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CROSSED-MOLECULAR-BEAMS REACTIVE SCATTERING OF
OXYGEN ATOMS

Robert J. Baseman
(Ph.D. thesis)

November 1982

LBL--15259

DEG3 004296

MASTER

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

Crossed-Molecular-Beams Reactive Scattering of Oxygen Atoms

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ABSTRACT

The reactions of $O(^3P)$ with six prototypical unsaturated hydrocarbons, and the reaction of $O(^1D)$ with HD, have been studied in high-resolution crossed-molecular-beams scattering experiments with mass-spectrometric detection.

The observed laboratory product angular and velocity distributions unambiguously identify parent-daughter ion pairs, distinguish different neutral sources of the same ion, and have been used to identify the primary products of the reactions.

The derived center-of-mass product angular and translational energy distributions have been used to elucidate the detailed reaction dynamics.

These results demonstrate that $O(^3P)$ -unsaturated hydrocarbon chemistry is dominated by single bond cleavages, leading to radical products exclusively.

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS	v
I. INTRODUCTION	
1. Opening Remarks	1
2. Experimental Method	2
3. Data Analysis 1: Product Identification	4
4. Data Analysis 2: Product Center of Mass Angular and Translational Energy Distributions	7
5. Interpretation of the Product Center of Mass Angular and Translational Energy Distributions	8
6. Potential Energy Barriers for 1,2 Migrations and Four Center Molecular Eliminations	11
References	13
Figure Captions	15
Figures	16
II. PRODUCTS OF THE REACTION OF $O(^3P)$ WITH TOLUENE	
1. Introduction	17
2. Energetics	18
3. Previous Results	21
4. Experimental	24
5. Primary Product Identification	25
6. Relative Cross Sections	29
7. Dynamics	33
8. Comparison of $O(^3P) + \text{Toluene}$ and $O(^3P) + \text{Benzene}$: Final Comments	35
References	37

Figure Captions.	39
Figures	40
III. THE REACTION OF $O(^3P)$ WITH ETHYLENE	
1. Introduction	46
2. Reaction Energetics.	47
3. Previous Results	50
4. Experimental	60
5. Identification of Primary Products	
A. On the Formation of Vinyloxy and Ketene	61
B. On the Formation of CH_3 and CHO	62
6. Relative Cross Sections	65
7. Dynamics of Vinyloxy Radical Formation	67
8. Formation of CH_3 and CHO : Summary	71
References	79
Figure Captions.	83
Figures	84
IV. PRIMARY PRODUCTS OF THE REACTIONS OF $O(^3P)$ WITH SUBSTITUTED ETHYLENES	
1. Introduction	96
2. Products of the Reaction of $O(^3P)$ with Propylene	97
3. Products of the Reaction of $O(^3P)$ with Vinyl Bromide	100
4. Products of the Reaction of $O(^3P)$ with 1,1 and 1,2 Dichloroethylene.	100
5. Summary	102
References	103

Figure Captions.	104
Figures	105
Appendix	108
V. THE REACTION OF $O(^3P)$ WITH ACETYLENE	
1. Introduction	139
2. Energetics	141
3. Previous Results	144
4. Experimental	153
5. Identification of Primary Reaction Products.	156
6. Center of Mass Product Angular and Translational Energy Distributions	
A. $H + HC_2O$	159
B. $CO + CH_2$	161
7. Relative Cross Sections.	165
8. Statistical Calculations: Comparison to Experiment	
A. Models.	167
B. Statistical Results	169
9. Summary.	176
References	177
Tables	180
Figure Captions.	184
Figures	186
VI. THE REACTION OF $O(^1D)$ WITH HD	
1. Introduction	205
2. Previous Results	208

3. Experimental	216
4. Center of Mass Product Angular and Translational Energy Distributions	
A. OD Product	221
B. OH Product	222
5. Relative Cross Sections	223
6. Statistical Calculations	224
7. Reaction Mechanism	227
References	230
Figure Captions	233
Figures	234

ACKNOWLEDGEMENTS

First, of course, I would like to thank Professor Y. T. Lee for the opportunity to study in his group and for all his invaluable help in completing, understanding, and interpreting these experiments.

I would also like to thank Richard Buss, who introduced me to reactive scattering and participated in most of these experiments, P. Casavecchia, G. Z. He, R. Tse, and A. Wodtke, who participated in some of these experiments, and all the other members of the Lee group that have assisted me in various aspects of this work.

I would like to acknowledge the generous support of a Fannie and John Hertz graduate fellowship during my years at the University of California, Berkeley.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Dept. of Energy under Contract No. DE-AC03-76SF00098.

Finally, and most importantly, I would like to thank my family, my wife, Ruth, and parents in particular, for their selfless help (in innumerable ways), never-ending patience, and everyday encouragement.

1. INTRODUCTION

1. OPENING REMARKS

During the last twenty years crossed molecular beams scattering experiments have been an unprecedented source of detailed information about elementary chemical and physical processes including photo-dissociation, elastic, inelastic, and reactive scattering. The results of crossed beams reactive scattering experiments can include determinations of entrance and exit channel potential energy barriers, preferred orientations of reactant attack and products separation, complex lifetime relative to its rotational period, the degree of energy randomization in a collision complex, the partitioning of excess product energy among the products' degrees of freedom, etc., and so allows connections to be made between the governing first principles of mechanics and observed macroscopic chemistry.

The $O(^3P) + \text{unsaturated hydrocarbon}$ crossed molecular beams scattering experiments described in this work, differ in one important way from most previous crossed beams reactive scattering experiments. For the most part, previous experiments have sought dynamical information about already clearly defined chemical processes, e.g., in $F + H_2 \rightarrow HF + H$,¹ both the reactants' and products' chemical identity are clearly known prior to the experiment. Here, however, the crossed beams experiments have been used simultaneously to establish the identity of the products of chemical reactions and to study the associated reaction

dynamics. In this introductory chapter, the experimental method, data analysis, and a few dynamical principles common to most of these reactions will be presented. We begin with a brief resume of the experimental method.

2. EXPERIMENTAL METHOD

The object of crossed molecular beams scattering experiments is to obtain the laboratory angular and velocity distributions of the particles scattered as the result of single bimolecular collisions. Two intense, highly collimated (in space, full width at half maximum $\sim 3^\circ$; in velocity, full width at half maximum ~ 10 percent of peak velocity), triply differentially pumped, supersonic beams cross at right angles in a collision chamber maintained at $\sim 1 \times 10^{-7}$ torr. This pressure is maintained low enough to provide a several meter mean free path in the collision chamber and insure that the only collisions that take place are single bimolecular collisions. Particles that are scattered out of the collision region ($\sim 27 \text{ mm}^3$) are detected by a detector which rotates about the collision center, in the plane of the two beams. Two different crossed beams machines were used in these experiments. The 25" machine's² detector is mounted on a 25" diameter rotating lid, while the 35" machine's detector is mounted on a 35"³ diameter rotating lid. The angular ranges covered by the 25" and 35" machines are 130° and 170° , centered 45° between the two beams, respectively. The detector itself is triply differentially pumped, with three nested regions maintained at 10^{-9} , 10^{-10} , and 10^{-11} torr during the experiment. Scattered particles which enter the detector are ionized by

an electron bombardment ionizer, housed in the innermost region of the detector (ionizer ~34 cm from the collision center in the 35" machine, ~20 cm from the collision center in the 25" machine), mass selected with an electric quadrupole mass spectrometer, and then counted, with a Daly detector (high voltage cathode, scintillator and photomultiplier combination).

To obtain the laboratory angular distribution of a given ion formed from scattered neutrals, one of the two beams is mechanically chopped at 150 Hz with a tuning fork. The tuning fork driving signal also triggers a dual channel scalar, so that signal and background is collected in one channel and only background in the other. The net ion signal is recorded as the difference between these two counts. Frequently it is also necessary to mechanically flag the unchopped beam, to obtain a second count and account for modulated background.

The laboratory velocity distributions are obtained with a time of flight technique. A slotted wheel (~17.5 cm in diameter) is mounted on the front of the detector and spun at several hundred Hz. The slots briefly admit a short neutral pulse train to the detector. Synchronous with the detector opening, a matched photodiode set triggers a fast (256) multichannel scalar. Thus the intensity of particles arriving at the detector is obtained as a function of flight time (from the wheel to the Daly detector). A wheel with four or eight equally spaced slots is used to measure the beams' original velocity distributions, or very high signal/noise product scattering. Most of the time, and in all of these experiments, a cross correlation time of flight technique is used.⁴ With this technique, the wheel is slotted in a pseudo-random fashion to

modulate the product. The original time of flight distribution is recovered from the observed modulated signal by correlating the pseudo-random sequence and the observed signal.

These two measurements constitute the crossed molecular beams scattering experiment. Next the general interpretation of these experimental results is discussed.

3. DATA ANALYSIS 1: PRODUCT IDENTIFICATION

The angular and velocity distributions obtained in a crossed beams scattering experiment are obtained in the laboratory frame of reference. Our methods for using these distributions for primary product identification and unraveling the reaction dynamics are most easily understood when the distributions are viewed from the center of mass reference frame. The conversion from laboratory to center of mass frames is made most easily with the use of a Newton diagram.⁵

A typical Newton diagram for the reaction of $O(^3P)$ with ethylene is shown in Figure 1. All the vectors in the Newton diagram are velocity vectors. Laboratory (reference frame) velocities are referenced to the origin (the laboratory oxygen, ethylene, and center of mass velocities are shown). Center of mass velocities are referenced to the terminus of the center of mass velocity vector.

When a chemical reaction takes place, some fraction of the excess energy available to the products will be deposited into the relative translation of the products. In the center of mass reference frame, one given translational energy corresponds to one center of mass speed. The direction of the separating particles is unknown, but the speed is

uniquely determined. The specification of the center of mass speed only, sweeps out a circle, centered on the terminus of the center of mass velocity vector, in the Newton diagram, representing the possible range of scattering. In the $O(^3P) + \text{ethylene}$ figure, two circles are shown; one representing the maximum center of mass speed for CH_2CHO product, the other, representing the maximum possible center of mass speed for CH_2CO product. The CH_2CO is spread over a much wider laboratory angular range. This is a manifestation of two factors, (1) there is more energy available for translation when CH_2CO is formed and more importantly, (2) the ratio of the operating products masses changes greatly from $\text{CH}_2\text{CO} + \text{H}_2$ (21:1) to $\text{CH}_2\text{CHO} + \text{H}$ (43:1). The laboratory angular and velocity distributions are determined solely by the neutral dynamics. No matter what ions are formed from a given neutral in the electron bombardment process, as long as the neutral parent is the same for all of the ions, then the laboratory angular and velocity distributions for all the ions will be identical.

Ideally, no dissociative ionization would occur in the electron bombardment ionizer, and primary reaction products would be identified solely by their masses. However, extensive fragmentation during ionization does occur, so ions of many different masses are formed from a given neutral product. Several different possible neutral products may lead to the same mass ions as well. Primary product identification, based upon mass spectroscopy alone then is nearly impossible.

The laboratory angular and velocity distributions, can be coupled with the kinematic constraints of energy and momentum conservation to identify primary reaction products. Specifically, the distributions can

be used to unambiguously identify parent daughter ion pairs, and distinguish different neutral sources of the same ion.

In the reaction of $O(^3P) + \text{ethylene}$, if CH_2CHO is formed, we would expect to see a mass 43 angular distribution between 11° and 45° in the laboratory frame. We would also measure an identical angular distribution for the many daughter ions, masses 42, 29, 15, etc., formed from CH_2CHO . If CH_2CO were formed we would expect to see a mass 42 angular distribution spread over a wider angular range (-27° to 83°). A comparison of the mass 42 and 43 angular distributions will reveal whether both mass 42 and 43 ions originate from the same neutral product. In the event that the 42 and 43 distributions are not identical, then the mass 43 distribution (nominally CH_2CHO) can be subtracted from the mass 42 distribution, to remove the contribution from dissociatively ionized CH_2CHO to the mass 42 distribution, and obtain the mass 42 angular distribution from CH_2CO alone.

The laboratory time of flight distributions can be used in a similar scheme. Any mass 42 or 43 ions originating from CH_2CHO must have lab velocities less than 1500 m/sec. Mass 42 ions from CH_2CO would have velocities up to 2100 m/sec, so a comparison of the mass 42 and 43 time of flight distributions will also determine whether one or both products are formed.

These techniques will be applied repeatedly in the experiments described in the following chapters.

4. DATA ANALYSIS 2: PRODUCT CENTER OF MASS ANGULAR AND TRANSLATIONAL ENERGY DISTRIBUTIONS

As mentioned earlier, it is of great interest to convert the observed laboratory angular and velocity distributions into center of mass angular and translational energy distributions. In a perfect experiment, the molecular beams would have a negligible spread in velocity and spacial profile, and the observed laboratory distributions could be directly inverted to the center of mass reference frame with a single Newton diagram. However, the beams do have an appreciable spread in velocity and space, making the lab to center of mass transformation non-unique. Siska⁶ has developed an iterative method for directly deconvoluting the lab data to the center of mass reference frame, but this method requires either extensive smoothing of the lab data or extremely high signal to noise to be effective.

An alternate method for recovering the center of mass angular and velocity distributions, employed exclusively in these experiments, is a forward convolution method. In this method, center of mass product angular and translational energy distributions are assumed, transformed to the laboratory frame, averaged over experimental parameters, and then the predicted laboratory distributions are compared with the experimental. Various center of mass angular and translational energy distributions can be considered to determine which adequately predicts the observed distributions.

In the program developed by Buss,⁷ the distribution of center of mass product flux (as a function of center of mass translational energy E' and scattering angle θ') is assumed to be separable into the product

of an energy ($P(E')$) and angular ($T(\theta')$) part. By including the appropriate transformation Jacobians, this assumed distribution is transformed into laboratory number density (as a function of lab velocity and lab scattering angle): $N(v, \theta) = kv/u P(E') T(\theta')$, where k is a normalization constant, v is the laboratory velocity, and u is the center of mass velocity.

The molecular beam (velocity) spreads are then taken into account by averaging the predicted $N(v, \theta)$ over a discrete set (typically 200) of Newton diagrams to obtain the predicted laboratory angular distribution $\bar{N}(\theta) = \int_0^\infty \bar{N}(v, \theta) dv$, with $\bar{N}(v, \theta) = \sum_n f_n N(v, \theta)$. The weighting function f_n , includes factors modeling the number density of velocities in each beam, assumed to be of the form $kv^2 e^{-\beta(v-v_0)^2}$. (The parameters, β and v_0 , for each beam are determined in separate beam TOF calculation experiments). The time of flight distributions $= kv^2 \bar{N}(v, \theta)$, are further averaged over a rectangular ionizer and trapezoidal (wheel) slit function prior to comparison with the observed distributions.

5. INTERPRETATION OF THE PRODUCT CENTER OF MASS ANGULAR AND TRANSLATIONAL ENERGY DISTRIBUTIONS

Basically, center of mass angular distributions can be divided into isotropic and anisotropic distributions. It is worthwhile to further subdivide the anisotropic distributions into forward-backward symmetric, and non-forward-backward symmetric distributions. The center of mass angular distribution provides what complex lifetime information is available from the crossed beams experiment. That is, when two particles come together to form a collision complex, if that complex

lives for at least several rotational periods (typically 1-3 picoseconds), then memory of the initial direction of attack is forgotten, and a forward-backward symmetric angular distribution is expected. Thus, forward-backward asymmetry implies a sub-rotational complex lifetime. A long (on a rotational time scale) complex lifetime implies forward-backward symmetry. However, forward-backward symmetry does not imply a long complex lifetime.

The exact details of an anisotropic center of mass angular distribution can be interpreted in several different ways. In particular, it can lead to information about preferred orientations of reactants' attack or products' separation, as in $F + C_2H_4$ ⁸ or be interpreted in terms of product angular momentum partitioning as in the reactions of Cl and F with vinyl bromide.⁹

The center of mass translational energy distributions can be regarded either as statistical or nonstatistical. Statistical theories calculate the probability of observing a given translational energy on the basis of the total state density of the transition state leading to that translational energy. Both phase space¹⁰ and RRKM-AM calculations¹¹ have been used in these studies to predict translational energy distributions (as well as unimolecular reaction rates).

If the observed distribution is represented well by the statistical calculation, then the conclusion is reached that the assumptions implicit (equal probability of forming all states consistent with energy and momentum conservation, absence of significant exit channel effects, etc.) in the statistical calculations appropriately describe the reaction considered. Two general types of deviations from statistical behavior can be considered.

The observed translational energy distribution may be colder than the statistical prediction. In this case, a dynamical feature of the reaction effectively channels product excess energy into rotational or vibrational degrees of freedom--in the reaction of $O(^1D) + H_2$ the highly excited bending motion of the H_2O complex apparently efficiently couples to OH product rotation at the expense of OH + H translation.¹² It is also conceivable that a colder than statistical distribution may result from dissociation prior to complete randomization of complex energy among all complex vibrational and rotational degrees of freedom prior to dissociation.

The observed distribution may also be hotter than statistical. Some of the first reports of these distributions (F + aromatics¹³) were interpreted in terms of incomplete energy randomization. However, since that time, a more detailed picture has developed. Statistical calculations assume that once the transition state is reached no further interaction between separating particles takes place. However, very frequently there is a potential energy barrier (at least part centrifugal) in the exit channel. RRKM-AM and phase space calculations do not include these exit channel effects. Following Marcus¹⁴ original suggestion, Hase's classical trajectory calculations¹⁵ have demonstrated that the potential energy released in descending the exit channel barrier is efficiently (~100 percent of the centrifugal barrier and as much as 80 percent of the mechanical barrier) converted to product translation. In these crossed beam studies, excess translational energy beyond statistical predictions is interpreted as manifestations of the exit channel interaction in those reactions where significant exit channel potential energy barriers are expected.

6. POTENTIAL ENERGY BARRIERS FOR 1,2 C-C MIGRATIONS AND FOUR CENTER MOLECULAR ELIMINATIONS

1,2 C-C migrations and three or four center molecular eliminations are considered extensively in some O(³P)-unsaturated hydrocarbon reaction mechanisms. Here, some general observations about these processes are presented.

First we address 1,2 C-C migrations. Molecular rearrangements by 1,2 migrations have been long regarded as interesting processes.¹⁶ Generally experimental studies have demonstrated that migrations occur most frequently in cations, less frequently in radicals, and least often in anions. Moreover, as the migrating group gains in electronic complexity, from hydrogen atoms and alkyl groups to halogens and phenyl groups, the migration becomes more facile. The general trends can be easily explained at a Huckel theory level,^{16,17} in terms of transition state stabilization. More detailed experimental results have suggested that while 1,X for X = 4, 5, 6 hydrogen migrations,¹⁸ and 1,2 halogen migrations take place in radicals¹⁹ the 1,2 C-C hydrogen migration is in Schaefer's words "unknown."²⁰ Recent calculations by Harding²¹ indicate that a 50 kcal/mole potential energy barrier accompanies the 1,2 C-C hydrogen migration in radicals.

We are concerned more specifically with 1,2 C-C migrations on triplet surfaces. Much less experimental information is available addressing migration probabilities in open shell singlet and triplet species. What evidence is available, describing migrations in carbenes, indicates that 1,2 hydrogen and alkyl group migrations take place readily on the singlet, but not the triplet surface, while phenyl group

migrations may take place on the triplet surface.²⁰ Recent calculations by Schaefer²⁰ and Harding²¹ modeling 1,2 migrations in carbenes demonstrate that the 1,2 C-C hydrogen migration is accompanied by a ~50 kcal/mole barrier on the triplet surface, but only a small < 5-10 kcal/mole barrier on the singlet surface. We will assume that, in general, a large barrier is associated with 1,2 C-C hydrogen and alkyl group migrations on triplet surfaces.

It is also of interest to point out that in general four center (and most three center) molecular product eliminations are accompanied by large (~50 kcal/mole, although frequently much larger) potential energy barriers. The large barriers are probably associated with the large energy outlay required to break two chemical bonds before the resulting product bond has formed to any great extent.

In any event, large barriers have been established for the eliminations of HCl from $\text{CH}_3\text{CF}_2\text{Cl}$ and CH_3CCl_3 ,²² for the eliminations of HF and DF from CD_3CHF_2 and CH_3CHF_2 ,²³ and for the elimination of H_2 from formaldehyde.²⁴ While these barriers have been established on singlet surfaces we expect the overriding principles to carry over to the triplet surface, and a large potential energy barrier to accompany three or four center molecular eliminations from triplets as well.

REFERENCES: CHAPTER I

1. Y. T. Lee, Ber. Bunsenges Phys. Chem. 86, 378 (1982).
2. Y. T. Lee, J. D. McDonald, P. R. LeBreton, D. R. Herschbach, Rev. Sci. Inst. 40, 1402 (1969).
3. R. K. Sparks, Crossed Beam Studies of Full and Half Collisions, Ph.D. Thesis, University of California, Berkeley (1980).
4. C. U. Nowikow, R. Grice, J. Phys. E 12, 515 (1979).
5. R. D. Levine, R. B. Bernstein, Molecular Reaction Dynamics, Oxford, New York (1974).
6. P. E. Siska, J. Chem. Phys. 59, 6052 (1973).
7. R. J. Buss, Crossed Molecular Beam Studies of Unimolecular Reaction Dynamics, Ph.D. Thesis, University of California, Berkeley (1979).
8. J. M. Parson, Y. T. Lee, J. Chem. Phys. 56, 4658 (1972).
9. R. J. Buss, M. J. Coggiola, Y. T. Lee, Disc. Farad. Soc. 67, 162 (1979).
10. J. C. Light, Disc. Farad. Soc. 44, 14 (1967). Program provided by K. Shobatake.
11. P. J. Robinson, K. A. Holbrook, Unimolecular Reactions, Wiley Interscience, London (1972). S. A. Safron, N. D. Weinstein, D. R. Herschbach, Chem. Phys. Lett. 12, 564 (1972). Program provided by W. L. Hase and D. L. Bunker.
12. P. A. Whitlock, J. T. Muckerman, E. R. Fisher, J. Chem. Phys. 76, 4468 (1982).
13. K. Shobatake, S. A. Rice, Y. T. Lee, J. Chem. Phys. 59, 1435 (1973).
14. R. A. Marcus, Disc. Farad. Soc. 55, 379 (1973).

15. W. L. Hase, K. C. Bhalla, J. Chem. Phys. 75, 2807 (1981).
W. L. Hase, R. J. Wolf, J. Chem. Phys. 75, 3809 (1981).
16. N. F. Phelan, H. H. Jaffe, M. Orchin, J. Chem. Ed. 44, 626 (1967).
17. H. E. Zimmerman, A. Zweig, J. Amer. Chem. Soc. 83, 1196 (1961).
18. J. W. Wilt in Free Radicals, Volume I, J. K. Kochi, Ed., Wiley Interscience, New York (1973).
19. See, for example, W. H. Urry, J. W. Wilt, J. Amer. Chem. Soc. 76, 2594 (1954); W. H. Urry, J. R. Eiszner, J. Amer. Chem. Soc. 74, 5822 (1952); W. H. Urry, J. R. Eiszner, J. W. Wilt, J. Amer. Chem. Soc. 79, 918 (1957).
20. H. F. Schaefer III, Acc. Chem. Res. 12, 288 (1979).
21. L. B. Harding, J. Amer. Chem. Soc. 103, 7469 (1981).
22. Aa. S. Sudbo, P. A. Schulz, Y. R. Shen, Y. T. Lee, J. Chem. Phys. 69, 2312 (1978).
23. K. C. Kim, D. W. Setser, B. E. Holmes, J. Phys. Chem. 77, 725 (1973).
24. P. Ho, D. J. Bamford, R. J. Buss, Y. T. Lee, C. B. Moore, J. Chem. Phys. 76, 3630 (1982).

FIGURE CAPTIONS: CHAPTER I

1. Typical Newton diagram for the reaction of $O(^3P)$ with ethylene.

FIGURE 1-1

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II. PRODUCTS OF THE REACTION OF $O(^3P)$ WITH TOLUENE

1. INTRODUCTION

Two competing reaction channels were observed in a crossed molecular beams investigation of the reaction of $O(^3P)$ with benzene in our laboratory.¹ One channel produces phenol, the other leads to hydrogen atom and phenoxy radical products. Aside from primary product identification, this experiment showed that (1) the addition channel is favored as the collision energy is increased, and upon deuteration of the aromatic ring, and (2) a large fraction of the available energy from oxygen atom substitution is deposited into the relative translation of the products, indicative of a potential energy barrier in the exit channel for C-H bond cleavage. Until this study, the identity of the primary reaction products was uncertain, and dynamical information about the reaction, such as product translational energy distributions, was unavailable. The ability to measure the velocity and angular distributions of all the ions formed from parent neutral products was crucial to the correct identification of parent-daughter ion pairs, and the primary reaction products.

As the next step in investigating the reactions of $O(^3P)$ with aromatics, we have studied the $O(^3P) + \text{toluene}$ reaction to clear up a similarly clouded picture of the primary reaction products, and to determine what dynamical effects and new products are associated with the methyl substituent on the benzene ring.

2. ENERGETICS

Figure 1 shows the standard heats of formation at 300°C of the relevant species. Cvetanovic's original belief² that the $O(^3P)$ atom is electrophilic in nature has been generally accepted, and there is little doubt that the oxygen atom initially adds to the electron rich aromatic framework. The several kilocalorie/mole activation energy for the reaction is also indicated.³ $O(^3P)$ addition to the saturated benzylic carbon is unexpected.

Abstraction by oxygen of an aromatic proton or the methyl group to form hydroxyl and methylphenyl or methoxy and phenyl radicals is very nearly energetically impossible with only 10 kcal/mole of collision energy. As our experiment was carried out at ~10 kcal/mole collision energy these channels need not be considered. Abstraction of a benzylic hydrogen to form benzyl and hydroxyl radicals is, however, nearly 18 kcal/mole exothermic.

Any of several diradicals may be formed when $O(^3P)$ adds to the aromatic framework. (Entrance channel effects determine exactly which one would be formed in any given collision.) Both singlet and triplet species are conceivable. Even within the triplet or singlet manifolds several different diradicals can be formed. We understand the nature of these electronic configurations best for the simpler but prototypical $O(^3P) + \text{ethylene}$ system, discussed later. By analogy we can make some general observations. If we regard one unpaired spin as primarily localized on the oxygen, and the other on the ring, then the most crude differences within the triplets and singlets can be easily understood. In the lowest energy configuration the ring unpaired spin

almost certainly has mainly π bonding character while the unpaired spin on oxygen probably resides in a nearly in plane atomic p orbital, with the oxygen lone pair lying out of the benzene plane. A next (slightly) higher configuration would have the oxygen unpaired spin lying out of molecular plane, with the lone pair orbital in plane. Further higher energy configurations would arise from the excitation of the aromatic spin from π to π^* character.

The energy of the lowest energy triplet diradical can be estimated either from Benson's rules,⁴ or by using 83 kcal/mole⁵ as a typical $S_0 \rightarrow T_1$ excitation for an aromatic phenol and the standard heat of formation for cresol, ~ -30 kcal/mole. Both methods give $\Delta H^\circ_{f300} = 53 \pm 2$ kcal/mole.

There are three possible product forming routes for the diradical, (1) the diradical has a long enough lifetime to be detected as a product, or isomerizes to a different relatively long lived (stable) species, (2) the diradical decomposes to stable molecular products or (3) the diradical decomposes into radical products.

Ortho, meta, para cresols or anisole are possible products arising from the first route. The three or four center elimination of H_2 with oxygen migration to form benzaldehyde and H_2 is representative of the second route, although a large potential energy barrier must be expected for that process. Finally, single bond cleavages, eliminating H or CH_3 from the diradical, are the most likely routes leading to radical products. The single bond cleavages, C-H and C- CH_3 , are shown in Figure 1 to have potential energy barriers in the exit channels. These barriers are presented to reproduce the

known activation energies for the reverse reactions of H and CH_3 adding to double bonded carbon atoms (barriers of ~ 3 and ~ 10 kcal/mole respectively).⁶ In none of the important resonance structures below for phenoxy or methylphenoxy does the carbon of interest acquire much radical character, so even though H or CH_3 reattaches to the carbon

it was originally bonded to, the reverse reaction is thought of as the addition of H or CH_3 to an aromatic carbon or carbonyl carbon rather than a radical center. (The decomposition of a diradical into two radicals whose recombination is most like the addition of a radical to an olefin is a peculiarity that is standard in these $\text{O}(^3\text{P})$ -unsaturated hydrocarbon systems.) Moreover, as will be shown, there is experimental evidence in the center of mass translational energy distributions for these channels of a small potential energy barrier in the exit channels for C-H and C-C bond cleavages.

Many previous experiments have been directed, at least in part, to determining which path(s) really represent the fate of the O-toluene diradical. Some of these efforts and their results are reviewed next.

3. PREVIOUS RESULTS

In 1961 Jones and Cvetanovic⁷ generated ground state oxygen atoms by the mercury sensitized decomposition of NO_2 and studied the reactions of $\text{O}(^3\text{P})$ with benzene and toluene in a circulating reaction system. The rate of the $\text{O}(^3\text{P}) + \text{toluene}$ reaction was measured relative to that of $\text{O}(^3\text{P}) + \text{cyclopentene}$. A pre-exponential factor equal to that of $\text{O}(^3\text{P}) + \text{cyclopentene}$ and an activation energy of between 3.8 and 4.1 kcal/mole were obtained. Jones and Cvetanovic also analyzed the reaction products and found the major reaction product to be a "material of low volatility." The volatile reaction products were CO , H_2O , and cresols. Of the cresols, little meta cresol was formed, and ortho dominated para roughly 3 to 1.

Following the Jones and Cvetanovic study, absolute measurements of the $\text{O}(^3\text{P}) + \text{toluene}$ reaction rate have been made by Mani and Sauer⁸ (pulsed radiolysis and transient absorption spectroscopy), Atkinson and Pitts⁹ (modulation-phase shift technique), Furuyama and Ebara¹⁰ (microwave discharge-fast flow), Colussi, Singleton, Irwin, and Cvetanovic¹¹ (phase shift chemiluminescence), and finally by Atkinson and Pitts again³ (flash photolysis- NO_2 chemiluminescence). With the exception of the absorption work of Mani and Sauer, all these measurements agree³ on a room temperature rate constant of $\sim 8 \times 10^{-14}$ cc/molecule sec (range 5.7 to 10.8) and an activation energy of 2.9 kcal/mole (range of 2.7 to 3.2).

In general, agreement has also been reached on the final reaction products. Grovenstein and Mosher,¹² using the mercury sensitized decomposition of nitrous oxide to make $\text{O}(^3\text{P})$ atoms in a flow system,

found that 95 percent of the volatile addition products were phenolic. Unlike the initial study by Jones and Cvetanovic, they reported phenol as a product from $O(^3P)$ -alkylated benzene reactions. A polymeric tar was again the major reaction product. Gaffney, Atkinson, and Pitts¹³ concluded that between 75 and 85 percent of the oxygen atoms consumed during the reaction ultimately went into a tar, which they were able to characterize as nonaromatic with a broad carbonyl infrared absorption. The remainder of the $O(^3P)$ concentration produced volatile products. Cresols were found, ortho dominating para with little meta, and like Grovenstein, phenol. In addition, small amounts of methane and ethane were detected. Finally, Akimoto et al.¹⁴ found cresols, but no phenol in an oxidation system that included NO_2 . Benzaldehyde was observed as a product in this experiment, but only when O_2 was present.

Details of the reaction mechanism, and the identity of the primary products formed, have mainly been inferred from these final product analyses. Cvetanovic's original suggestion that the oxygen atom acts as an electrophile and attacks the aromatic nucleus is widely accepted. Assuming that the relative amounts of the cresols and phenols formed reflect the likelihood of the $O(^3P)$ adding to the corresponding carbon atoms, then all studies agree that addition to the ortho and para positions is greatly favored over the meta position, as in other typical electrophilic benzenoid substitutions¹⁵ with electron releasing substituents on the benzene ring. Grovenstein and Mosher¹² explicitly calculated the partial rate factors at each carbon atom in the ring: 2.1 methyl substituted, 7.7 ortho, 2.0 meta, and 4.7 para.

The methyl group, in addition to being orth-para directing, would also be expected¹⁵ to activate the ring towards addition. Indeed the activation energy for $O(^3P) + \text{toluene}$ is found to be ~ 1 kcal/mole less than the $O(^3P) + \text{benzene}$ case,³ and the activation energy for the reaction decreases with further alkylation.³ (Mani and Sauer⁸ point out that the methyl group would, through hyperconjugation, be expected to release electrons to the aromatic ring. However, were hyperconjugation the dominant effect, ethylbenzene would react more slowly than toluene, in contrast to experiment, suggesting that inductive effects must be the important electron donating mechanism for the methyl group.)

In any event, the electrophilic character of the reaction is clearly established. However, the nature and initial fate of the $O(^3P)$ -toluene adduct is unclear. Absorption spectra⁸ suggested that an initially formed triplet biradical converts into methyl substituted benzeneoxide or oxepin with a half life of 4 microseconds, but little more than that is known.

The most serious attempt to identify specifically the primary products of $O(^3P) + \text{toluene}$ to date has been made by T. M. Sloane¹² in a crossed beam experiment. Two uncollimated, effusive beams were crossed at 60° and products detected with an electron bombardment ionization mass spectrometer. The electron (ionization) energy was varied to measure the ionization appearance potential of ions, aiding in the identification of neutral products. Some adducts observed may have been stabilized by secondary collisions.

Products were observed at $m/e = 108, 106$, and 80 . A structure for the mass 108 adduct could not be assigned on the basis of the observed appearance potential because the differences between the ionization potentials of the cresols and anisole were beyond the experimental resolution. Sloane considered that the $m/e = 106$ signal might have been a daughter ion of the 108 adduct, but concluded that the 106 was a parent benzaldehyde ion. The $m/e = 80$ signal was attributed to a third and final product, most likely the open chain olefin $\text{CH}_2(\text{CH})_4\text{CH}_2$. No mass 107 product was reported.

While Sloane's observation of a stabilized mass 108 adduct is in concert with the observation of phenol in this group's $\text{O}(^3\text{P}) + \text{benzene}$ experiment, one must wonder about the apparent absence of the O for H substitution channel, as in $\text{O} + \text{benzene}$, the absence of the analogous O for CH_3 substitution, about the likelihood of a 3 or 4 center elimination of H_2 , and the likelihood of a ring opening reaction (large activation energy required to open the aromatic ring and loss of the stability associated with the benzene ring).

4. EXPERIMENTAL

In this experiment a 5 percent oxygen in helium mixture was used in the atomic oxygen source.¹⁷ Two hundred watts of RF power was discharged through the mixture prior to expansion through a $.0076''$ nozzle. The beam was skimmed by a $.032''$ diameter by $.55''$ long conical boron nitride skimmer, mounted $.75''$ from the nozzle, and finally passed through a $.081'' \times .120''$ rectangular slit mounted on the differential pumping wall ($2.375''$ from skimmer and $.625''$ from the

collision center) prior to entering the main scattering chamber.¹⁹ This oxygen beam had a peak velocity of $V_0 = 2.35 \times 10^5$ cm/sec and a speed ratio of 6.6.

A molecular beam of toluene was formed by flowing toluene vapor (in equilibrium with the neat liquid at 75°C) through a heated quartz tube and expanding it through a .004" nozzle. The beam was skimmed by a .043" diameter, .423" long conical skimmer and then passed through another conical skimmer, .064" diameter, .4" long, mounted .600" from the base of the first skimmer, and a .093" x .119" rectangular slit mounted on the differential pumping chamber wall 1.500" from the nozzle and .375" from the collision center. This toluene beam had a $V_0 = 6.72 \times 10^4$ cm/sec and a speed ratio of 3.7. With these two beams, the nominal collision energy for the reaction was 10 kcal/mole.

Product angular distributions shown are the results of at least five 100 second counts at each angle, taken every 2.5 (laboratory) degrees. Time of flight (TOF) product spectra were obtained at the canonical center of mass angle, using the cross correlation TOF method.¹⁸ Typical TOF distributions shown are the result of 1 to 2 x 10⁶ sweeps of our 256 multichannel²⁰ scaler, 12 μsec/channel, with a total counting time of 1.7 hours. Error bars shown in the figures are ±1 standard deviation of the mean value reported.

5. PRIMARY PRODUCT IDENTIFICATION

Angular distributions of ions formed from reactively scattered neutrals were measured for $m/e = 78, 79, 106, 107, \text{ and } 108$. The mass 107 angular distribution shown in Figure 2 was the most intense

signal, roughly 200 counts/second at its peak. This distribution peaks at the center of mass angle, 60.5° and is, as reactive angular distributions go, quite narrow. These characteristics are those expected for the angular distribution of a product formed as the result of the elimination of a very light particle from a relatively heavy O-toluene adduct. Oxygen substitution for hydrogen to give methyl substituted phenoxy (cresoxy) radical is the most likely possibility. Examination of the other angular distributions and their intensities confirms the nature of the product.

All of the other angular and TOF distributions ($m/e = 78, 79, 106, 107, 108$) are superimposable on the mass 107 angular and TOF distributions. Since the angular and velocity distributions of the ions are determined solely by the neutral dynamics, this means that the mass 78, 79, 106, 107, and 108 ions all originate from a common neutral parent.

If C-H single bond cleavage leading to H and methylphenoxy radical is the product forming route, we would expect to see parent mass 107 ions, daughter ions of various masses including masses 106, 78, and 79, and some mass 108 ions due to ^{13}C and ^2H isotopic impurities in the 107 product. On the basis of the ^{13}C and ^2H natural abundances this 108/107 ratio would be ~ 0.077 .

On the other hand, if stabilized mass 108 product were being formed (or if it were being formed as well as a 107 neutral product) the 108 signal would have to be greater than or equal (equal only in the extremely unlikely case that no mass 108 ions would be formed from a neutral mass 108 product) that due merely to isotopic impurities in the 107 signal.

Experimentally, the 108/107 intensity ratio is $.075 \pm .003$, that expected solely due to isotopic impurities in a 107 primary neutral product. We see no m/e 108 signal from a C_7H_8O product and conclude there is little or no stabilized adduct formed, while oxygen readily substitutes for hydrogen on the ring.

Having seen that C-H single bond cleavage following $O(^3P)$ attack is an important product forming route, the question arises as to whether C-C single bond cleavage is also important. If C-C single bond cleavage following $O(^3P)$ attack does occur then the products formed would be phenoxy and methyl radicals. Relatively scattered $m/e = 93$ or $m/e = 15$ particles are difficult to detect. $m/e = 93$ particles are hard to detect because of the ^{13}C and 2H impurity in the intense toluene beam leading to intense elastic scattering and background $m/e = 93$ signal. The methyl radical product is difficult to detect because were it formed, it would be scattered over the complete laboratory angular range. We abandoned hope of seeing a $m/e = 93$ or $m/e = 15$ product angular distribution for these reasons.

However, TOF distributions are able to separate different contributions to the same ion at a given laboratory angle, due to the different velocity distributions of the various sources. Shown in Figure 3 is the mass 91 (identical to mass 92) TOF distribution at the center of mass angle. Two contributions are immediately apparent. The first sharp feature is the elastically scattered toluene TOF, while the second component is a $\sim 320^\circ$ Maxwell Boltzman distribution representing the effusion of toluene from the main chamber into the detector. The mass 93 TOF should show both these two, and a third

contribution if phenoxy were formed, but the two nonreactive sources are so intense that any third contribution is obscured. However, by looking for a daughter ion of the phenoxy radical, mass 65, which is a relatively less important daughter ion of toluene, a third contribution, if present, would be observed. Figure 3 also shows the mass 65 TOF distribution, and a third contribution, centered between the elastic and Maxwell Boltzman is obvious.

The third (reactive) contribution can be obtained by subtracting the 91 from the 65 spectra. Any reasonable subtraction scheme evinces this third contribution. The data shown in Figure 4 is obtained after shifting the 91 distribution $\sim 1/3$ channel faster to account for the difference in detector ion flight times, then vertically scaling the two spectra such that their least square differences are minimized from channels 41-80 (the slow tail of the Maxwell Boltzman distribution). The shape of the fast side of this line is relatively insensitive to what subtraction scheme is used, whereas the slow side, buried for the most part underneath the rapidly increasing fast side of the Maxwell Boltzman line, is much more sensitive and less attention was paid to this part of the data in the fitting process. This TOF distribution is shown in Figure 4 and can be compared with the mass 107 TOF. The displacement in time and increased breadth unambiguously confirm a different neutral product origin, phenoxy radical.

Two different sets of products have been identified, $H + C_6H_5OCH_3$ and $CH_3 + C_6H_5O$. We have found no evidence for molecular products, stabilized C_7H_8O or otherwise.

6. RELATIVE CROSS SECTIONS

The relative cross sections for the formation of H and methylphenoxy or methyl and phenoxy, may be estimated from the observed signal intensities. At 60° in the lab, the intensity of the CH₃ elimination product is 4.8 times that of the H elimination route. (The ratio is obtained by integrating the two TOF distributions at that angle.)

The observed intensity ratio is the product of several factors. First, of course, is the ratio of the cross sections (σ). The observed signal ratio will be proportional to the actual cross section ratio. Second, there is a kinematic factor (kine), the ratio of the integrals of the center of mass angular and energy distributions. This factor takes into account that different fractions of the volume products are scattered into are sampled by the detector in a given measurement. That is, in this experiment, the detector samples a proportionately smaller volume when detecting phenoxy radicals compared to methylphenoxy, since the phenoxy is much more widely scattered. Third, there is the relative likelihood of ionization, assumed to be proportional to the square root of the neutrals' polarizability (α). Fourth, the likelihood of the neutral cracking during ionization to the detected m/e (f), and finally the ion detection efficiency (det eff).

$$\frac{\sigma_H}{\sigma_{CH_3}} \cdot \frac{kine_H}{kine_{CH_3}} \cdot \frac{\alpha_H^{1/2}}{\alpha_{CH_3}^{1/2}} \cdot \frac{f_{ionH}}{f_{ionCH_3}} \cdot \frac{det\ eff_H}{det\ eff_{CH_3}} = \frac{obs_H}{obs_{CH_3}}$$

From the $P(E')$ and $T(\theta')$ presented later, $k_{\text{ine}_H}/k_{\text{ine}_{\text{CH}_3}} = 1/.05$. For the rather crude estimate we obtain, and for the relatively small errors incurred therein, we set $\alpha_H = \alpha_{\text{CH}_3}$ and $\text{det eff}_H = \text{det eff}_{\text{CH}_3}$. The only remaining factors are the fraction of the phenoxy ions detected as mass 65 and the fraction of the methylphenoxy ions detected at mass 107. Here we are forced to rely on analogy with the mass spectra of stable species.²¹ Unfortunately the mass spectra of phenol and the cresols are quite different, and this makes predictions somewhat uncertain. The mass spectrum of phenol shows that CO loss, $m/e = 66$, is a prominent peak, nearly .1 of the total ion counts. (However, only $\sim .02$ of the ions formed from the cresoles have $m/e = 80$). Assume then, that .1 of the phenoxy radical product is detected as $m/e = 65$. The parent ion is abundant for cresol, roughly .2 of the total ions formed. Using that value as the fraction of methylphenoxy detected as mass 107, one obtains finally $\sigma_H/\sigma_{\text{CH}_3} = .005$.

RRKM-AM lifetime calculations²² for the decomposition of an O-toluene diradical were performed to obtain further information about this question. The energetics were as pictured earlier, the transition state for CH_3 elimination 2 kcal above the diradical level, the transition state for H elimination 5 kcal above the diradical level. Normally the activated complex and energized molecule are modeled to accurately reproduce the high pressure A factor for the unimolecular reaction. In this case no A factor is known for the decomposition of an O-toluene diradical.

In other systems, if H atoms or methyl groups are eliminated and the other remaining products are radicals, A factors are commonly near

$10^{14.5}$ and 10^{16} respectively.⁴ The elimination of H from ethyl radical has an A of $10^{13.5}$,⁴ however, reflecting the tighter nature of the transition state, i.e., an activation barrier for the reverse reaction. A factors for the H and CH_3 eliminations were then estimated to be $10^{13.8}$ and $10^{15.3}$ respectively.

The models were as simple as possible, varying only the C-H or C- CH_3 bond distance in the transition state (two vibrational frequencies and two moments of inertia varied) until a $\Delta S^\ddagger$ that gave the required A factor was achieved.

These calculations showed $a_{\text{H elim}}/a_{\text{CH}_3 \text{ elim}} = .05$, in rough accord with the experimental result. However, an assumption implicit in doing RRKM-AM calculations and trying to estimate relative cross sections from the results, is that the two channels are really competitive decay processes. That is, either the two channels must compete in the decay of one given activated molecule, or if two different activated molecules are considered, there should be no entrance channel effects that lead preferentially to the formation of one or the other activated molecules. If these conditions are not satisfied, the actual cross section ratio could be determined by dominating entrance channel effects, and RRKM-AM calculations of the decomposition would be misleading.

If the oxygen atom attacks the ring, but does not localize on a specific carbon, i.e., if it either readily makes 1,2 shifts or just remains associated with the π system as a whole, then the C-H cleavage and C- CH_3 cleavage would really be competing processes for the unimolecular decay of the O-toluene diradical. (Assuming that the movement of oxygen is rapid relative to decomposition.)

However, typical electrophilic substitutions are generally regarded as resulting from a localized attack of the electrophile. It is certainly clear that in the reactions of $O(^3P)$ with olefins, an asymmetric addition occurs (see Chapter 3) with the oxygen binding to one given carbon. Therefore, we favor a picture of the reaction in which oxygen localizes, forms a σ bond to, one specific aromatic carbon.

Since different activated diradicals probably are formed, leading to C-H and C-CH₃ cleavages, an understanding of the relative cross sections must include a consideration of any relevant entrance channel effects. Four factors must be considered. First, there are five hydrogenated carbons on the ring, clearly favoring C-H bond cleavage. Second, the methyl group sterically hinders the addition of oxygen to the methylated carbon, again favoring C-H cleavage product. Third, the methyl group donates electrons to the ring, and that effect would be greatest at the methylated carbon, attracting oxygen to the methylated carbon, favoring CH₃ elimination. Fourth, we consider the stability of the diradicals formed. In the addition of $O(^3P)$ to propylene, the addition of oxygen to the methylated carbon leads to a 1,3 diradical in which a 1° carbon radical center is formed. Addition of oxygen to the perhydro end of the molecule leads to a 1,3 diradical in which the carbon radical center is more nearly 2°. Given the accepted ordering of carbon radicals' stability, addition at the less substituted end is clearly favored.²³ In the case of $O +$ toluene, however, the differences are much less dramatic. In either case the nominally important resonance structures have one unpaired spin on

oxygen and one on the ring. In one of these resonance structures the ring spin lies at the methylated carbon, but overall little difference in the stability of the two diradicals is expected. (As such only one diradical level is shown in the energy level diagram.) Taken together, entrance channel effects probably favor C-H bond cleavage products, but not to a great extent.

While entrance channel effects may favor H elimination somewhat, both the energetics of the transition state, as well as the A factors favor CH_3 elimination. The RRKM-AM calculation, based on these factors is in rough agreement with the experimental result, so it appears that these factors dominate, entrance channel effects are probably relatively small, and CH_3 elimination is roughly 100 times as likely as H elimination.

7. DYNAMICS

Most of our information about the dynamics of this reaction is obtained by considering the center of mass angular ($T(\theta')$) and translational energy ($P(E')$) distributions required to fit the observed laboratory angular and time of flight distributions. Shown in Figure 5 is the $P(E')$ used to fit the H atom elimination angular and velocity distributions. An isotropic center of mass angular distribution was adequate. The error bars shown on the $P(E')$ are determined by an arbitrary estimate of what constitutes an acceptable fit to the data. The errors for this channel are quite large, because the detected particle is so heavy relative to the leaving group, and the fraction of the translational energy deposited into particle 1 is

$m_2/(m_1 + m_2) = \sim .01$. Also shown in the figure are the $P(E')$ obtained by the RRKM-AM calculations mentioned earlier, and by a phase space calculation. These calculations indicate that an average of ~ 2.5 kcal/mole go into translation, while the best fit $P(E')$ indicates that really about 3.6 kcal/mole go into translation. A forward-backward symmetric center of mass angular distribution, in particular an isotropic one, indicates that the complex lives for at least a rotational period (several picoseconds). It is unlikely then that the excess energy in translation observed is a result of incomplete sharing of the internal energy among internal modes of the complex. Rather, this excess energy is taken to be evidence for a several kilocalorie/mole potential energy barrier in the exit channel for C-H bond cleavage, as expected from the energetics discussion.

The CH_3 elimination TOF data is also fit with an isotropic center of mass angular distribution, and the $P(E')$ shown in Figure 6. Also shown in Figure 6 are typical results of phase space and RRKM-AM calculations of the translational energy distribution. The experiment shows again that more energy is deposited into translation than that expected for the unimolecular decay of the diradical without an exit channel potential energy barrier. (An experimental best fit average of 8.0 kcal/mole versus the calculated 3.6 kcal/mole average.) This is not surprising in light of the activation energy expected for the reverse reaction as mentioned before.

8. COMPARISON OF $O(^3P) + \text{TOLUENE}$ AND $O(^3P) + \text{BENZENE}$: FINAL COMMENTS

As a means of summarizing the $O + \text{toluene}$ results, we compare the two reactions, $O(^3P) + \text{benzene}$ and $O(^3P) + \text{toluene}$. The previous crossed beam experiments showed that $O(^3P) + \text{benzene}$ leads to either phenol or $H + \text{phenoxy}$. A broad $P(E')$, indicative of an exit channel potential energy barrier, was observed for the $H + \text{phenoxy}$ channel.

H atom elimination is also observed in $O + \text{toluene}$. While the best fit $P(E')$ is not quite as broad as that reported for $O + \text{benzene}$, a very broad distribution like that for $O + \text{benzene}$ is certainly within the errors of the $O + \text{toluene}$ experiment, and even the best fit $P(E')$ clearly points to an exit channel potential energy barrier of several kcal/mole.

While phenol was observed as a primary product in $O + \text{benzene}$ no corresponding stabilized adduct is observed in $O + \text{toluene}$. The cross section for the formation of phenol was apparently of the same order of magnitude as that for H elimination in $O + \text{benzene}$. In $O + \text{toluene}$ we see that H elimination is a rather minor channel compared to methyl radical elimination. If H elimination is favored over stabilization, even to a small extent, then the addition channel will be, as is observed, a very small, if not zero, contribution. The absence of stabilized adduct is regarded as mainly the effect of having a new relatively very fast channel open up in the toluene system.

In contrast to previous results, the primary products of $O + \text{toluene}$ are seen to be radical products exclusively. Radical chain type mechanisms can easily lead to the many polymeric products

observed in the bulk phase studies. Both C-H and C-C single bond cleavages occur, with potential energy barriers in the exit channels.

No evidence for molecular decomposition products, or stabilized adducts was obtained, reinforcing our notions about the potential energy barriers associated with 3 or 4 center molecular eliminations, and the relative rates of intersystem crossing and single bond cleavages.

REFERENCES: CHAPTER II

1. S. J. Sibener, R. J. Buss, P. Casavecchia, T. Hirooka, Y. T. Lee, J. Chem. Phys. 72, 4341 (1980).
2. R. J. Cvetanovic, J. Chem. Phys. 23, 1375 (1955).
3. R. Atkinson, J. N. Pitts, Jr., Chem. Phys. Lett. 63, 485 (1979); R. Atkinson, J. N. Pitts, Jr., J. Phys. Chem. 79, 295 (1975).
4. S. W. Benson, Thermochemical Kinetics, Wiley Interscience, New York (1976).
5. G. N. Lewis, M. Kasha, J. Am. Chem. Soc. 66, 2100 (1944).
6. V. N. Kondratiev, Rate Constants of Gas Phase Reactions, U.S. Department of Commerce, Washington, D.C. (1972).
7. G. R. H. Jones, R. J. Cvetanovic, Can. J. Chem. 39, 2444 (1961).
8. I. Mani, M. C. Sauer, Jr., Advances in Chemistry 82, 142 (1968).
9. R. Atkinson, J. N. Pitts, Jr., J. Phys. Chem. 78, 1780 (1974).
10. S. Furuyama, N. Ebara, Int. J. Chem. Kinetics VII, 689 (1975).
11. A. J. Colussi, D. L. Singleton, R. J. Cvetanovic, R. S. Irwin, J. Phys. Chem. 79, 1900 (1975).
12. E. Grovenstein, Jr., A. J. Mosher, J. Am. Chem. Soc. 92, 3810 (1970).
13. Gaffney, Atkinson, J. N. Pitts, Jr., J. Am. Chem. Soc. 98, 1828 (1976).
14. H. Akimoto, M. Hoshino, G. Inoue, M. Okuda, N. Washida, Bull. Chem. Soc. Japan 51, 2496 (1978).
15. R. T. Morrison, R. N. Boyd, Organic Chemistry, Allyn and Bacon, Boston (1973).

16. T. M. Sloane, J. Chem. Phys. 67, 2267 (1977).
17. S. J. Sibener, R. J. Buss, C. Y. Ng, Y. T. Lee, Rev. Sci. Inst. 51, 167 (1980).
18. C. U. Nowikow, R. Grice, J. Phys. E 12, 515 (1979).
19. Y. T. Lee, J. D. McDonald, P. R. LeBreton, D. R. Herschbach, Rev. Sci. Inst. 40, 1402 (1969).
20. R. Sparks, Crossed Beams Studies of Full and Half Collisions, Ph.D. Thesis, University of California, Berkeley (1980).
21. E. Stehhagen, S. Abrahamsson, F. W. McLafferty, Eds., Atlas of Mass Spectral Data, Wiley Interscience, New York (1969).
22. P. J. Robinson, K. A. Holbrook, Unimolecular Reactions, Wiley Interscience, London (1972); S. A. Safron, N. D. Weinstein, D. R. Herschbach, Chem. Phys. Lett. 12, 564 (1972).
23. M. Dupuis, W. Wendoloski, T. Takada, W. A. Lester, Jr., J. Chem. Phys. 76, 481 (1982).

FIGURE CAPTIONS: CHAPTER II

1. $O(^3P) + \text{toluene}$ energy level diagram. Heats of Formation at 300° in kcal/mole.
2. Mass 107, C_7H_7O product laboratory angular distribution.
3. Mass 91, elastic and Maxwell Boltzman toluene TOF; Mass 65, elastic and Maxwell Boltzman toluene TOF; C_6H_5O product TOF.
4. Mass 65 (C_5H_5) C_6H_5O product TOF, Mass 107 C_7H_7O product TOF, both at 60° in laboratory.
5. C_7H_7O product center of mass translational energy distribution. Solid line, experimental best fit. Cross hatched area, experimental error. Dotted line, statistical calculations.
6. C_6H_5O product center of mass translational energy distribution. Solid line, experimental best fit. Cross hatched area, experimental error. Dotted line, statistical calculations.

XBL 8211-3237

FIGURE 2-1

XBL 7912-13563

FIGURE 2-2

XBL 802-8223A

FIGURE 2-3

XBL 7912-13564

FIGURE 2-4

FIGURE 2-5

FIGURE 2-6

III. THE REACTION OF $O(^3P)$ WITH ETHYLENE

1. INTRODUCTION

The reaction of $O(^3P)$ with ethylene has received a great deal of attention during the last thirty years. In the set of experiments described here, studying the reactions of $O(^3P)$ atoms with unsaturated hydrocarbons, it occupies a prominent position as the prototypical oxygen + unsaturated hydrocarbon reaction. There are practical aspects to understanding the reactions of $O(^3P)$ with olefins as well, as these reactions are believed to be important participants in some combustion systems,¹ atmospheric models,² and in smog formation.³

From a purely scientific view, the reactions of $O(^3P)$ with olefins are exceptionally challenging and rich systems to study. The reactions are exceedingly fast, display some unusual kinetic features (i.e., apparent negative activation energies in some cases) and have proven difficult to characterize kinetically. The primary reaction products are rapidly reacting radical species whose identities have been difficult to determine. Finally, the open shell diradical structures characterizing the transition states and the open shell products are exceedingly difficult to handle theoretically.

In spite of (or perhaps due to the attractions of) these difficulties a large number of groups and techniques have been applied to the study of the reaction of $O(^3P)$ with ethylene, and not a few

controversies have developed through the years, most notably dealing with the identity of the primary products.

In this chapter we discuss the reaction of $O(^3P)$ with ethylene itself. The reactions with some substituted ethylenes are discussed later as a coherent reaction mechanism emerges.

2. REACTION ENERGISTICS

Before proceeding to a brief review of some previous results, the nominally relevant thermochemistry is presented in Figure 1. Without a doubt, $O(^3P)$ first adds to one side of the double bond creating a diradical. The heat of formation for that species is estimated to be 42 kcal/mole from Benson's rules.⁴¹ Only one diradical is shown, but in fact four different triplet diradicals with similar energies can be formed. If we regard one unpaired spin as residing in an oxygen p orbital (with the oxygen lone pair in another oxygen p orbital) and the other unpaired electron in an atomic p orbital centered on the terminal carbon, then the four possible configurations for triplet species arise from the four possible orientations of these spins, i.e., both out of the CCO plane, one in one out, etc. One of these triplets, the lowest energy triplet, correlates, through C-H single bond cleavage to ground state vinyloxy radical product. The next highest triplet correlates to the first excited state of vinyloxy. (A more detailed description of these species is presented later.)

In this system, like toluene, and as in all other $O(^3P)$ unsaturated hydrocarbon reactions we have studied, we believe that inter-

system crossing by the collision complex is a relatively slow process compared to the complex lifetime. This is based on our chemical intuition about these small species, some calculations reviewed later, and the fact that intersystem crossing need not be considered to fully explain our results.

The most stable products that conceivably could be formed from $O(^3P)$ and ethylene are ethylene oxide and acetaldehyde, and these have been proposed as intermediates in the reaction. However, formation of acetaldehyde, even an excited triplet state, requires a 1,2 C-C hydrogen migration on the triplet surface which is expected to have a potential energy barrier so large (~50 kcal/mole) that acetaldehyde formation is very unlikely. Ring closure to form triplet ethylene oxide is also energetically unlikely, and the singlet manifold is not under consideration. Ketene and H_2 are the last stable products that have been considered to be likely primary products. However, the 3 or 4 center elimination of H_2 is almost certainly accompanied by a prohibitively large potential energy barrier given the 15-25 kcal/mole excitation of the complex. If singlet acetaldehyde were formed, following intersystem crossing and a 1,2 H migration, then even a ~100 kcal barrier to the 3 center elimination could be surmounted, but lack of access to the singlet manifold again makes this unlikely. Then, by considering these various paths leading to possible stable products, we can say no stable products are likely.

The possible radical products include $CH_3 + CHO$, $CH_2 + CH_2O$, and $C_2H_3O + H$. $CH_3 + CHO$ product requires a 1,2 hydrogen migration on the triplet surface, prior to C-C bond cleavage and is unlikely

because of the large potential energy barrier to the 1,2 migration on the triplet surface. Formaldehyde and triplet methylene production is nearly thermoneutral. Any activation energy for the reverse reaction (not yet experimentally known) would imply a barrier in the exit channel for methylene + formaldehyde products, and an activation energy of more than ~10 kcal/mole would make this path energetically impossible as well. ($\text{CH}_2 + \text{CH}_2\text{O}$ is isoelectronic with $\text{O} + \text{CH}_2\text{CH}_2$ which has a several kilocalorie/mole barrier. Moreover, the addition of $^3\text{CH}_2$ to olefins is known to have a ~6 kcal barrier,⁴⁸ so a considerable barrier could be expected for $^3\text{CH}_2 + \text{CH}_2\text{O}$.) The most recent studies of $\text{O}(^3\text{P}) + \text{ethylene}$ do not consider this an important process. Finally, there is the single C-H bond cleavage route forming vinoxy radical and hydrogen atoms. A small ~5 kcal/mole barrier is presented in the exit channel to reproduce the known activation energy for the addition of H atoms to double bonded carbon atoms. That is, even though $\text{H} + \text{vinoxy}$ is a radical recombination, the radical center shifts away from the carbon that the hydrogen was initially bonded to, and the addition is like an addition to a double bonded carbon. Although there is a potential energy barrier in the exit channel, this barrier is small enough, given the diradical stability that the barrier should not inhibit the formation of $\text{H} + \text{vinoxy}$ products.

Some of the previous efforts directed at assessing the relative likelihood of these possible products are reviewed next.

3. PREVIOUS RESULTS

Various authors have reviewed $O(^3P)$ + ethylene kinetic experiments,⁴⁻⁶ here a rather brief overview is presented to display the wide variety of techniques used in these studies. In 1955 Cvetanovic⁹ attempted to determine the reaction mechanism from a final product analysis of a static system, and kinetic parameters from competitive experiments with n-butane. The stoichiometry of the reaction at negligible conversions is

It is extremely difficult to make unique and accurate inferences about what the identity of the primary products are, given the complexity of the final product mixture. Nonetheless, the mechanism developed by Cvetanovic⁶ (vide infra) apparently explained all the experimental data adequately until the last few years.

Following Cvetanovic's original work, a wide variety of methods have been used to study the kinetics of $O(^3P)$ + ethylene. Cvetanovic,¹⁰ again using mercury sensitized decomposition of nitrous oxide to produce oxygen atoms, and final product analysis, determined relative Arrhenius parameters for the reaction, in competitive experiments with cyclopentene. The first of several controversies revolving around this reaction started after Elias¹¹ measured the absolute rate constant in a fast flow system, where $O(^3P)$ was made in a low pressure discharge,

and the oxygen concentration was monitored by observing the emission from NO_2^* when NO was introduced into the system. While the rates Elias measured agreed with those of Cvetanovic, the Arrhenius parameters differed outside of the combined experimental errors. Cvetanovic had concluded that, in substituted olefins the A factors were essentially constant, and the different rates of reaction were due solely to changes in the activation energies. Elias believed that both the A factor and the activation energy were changing. Brown and Thrush¹² made oxygen atoms by titrating NO with N atoms made in a microwave discharge, and measured the rate constant in a fast flow system with electron spin resonance detection of the oxygen atom concentration. Niki, Daby, and Weinstock¹³ used the NO titration of N atoms as well, in a fast flow system, but used a time of flight mass spectrometer to measure the ethylene concentration in rate measurements. Westenberg and deHaas¹⁴ also used a fast flow system with esr detection to make absolute rate measurements, but incorporated an auxiliary mass spectrometer in their experiment. Cvetanovic returned to the kinetic problem, with Atkinson,¹⁵ and measured absolute rate constants in a modulation-phase shift experiment, using modulated mercury resonance radiation to sensitize the decomposition of N_2O to O atoms and observing the NO_2 afterglow phase shift following NO titration of the remaining O atoms. Stuhl and Niki¹⁶ used vacuum uv radiation to photolyze NO to produce oxygen atoms, and measured the absolute $\text{O} + \text{C}_2\text{H}_4$ rate by again monitoring the NO_2 chemiluminescence after NO titration. Huie, Herron, and Davis¹⁷ flash photolyzed O_2

to make oxygen atoms and looked at the resonance fluorescence from oxygen atoms in order to get an absolute rate in one experiment, and used a discharge flow system¹⁸ coupled to a mass spectrometer in another. In yet another set of experiments, Atkinson, Pitts, and Cvetanovic^{19,21} used their modulation experiment to obtain Arrhenius parameters, and established negative activation energies for the $O(^3P) + \text{tetramethylethylene}$ reaction. Kurylo and Huie²⁰ repeated flash photolysis-resonance experiments and argued that the experiments with chemiluminescent detection ($O + NO \rightarrow NO_2^*$ or $O + CO \rightarrow CO_2^*$) were systematically underestimating the rate constant. Finally Atkinson and Pitts²⁰ obtained Arrhenius parameters for ethylene and some other olefins in a flash photolysis- NO_2 chemiluminescence experiment. (Another more complete bibliography of the kinetic studies of this reaction is contained in their report.) The recommended value as of several years ago is $3.3 \times 10^{12} \exp(-1124/RT)$,⁴ while the most recent value of Atkinson and Pitts²² is $9.2 \times 10^{12} \exp(-1475/RT)$ cc/mole sec.

While the bimolecular rate constant was being determined, parallel studies were in progress to determine the reaction mechanism. The generally accepted mechanism as of several years ago is reviewed by Huie and Herron,⁷ Cvetanovic⁶, and Lin.⁸

The first experiments directed at determining the reaction mechanism were, of course, studies of the final product distributions obtained in static systems. Cvetanovic likened the final $O + \text{ethylene}$ product distribution to that from the thermal decomposition of ethylene oxide,⁹ and suggested that oxygen initially adds to one carbon, creating a diradical. Ultimately, Cvetanovic⁶ developed a complete

mechanism to explain the products he observed in the static gas experiments: Step 1, addition of $O(^3P)$ to the least substituted side of the C-C double bond where rotation about the former C-C double bond would be possible, and Step 2, unimolecular reactions of the excited adducts formed in the addition step. Several general unimolecular reaction types were proposed, (1) pressure independent fragmentation of the diradical adduct; either the oxygen would displace a group originally bound to carbon or the C-C bond would break, (2) ring closure to form a hot epoxide which would either fragment or be stabilized as a function of pressure or (3) 1,2 C-C migration of hydrogen or a radical group to form an excited carbonyl which would either be stabilized or fragment as a function of pressure. In particular, Cvetanovic estimated that less than 10 percent of the reaction products were formed by pressure independent fragmentation of the O-ethylene adduct, to give $CH_2CHO + H$. Brown and Thrush¹² used the overall stoichiometry and the yield of hydrogen atoms to assess the reaction mechanism, did not consider that hydrogen atoms might be primary products, and decided that the primary products of the reaction were most likely CH_3 and CHO .

Scheer and Klein²³⁻²⁵ observed the final products formed in the low ($\sim 100^\circ K$) temperature reactions of $O(^3P)$ with butenes and pentene and proposed an interestingly different intermediate. Rather than an open diradical structure, they found it necessary to propose a rigid intermediate (shown below for cis and trans 2-butene) to explain the conformations of the products they observed. Cvetanovic,²⁶ however,

argued that such structures were unnecessary, and little or no mention of them has appeared since.

By the end of 1970 there was general agreement that the initial addition of $O(^3P)$ to ethylene resulted in the 1,2 open diradical. However, the primary products of the diradical's decomposition were still uncertain. At the 12th International Symposium on Combustion, Niki et al., argued that CH_3 and CHO were the most likely major products by arguing against the formation of CH_2 and CH_2O , then considered the other most likely candidates. The large H atom and CH_2O yields in the Niki experiment were ascribed to the secondary reactions $O + CH_3 \rightarrow CH_2O + H$ and $O + CHO \rightarrow CO_2 + H$. Westenberg and deHaas however, argued on the basis of the large H_2CO production in their experiment, and the absence of formaldehyde in $O + CH_4$ systems (where $O + CH_3$ would be expected) that formaldehyde and CH_2 were the important primary products.

More straightforward attempts to determine the primary products of $O(^3P)$ -olefin reactions have been made using either very low pressure mass spectrometric or crossed molecular beam mass spectrometric techniques. Gutman et al.,^{27,28} crossed high intensity molecular beams and used photoionization mass spectroscopy to identify

products. They observed major CH_3^+ , CHO^+ , and $\text{C}_2\text{H}_2\text{O}^+$ signals, noted that any CH_2^+ was less than .07 of the CH_3^+ signal, that any $\text{C}_2\text{H}_3\text{O}^+$ signal was less than .25 of the $\text{C}_2\text{H}_4\text{O}^+$ signal and concluded that two channels were important, formation of CH_3 and CHO , and formation of ketene and H_2 . In a later experiment, using a fast flow system with photoionization detection as well, the absolute rate of the overall reaction, and the ketene formation rate were measured. Gutman, assuming no other important primary processes, arrived at a branching ratio of .95 for $\text{CH}_3 + \text{CHO}$, and .05 for $\text{H}_2 + \text{C}_2\text{H}_2\text{O}$. In an independent set of experiments³⁰ Blumenberg, Hoyer mann and Sievert used a crossed free jet arrangement and a laval nozzle reactor to identify products and determine product branching ratios. Controlled ionization energy mass spectroscopy was employed in these experiments also, but here a narrow energy spread (.3 ev in 4.5 to 70. ev) electron beam was the ionization source. The results were essentially identical to Gutman's. These last two experiments have been regarded as definitive,⁸ and in essentially complete agreement with the Cvetanovic mechanism. Bogan³⁸ has further supported these conclusions in a calculation of the reactive branching ratios using an energy limited phase space calculation. This calculation, however, considered only the formation of H_2 and ketene, CH_2 and formaldehyde, and $\text{CH}_3 + \text{CHO}$.

While these last experiments, conducted under near single collision conditions, are much better suited to determining the primary products, they still suffer from several drawbacks that were not considered as carefully as they might have been.

First, these experiments are not truly single collision experiments. Even in Gutman's crossed beam arrangement, attenuation of the oxygen beam is on the order of 50 percent, and secondary collisions are possible.

Second, there are some complications in the mass spectrometry of the reaction products. As we have seen in the reaction of $O + \text{toluene}$, and as we shall see in the $O + \text{olefin}$ reactions, radical products dominate. Moreover, some of these radical products are formed with 10's of kcal/mole internal excitation. Taken together, ions may be formed from neutral reaction products at unusually low ionization potentials, compared to ionization potentials of known stable species, and appearance potentials may be misleading as an aid in product identification. Closely related to this problem is the extensive fragmentation some radicals undergo during ionization. In our mass spectrometer less than .02 of the ions formed from vinoxy radical are parent ions. (Others have reported essentially no parent ion from vinoxy.)^{31,32} Trying to determine whether a neutral radical is produced, by looking for parent ions then, can also be misleading. (Photoionization techniques were thought to minimize fragmentation, but in fact, vinoxy will yield CH_3^+ even with photoionization.)⁵² A final mass spectrometric problem is the non-uniqueness of appearance potentials in chemically complicated systems. 10.2 eV H Lyman α radiation will ionize CH_3 to CH_3^+ but the appearance of CH_3^+ at this energy²⁷ in a study of $\text{U}(^3\text{P}) + \text{ethylene}$ does not unambiguously confirm CH_3 neutral product, since vinoxy will also dissociatively ionize to yield CH_3^+ at 10.2 eV.

Third, and finally, these previous mass spectrometric-crossed beam experiments used a fixed detector arrangement. In any given orientation of beams and detector, the detection efficiency for various products varies due to kinematic factors. As an example, in Gutman's experiments the detector looks straight into the oxygen beam. Neglecting the appreciable spread in velocity and space of the beams, with the beams crossing at 90° , the center of mass velocity will be $\sim 30^\circ$ from the oxygen beam. Any product formed either as a stabilized (sans collisions) O-ethylene adduct, e.g. oxirane, or by the emission of a very light particle, e.g. vinoxy, will travel predominately in the direction of the center of mass velocity, while products formed by the emission of a relatively heavy particle, say CH_3 and CHO , will be much more widely scattered. The detector looking towards one beam is clearly biased towards some products (in the example, CH_3 and CHO) merely as a function of the kinematics. These effects can be accounted for correctly, and some mention was made of their possible importance,²⁹ but careful considerations were absent.

Gutman's and Blumenberg's results, $.95 \text{ CH}_3 + \text{CHO}$, $.05 \text{ H}_2 + \text{ketene}$, must be questioned in view of what we believe about the potential energy surfaces involved. In particular a 1,2 C-C hydrogen (or alkyl) group migration on a triplet surface (prior to C-C bond cleavage) is unlikely. We also expect a prohibitively large potential energy barrier to be associated with the 3 center²⁸ elimination of H_2 . If a crossing to the singlet manifold occurs, then the 1-2 migration is possible, but one must question the facility of the triplet to singlet inter-system crossing. Finally, the single C-H bond cleavage might be

expected to be at least competitive with these other channels, with no prohibitively large potential energy barriers, but no evidence for the importance of that channel has been obtained.

During the last five years a number of theoretical studies related to the $O(^3P) + \text{ethylene}$ reaction have been carried out. Most of these have been directed at understanding the geometry and electronic structure of the diradical intermediate.

Bader, Stephens, and Gangi³³ did SCF calculations of the additions of both $O(^1D)$ and $O(^3P)$ to ethylene. They found the addition of $O(^1D)$ to ethylene to be symmetric, concerted and yielded an excited ethylene oxide. The addition of $O(^3P)$ was asymmetric, the terminal methylene symmetric with respect to the CCO plane, an OCC angle of 105° , a relatively low barrier to rotation about the C-C bond, ~ 5 kcal, and lastly they found the lowest intersystem crossing from the triplet manifold of the diradical to lie 36 kcal/mole above the reactants' level. Baird, Gupta, and Taylor^{34,35} have published several studies of the applicability of "standard MO" level calculations for the predictions of free radical geometry, using systems isoelectronic with allyl as examples. Unfortunately, they were able to show that quite sophisticated calculations are required not only for the energetics of these species but for geometrical calculations as well--in contrast to calculations for closed shell species.

Bigot, Sevin, and Devaquet have considered³⁶ both a one and a two step formation of ground state ethylene oxide from $O(^3P)$ and ethylene, at the SCF STO-3G with limited configuration interaction level. The one step concerted addition required 23 kcal/mole activa-

tion energy, then intersystem crossing to an excited oxirane state, and can be ruled out as a possible process due to the large entrance barrier. However, their calculations for a two step process, first forming the CCO diradical, then closing the ring, indicate that singlet and triplet configurations are mixed so much in the diradical that ring closure to the oxirane ground state is possible. This calculation however, yields an 18 kcal/mole barrier to formation of the diradical, in marked contrast to experiment.

Finally, Yamaguchi et al.,³⁷ obtained optimized geometries for ring opened oxirane by their method of energy gradients at the UHF MINDO/3, STO-3G, and 4-31G levels. With their geometries, they obtained relative energies for the various diradicals, and a low barrier to rotation about the carbon-carbon bond. Yamaguchi speculated that intersystem crossing from triplet to singlet diradical might be facile, because the two p orbitals containing the unpaired spins are nearly orthogonal in the lowest triplet state, but gave no estimate of how high up on the ground state surface that crossing might be expected.

To summarize the previous experimental results, the generally accepted products of $O(^3P) + C_2H_4$ were .95 $CH_3 + CHO$, .05 $H_2 + C_2H_2O$, even though each channel should encounter significant potential energy barriers. Little importance was attached to $H + C_2H_3O$ products, while only a small barrier, at most, might be expected for a single bond cleavage route leading to $H +$ vinoxy products.

4. EXPERIMENTAL

The reaction of $O(^3P)$ with ethylene was studied at two different collision energies, and on two different machines. Our first experiment was performed at 8.3 kcal/mole collision energy on the 25" universal crossed beams machine. For this experiment, 200 watts of radio frequency power was discharged through 200 torr of a 5 percent oxygen in helium mixture. After expanding through a .007" nozzle the resulting beam was skimmed and collimated just as that reported for the $O + \text{toluene}$ experiment. This oxygen beam had a V_0 of 2.4×10^5 cm/sec and a speed ratio of 5.94.

Neat ethylene at ~400 torr was run through the same beam source that was used in the toluene experiment for the toluene beam, but the gas line was maintained at room temperature. This ethylene beam had a V_0 of 8.03×10^4 cm/sec and a speed ratio of 5.87.

The mass 42 signal at 30° from the oxygen source, near its peak, was nearly 800 counts/sec, and error bars such as those shown in Figure 2 were obtained by taking at least five 100 second counts at each angle. Cross correlation time of flight distributions, 12 microseconds per channel, of the mass 42 product signal were obtained at seven different laboratory angles, requiring counting times of 1 hour per angle.

The mass 15, 27, 29, 42, and 43 angular distributions at a collision energy of 8.3 kcal/mole were remeasured some time later on our 35" universal crossed beam machine. Counting times for the distributions shown below range from four 100 second counts/angle for mass 42 (~400 counts/second) to more than twenty 66 second counts/angle for mass 15 (~377 counts/second).

The mass 15, 27, 29, 42, and 43 angular distributions, as well as mass 42 cross correlation TOF distributions, were also obtained at a collision energy of 5.4 kcal/mole by using an oxygen in neon discharge source (with the 35" machine). 260 watts of power was discharged through 600 torr of a 5 percent oxygen in neon mixture prior to expansion through a .004" nozzle to obtain an oxygen atom beam with a $V_0 = 1.91 \times 10^5$ cm/sec and a speed ratio of 6.43. The ethylene beam was neat (250 torr) and at room temperature (as before) with a $V_0 = 8.09 \times 10^4$ cm/sec, speed ratio = 6.35.

The mass 42 low energy angular distribution shown below is the result of at least four 200 second counts per angle, while the mass 15 angular distribution represents twenty 200 second counts at each angle. In this experiment, at the peak of the mass 42 distribution $\sim 40^\circ$ away from the oxygen beam, there were ~ 140 counts/sec of mass 15 signal and ~ 140 counts/sec of mass 42. Ten microsecond per channel cross correlation time of flight of mass 42 signal was obtained at seven laboratory angles, requiring as much as six hours counting at each angle.

5. IDENTIFICATION OF PRIMARY PRODUCTS

A. ON THE FORMATION OF VINOXY AND KETENE

Figures 2 and 3 shown the mass 42 angular distributions at 8.3 and 5.4 kcal/mole. The mass 43 angular distributions were superimposable on these with in error bars, although that signal was much weaker and the error bars larger. Since the mass 42 and 43 distributions are identical, both the mass 42 and 43 ions are formed from

the same neutral primary product. The relative strength of the mass 42 signal, coupled with previous results, would seem to indicate that ketene is really the primary product, and the mass 43 signal we see is due to ^{13}C and ^2H isotopic impurities in same. However, it is also possible that the mass 43 signal is the parent ion, a $\text{C}_2\text{H}_3\text{O}$ primary product, that fragments extensively when ionized. Were ketene product formed, the mass 43 intensity would be $\sim .022$ of the mass 42 (based on ^{13}C and ^2H natural abundances). However, repeated measurements of the 43/42 intensity, under high resolution conditions to avoid any meaningful mass spectrometric crosstalk, gave $43/42 = .054 \pm .013$ in the helium seeded experiment and $43/42 = .050 \pm .009$ in the neon seeded experiment. In each experiment there was more than twice as much 43 signal than what could be expected due to isotopic impurities in ketene. This proves that the mass 42 signal is in fact a daughter ion of a parent $\text{C}_2\text{H}_3\text{O}$ neutral primary product. We initially favored CH_2CHO rather than CH_3CO for the structure of this product due to the large barrier expected for 1,2 C-C hydrogen migration on the triplet surface. This structure has now been firmly established spectroscopically (vide infra).

B. ON THE FORMATION OF CH_3 AND CHO

Even though it seems unlikely that CH_3 and CHO would be formed as primary products in this reaction, the repeated reports of these products made it attractive for us to study. Ideally a search for these products entails looking for reactively scattered signal at masses 15 and/or 29. However, the situation is complicated due to

dissociative ionization of ethylene and vinoxy, the C-H single bond cleavage product. Both of these neutrals will fragment to give ions of masses 15 and 29, so even in the absence of CH_3 and CHO product there would be both a reactively scattered and elastically scattered contribution to the mass 15 and 29 angular distributions.

However, we still can search for a third (second reactive) contribution in the mass 15 or 29 angular distributions. At any given angle of the mass 15 or 29 angular distribution, the fraction of the signal due to dissociatively ionized elastically scattered ethylene can be obtained by measuring the 15/27 or 29/27 ratios with the oxygen plasma on and off. For example, with the oxygen plasma cold (or equivalently by obtaining a mass spectrum of the ethylene source itself) in the neon seeded experiment we find $15/27 = .0049 \pm .0001$ and $29/27 = .0342$, while at 320° with the oxygen plasma hot $15/27 = .0098 \pm .0008$ and $29/27 = .0421 \pm .0003$. Thus we find that at 320° .504 $\pm$.043 of the mass 15 signal and .812 $\pm$.005 of the mass 29 signal is due to elastic scattering. Similarly we find .98 of the mass 29 and .90 of the mass 15 to be elastically scattered at 290° in the 8.3 kcal/mole experiment. The mass 42 angular distribution represents the vinoxy radical product alone, while the purely elastically scattered ethylene distribution is obtained from the mass 28 (or 27) angular distribution. Knowing what fractions of the mass 15 and 29 angular distributions are due to elastic scattering at a given angle, we assume for the moment that the only reactive contribution to the 15 and 29 signals is from vinoxy. Then the mass 42 and 27 distributions can be scaled to properly reproduce the elastic fraction, and summed

to provide a predicted mass 15 or 29 angular distribution in the absence of a second reactive component. If this predicted distribution accounts for the mass 15 and 29 signals observed, i.e., if no third contribution is apparent, then we can be sure that CH_3 and CHO are not primary products of the reaction.

In Figures 4 and 5 the mass 42 distributions are reproduced along with the purely elastically scattered mass 27. Below them are the mass 29 and 15 distributions, with curves obtained assuming that only vinoxy and ethylene contribute to the signals as discussed above. While the fits are much better for the low energy experiment, for the most part, the predicted distributions lie within the error bars of the observed distributions. There is some residual mass 15 at angles beyond 370° and some residual 29 near 340° and 300° in the high energy experiment. However, the shapes of these small residual signals do not support their identification as evidence of mass 15 or 29 primary products. The 15 lies completely to one side of the center of mass and implies that the 29, if from CH_3 and CHO , should lie completely on the other side of the center of mass angle, which is not the case. We conclude that our experimental observations are accounted for completely on the basis of vinoxy and ethylene contributing to the mass 15 and 29 angular distributions, and that if CH_3 and CHO are formed as primary products, that channel is relatively unimportant.

6. RELATIVE CROSS SECTIONS

Our experiments reveal evidence for only one set of primary products in the reaction of $O(^3P)$ and ethylene, vinoxy radical and hydrogen atom. We would like to estimate how large, relatively, the cross sections for ketene + H_2 and $CH_3 + CHO$ could be, given our experimental results. Of the various factors that affect our observed signal intensity mentioned in the relative cross section calculations for toluene, for these crude estimates we consider only the actual cross section ratio (σ), ionization efficiency (assumed proportional to the square root of the polarizability)(α), fragmentation patterns (f), and kinematic factors (k).

$$\frac{\sigma_1}{\sigma_2} \cdot \frac{\alpha_1^{1/2}}{\alpha_2^{1/2}} \cdot \frac{f_1}{f_2} \cdot \frac{k_1}{k_2} = \frac{\text{obs inten}_1}{\text{obs inten}_2}$$

First we have to estimate just how much signal from a given channel could have appeared in these experiments. We believe that the mass 42 signal we observe comes solely from the fragmentation of vinoxy radical at both 8.3 and 5.4 kcal/mole. A liberal estimate then, puts the observed mass 42 from ketene, at any angle, at $\sim .05$ of the peak intensity from vinoxy in both experiments. In the 8.3 kcal experiment we can say that mass 29 from HCO at any laboratory angle must be less than .2 of the 29 from vinoxy at 330° , and that the 15 from CH_3^+ at any angle must be less than .08 of the 15 from vinoxy

at 330°. In the 5.4 kcal experiment, 29 from CHO at any angle must be less than .2 of the 29 from vinoxy at 320° and the 15 from CH₃ at any angle must be less than .08 of the 15 from vinoxy at 320°.

In order to estimate the cross sections, an estimate of the cracking pattern of the relevant species is required. Published mass spectra³⁹ of ketene indicate that .3 of the total ions formed are parent ions. Nearly .90 of the ions formed from methane³⁹ have either mass 15 or 16, so we estimate that .4 of the CH₃ ions appear at mass 15. Finally, we estimate that 1/3 of the ions from CHO are parent ions. Our measurement in the O + ethylene reaction indicate that vinoxy fragments to give intensities 43 : 42 : 29 : 15 of .05 : 1. : .45 : .55. Assuming that ~2/3 of all ions formed appear at these masses, then fractional yields of 42, 29, and 15 from vinoxy are .32 : .15 : .18. For these calculations, suitable estimates of the polarizabilities of the neutrals may be obtained merely by summing the atomic polarizabilities. This method gives 2.2 Å³ for CHO and CH₃, 4. Å³ for C₂H₃O and 3.6 Å³ for ketene.

By far the most important factor in estimating the relative cross sections for these channels that have very different ratios of separating masses, is the kinematic effect on our detection sensitivity. Kinematic factors for vinoxy radical were those from the best fit analysis described below. Kinematic factors for ketene product were estimated by assuming that triplet ketene would be formed, with an isotropic center of mass angular distribution and a broad center of mass translational energy distribution, peaking at ~19 kcal/mole, with roughly a 18.5 kcal/mole average. This broad distribution was deemed

appropriate due to the expected exit channel barrier for a 3 center H_2 elimination. Kinematic factors for $CH_3 + CHO$ were estimated assuming an anisotropic forward-backward peaking center of mass angular distribution, [$T(0^\circ) = T(180^\circ) = 2T(90^\circ)$]. The $P(E')$ for this channel was designed to imitate one expected for the single C-C bond cleavage without an exit channel barrier (no activation energy expected for the $CH_3 + CHO$ recombination), peaking near 0 kcal/mole, decreasing monotonically with energy, having an average of ~ 8 kcal/mole. To illustrate the dominating nature of these effects Figure 6 shows the relative signal intensities expected for these three channels (four products) if they all had the same cross section (no other factors effecting detection efficiency included). Using these values we can put upper bounds on the relative cross sections as follows

$$\sigma_H/\sigma(CH_3 + CHO) \geq 1, \quad \sigma_H/\sigma(ketene + H_2) \geq 7.$$

There is only a very small difference in the limits at the two collision energies.

Production of vinoxy and hydrogen then certainly dominates formation of H_2 and ketene. However, we cannot rule out a significant cross section for $CH_3 + CHO$ from our experimental data, unlikely as that process may be, requiring a 1,2 C-C hydrogen migration on the triplet surface.

7. DYNAMICS OF VINOXY RADICAL FORMATION

The low collision energy angular distribution and TOF data for vinoxy product shown in Figures 3 and 7 is fit best with an isotropic center of mass angular distribution and the translational energy distribution shown in Figure 8. The poor fit at the extremes of the

angular distribution is due either to a high translational energy component in the oxygen beam, not modeled accurately in the calculation, or a contribution to vinoxy product from the small fraction of $O(^1D)$ in the beam. The translational energy distribution is very broad, peaking at ~ 12 kcal/mole, falling away only at the thermodynamic limit at ~ 23 kcal and represents, on average 11.5 kcal/mole deposited into translation.

The high energy data, Figures 2 and 9 are fit best with the slightly anisotropic center of mass angular distribution shown in Figure 10, and the center of mass translational energy distribution shown in Figure 11. This translational energy distribution is very similar to that required to fit the low energy data, though shifted to slightly higher energies, with the best fit average of 13.2 kcal/mole. The center of mass angular distribution is skewed to the forward direction (with respect to oxygen) with a $0^\circ/180^\circ$ ratio of ~ 1.7 , while peaking at $\sim 70^\circ$.

Phase Space and RRKM-AM calculations were performed to obtain estimates of the lifetime and translational energy distributions for a statistical decay of the O-ethylene diradical.

In the RRKM-AM model, the geometry of the diradical was taken from Dupuis' calculation⁴⁰ (C-C length 1.5 Å, C-O length 1.4 Å, C-C-O angle 113.5°), and the diradical vibrational frequencies were essentially the same as his as well. Since either of two hydrogen atoms could be eliminated, the reaction path degeneracy is 2.

An A factor for the unimolecular decay was estimated by analogy with the reaction $C_2H_5 \rightarrow C_2H_4 + H$. The A factor for that reaction is $\sim 10^{13.4}$, implying a ΔS of activation of .4 gibbs. However, there is an important difference between the loss of H from ethyl radical and the loss of H from the O-ethylene diradical. When H departs from ethyl, the C-C double bond starts to form and an internal rotation is lost in the transition state. As H starts to depart from the O-ethylene diradical, a C-O double bond is starting to form and there is no loss of internal rotation. A net loss of 2.6 gibbs can be attributed to the loss of internal rotor (loss of 3.3 gibbs for the 1 internal rotor, but it is replaced by an $\sim 500\text{ cm}^{-1}$ torsional vibration, $\sim .7$ gibbs at 300°) so a ΔS of activation of ~ 3 gibbs could be expected for the reaction $CH_2CH_2O \rightarrow H + CH_2CHO$. A simple model of the transition state kept roughly the same geometry, lost one C-H vibration (as the reaction coordinate) and varied a 1491 and 1193 cm^{-1} vibration until the required ΔS was achieved (final frequencies of 338 and 225 cm^{-1}). C_6 constants were estimated by using the known polarizabilities of O, H, and ethylene, using bond additivities (plus an additional contribution for a C 2p electron) to estimate the polarizability of vinoxy, and the relationship between polarizabilities and C_6 constants given by Hirschfelder.⁴² (Entrance channel C_6 of 1280 kcal Å⁶, exit channel C_6 of 523 kcal Å⁶.) vibrational frequencies of the vinoxy product, (required for the phase space calculation) were estimated by analogy with stable molecules. The thermochemical estimate of the diradical's heat of formation was used in the RRKM-AM calculations (30 kcal/mole stable with respect to O + ethylene), and the thermochemical value of -15 kcal/mole was used

for the overall reaction exothermicity. However, to estimate the lifetime of the O-ethylene diradical the decomposition was assumed to occur to a level ~ 5 kcal/mole above the products energy level (assuming total exit potential energy barrier of 15 kcal/mole).

The lifetime of the O-ethylene diradical was calculated to be .55 picoseconds with internal excitation corresponding to the 5.4 kcal/mole experiment and .30 picoseconds for the 8.3 kcal/mole experiment. The translational energy distributions calculated by the two methods were identical, and are also shown in Figures 8 and 11. These distributions are much narrower than the experimental, indicating an average of only 3.8 and 4.2 kcal/mole in translation for the 5.4 and 8.3 kcal experiments. Since the diradical lives for a long time, on a vibrational time scale, and because, as mentioned earlier, a barrier is expected in the exit channel for this C-H single bond cleavage, we take the observed excess energy in translation to be a manifestation of the exit channel potential energy barrier.

Lack of forward-backward symmetry in the center of mass angular distribution indicates that reaction products are separating, on the average, prior to a complete rotational period of the complex. A typical rotational period of the O-ethylene complex can be estimated by first obtaining the average impact parameter for the collisions. Average impact parameters of 2.1 Å and 2.3 Å were used at 5.4 kcal and 8.3 kcal. Given the average impact parameter, then the rotational period of the complex may be estimated by setting $(1/2)I\omega^2 = h^2/8\pi^2I [J(J+1)]$ with $J = 2\pi\mu vb/h$. In this way the rotational period at 5.4 kcal/mole is estimated to be .75 psec and .53 psec at 8.3 kcal/mole. Using the

RRKM-AM results, this means that on the average, complexes live for ~ 0.75 of a rotational period at 5.4 kcal/mole and for ~ 0.55 at 8.3 kcal/mole. The center of mass angular distributions indicated that at 5.4 kcal/mole the complex had a lifetime on the order of a rotational period while at 8.3 kcal the decay was becoming faster than a rotation. While not too much faith should be put on the absolute results of these RRKM-AM calculations, they certainly seem to indicate that the lifetime of the complex does go from a comparable to a sub-rotational period as the collision energy goes from 5.4 to 8.3 kcal/mole. A further argument for the presence of an exit channel potential energy barrier can be made on the basis of these lifetime calculations, since these (apparently appropriate) lifetimes are obtained by assuming that the diradical decomposes to a level ~ 5 kcal above the products' actual level.

8. FORMATION OF CH_3 AND CHO : SUMMARY

Conspicuous by their absence from the review of previous experiments were three experiments by Kleinermanns and Luntz,⁴⁴ Inoue and Akimoto,⁴⁵ and Hunziker, Knepe and Wendt,⁴⁶ as well as a set of calculations by Dupuis, Wendoloski, Takada, and Lester, Jr.^{40,47} These studies occurred simultaneously with our experiments and were at least in part inspired by our initial report of vinoxy product from the reaction of $\text{O}(^3\text{P}) + \text{ethylene}$.⁴⁹

Inoue and Akimoto⁴⁵ reported the first laser induced single vibronic level fluorescence of the CH_2CHO radical. Vinoxy was made by at least five different routes, including the mercury sensitized decomposition of ethylvinylether, the reaction of fluorine atoms with

acetaldehyde, and the reaction of $O(^3P)$ with ethylene. The same LIF spectrum was obtained in each case, and was clearly not that of CH_3CO . (Corresponding emission was observed for $Xe^* + \text{ethylvinylether}$.) Four strong peaks were measured in the excitation spectrum, the O-O band (at 28789 cm^{-1}) and excitation to 3 vibronic origins, $v_3 = 432$, $v_1 = 872$, and $v_2 = 1110\text{ cm}^{-1}$. The v_1 and v_2 vibrations were characterized as local C-O (v_1) and C-C stretches. In the ground electronic state, $v_1 = 1561$, $v_2 = 1155$, and $v_3 = 533\text{ cm}^{-1}$. These vibrational frequencies were used to estimate the C-C and C-O bond orders in the ground and excited states, so as to assess the relative importance of the two structures below, which contribute equally in the isoelectronic allyl radical, but were expected to contribute non-equally after the heteroatom introduction.

The C-O bond order in the ground state was 1.74, with a C-O distance of $1.27\text{ \AA}$, indicating that in the ground state the $C=O$ structure dominates. The significant decrease in v_1 in the excited state indicates a significantly lower C-O bond order.

Kleinermanns and Luntz⁴⁴ did a laser induced fluorescence study of CH_2CHO produced in crossed molecular beam reactions of $O(^3P)$ with several olefins. The same three vibrational bands that Inoue and Akimoto observed were seen by Kleinermanns and Luntz in the $O(^3P) + \text{ethylene}$, $O(^3P) + \text{propylene}$, and $O(^3P) + \text{butene}$ reactions. Kleinermanns and Luntz were able to put upper limits on the amount of vibrational

excitation in the CH_2CHO products formed in the reaction, for the three optically accessible modes, and found that very little energy was deposited therein. (Upper limit of observed density $< .05$ for $\nu_i'' = 1$ $i = 1, 2$ or 3 .) Much less energy was deposited into vibrations than that predicted by a statistical model (i.e., $.94$ for $\nu_3'' = 1$). Some evidence was presented to support the possibility that some vibrational excitation occurs in the non-optically accessible modes. Finally, they found that the dynamic thresholds for CH_2CHO production (~ 1 kcal/mole) were not equal in all cases to the reported activation energies, implying that CH_2CHO is formed independently from the processes leading to the electrophilic addition products observed in the experiments leading to the accepted kinetic parameters.

Dupuis^{40,47} et al., have done ab initio multi-configuration hartree fock calculations to characterize the addition of $\text{O}(^3\text{P})$ to ethylene as well as to describe the electronic states of vinoxy. In their study of the $\text{C}_2\text{H}_4\text{O}$ diradical they obtained geometries, vibrational frequencies and relative energies for the eight various diradical states, as well as a description of the addition transition state. The transition state was again found to be asymmetric, O attaching to one of the carbons at a $\sim 107^\circ$ CCO angle. The CCO plane is maintained as a symmetry plane throughout the reaction. Labeling p orbitals as σ if they lie in the CCO plane and π if they lie out of the CCO plane, then the ordering of the triplets was found to be lowest $^3\text{A}'(\sigma, \pi)$, next lowest $^3\text{A}''(\pi, \pi)$, then $^3\text{A}''(\pi, \sigma)$ and highest $^3\text{A}'(\sigma, \sigma)$. (First character σ or π refers to the unpaired spin on the methylene

carbon, second character to the spin on the oxygen atom.) An energy range of only ~2 kcal/mole covers the entire range of four energies. A vibrational analysis of the $^3A''(\sigma, \pi)$ state was also presented.

Dupuis' study of the vinoxy radical predicted the relative energies of the lowest two states of A'' symmetry and the relative energy of the lowest A' state. The necessity of including polarization functions to distinguish between $C=C$ and $C=O$ structures was stressed. The lowest state of vinoxy and the first excited state of A'' symmetry (in C_s) are mixes of the ethenyloxy and formylmethyl radicals shown below. The ground state resembles formylmethyl more than the ethyleneoxy, as formylmethyl is the lower energy structure.

A third intermediate energy level has a $C-C$ double bond, the oxygen lone pair out of the CCO plane and has A' symmetry. The A'^2A'' state was calculated to be 74 kcal($25,800\text{ cm}^{-1}$) above the X state, and the best estimate of the energy of the A' state was between .9 and 1.25 eV above the X state ($\sim 8000\text{ cm}^{-1}$).

Finally Hunziker, Knepe and Wendt⁴⁶ studied the spectroscopy of O -olefin reactions using a photochemical modulation technique, in a static system from 40 to 760 torr. Hunziker observed two electronic transitions in vinoxy, one at $3477\text{ \AA}$ ($28,800\text{ cm}^{-1}$) and one at .99 eV (7960 cm^{-1}). Both the C_2H_3O and CHO yields from $O + \text{ethylene}$, propylene and butene were measured. The CHO yield in $O + \text{ethylene}$ was ~.55 and

the CH_2CHO yield was .36 over the entire 40-760 torr pressure range. Hunziker showed that with these yields, Cvetanovic's original final product distribution could be accounted for. The $\text{C}_2\text{H}_3\text{O}$ yield for $\text{O} + \text{propylene}$ showed a marked pressure dependence, going from .18 at 40 torr to ~.3 at 760 torr, while the $\text{C}_2\text{H}_3\text{O}$ yield from butene was constant at .18. From this pressure dependence Hunziker was able to surmise that there were two CH_2CHO formation mechanisms in the reactions of $\text{O}(^3\text{P})$ with olefins, one operating independent of pressure, one pressure dependent, and saturating below 40 torr in the oxygen-ethylene system.

A coherent mechanism explaining all the recent experiments has been offered independently by Luntz and Dupuis. We note first that the observed electronic transitions in vinoxy are certainly those corresponding to the $X^2A'' \rightarrow a^2A'$ and $X^2A'' \rightarrow A^2A''$ transitions calculated by Dupuis. The salient features of the mechanism must explain the product forming processes that form only $\text{H} + \text{CH}_2\text{CHO}$ in the absence of collisions, form H and CH_2CHO by two different mechanisms in the presence of collisions, and may allow a path to $\text{CH}_3 + \text{CHO}$, etc., in a multiple collision environment.

Referring to Figure 12, an expanded energy level diagram, we recall that four different triplet diradicals may be formed from $\text{O} + \text{ethylene}$. The barrier to rotation about the former C-C double bond is small, so the $^3A''(\sigma, \pi)$ may easily convert to $^3A'(\pi, \pi)$ and $^3A''(\pi, \sigma)$ may convert to $^3A'(\sigma, \sigma)$. If total electronic symmetry is retained in the C-H single bond cleavage process, then we would expect $^3A''(\sigma, \pi)$ to correlate to the X^2A'' , $^3A''(\pi, \sigma)$ to the A^2A''

and $^3A'(\sigma, \sigma)$ to the $^2A'$ state of vinoxy. If $^3A''(\sigma, \pi)$ is formed initially, C-H bond cleavage would lead to ground state vinoxy, exothermic by ~ 15 kcal/mole. A potential energy barrier of ~ 5 kcal/mole is shown in the exit channel, on the basis of our translational energy distribution. (We note that in accord with the excess energy in translation we find, Luntz found much less vibrational energy than that expected statistically.) If the $^3A'(\pi, \pi)$ state is formed, rapid rotation about the C-C bond will take it into the $^3A''(\sigma, \pi)$ where C-H bond cleavage could take place. However, when either the $^3A''(\pi, \sigma)$ or $^3A'(\sigma, \sigma)$ states are formed, the only channel available is the reformation of reactants, since only for collision energies in excess of 8 kcal/mole (more if an exit channel potential energy barrier exists) is dissociation by $^3A''(\pi, \sigma)$ to the $^2A'$ of vinoxy energetically possible. If this diradical has a long enough lifetime prior to dissociation to $O(^3P) + \text{ethylene}$, then in a multiple collision environment, it may suffer collisions, and undergo collision assisted intersystem crossing. From the singlet manifold of the diradical, C-H single bond cleavage to give C_2H_3O should still be feasible (a second vinoxy route) and 1,2 C-C hydrogen migrations leading to CH_3 and CHO would be facile. Ring closure (to ethylene oxide) and stabilized aldehyde would also be possible.

One remaining question then, is whether the $^3A''(\pi, \sigma)$ diradical has a long enough lifetime to undergo a collision prior to redissociation to $O(^3P) + \text{ethylene}$ at 40 torr, as Hunziger's results show. To investigate this another RRKM-AM calculation was done on the O -ethylene diradical, considering its dissociation to $O(^3P) + \text{ethylene}$.

The diradical was modeled just as for the dissociation to $H + CH_2CHO$. The A factor for $C_2H_5 \rightarrow C_2H_4 + H$ is $10^{13.5}$. In the $C_2H_3O \rightarrow H + C_2H_4$ reaction an internal rotation is lost as in the ethyl radical decomposition so that A factor need be corrected only for the loss of a heavier atom. A factors for processes $X - CH_3 \rightarrow X^\cdot + CH_3$ are commonly 10^8 larger than those for $X - H \rightarrow X^\cdot + H$ (same X)⁵⁰ so an A factor of $10^{14.2}$, ΔS of activation 4.4 gibbs, was adopted. The transition state geometry (1.4 Å C-C distance, 1.8 Å C-O distance, 120° CCO angle) of Dupuis was used for the activated complex. The 316 cm^{-1} torsional vibration of the diradical was estimated to be $\sim 500\text{ cm}^{-1}$ in the transition state. A 1608 cm^{-1} vibration was lost as the reaction coordinate, and a 1300 and 700 cm^{-1} vibration were reduced to 235 and 125 cm^{-1} to complete the model. Dissociation to a level 32 kcal above the diradical level was considered, implying a barrier for the addition of $O(^3P)$ to ethylene of ~ 2 kcal/mole.

At 5.4 kcal/mole collision energy the diradical lifetime is calculated to be .8 nanoseconds (.4 nanoseconds for a 1 kcal $O(^3P)$ + ethylene barrier). Using elementary kinetic theory⁵¹ estimates of the mean free path and average molecular velocity at 40 torr, 300°C , and an average molecular mass of 20, the average time between collisions is ~ 2 nanoseconds. These calculations indicate that the collision induced processes should not be saturated at 40 torr, but certainly should be active. However, given the many uncertainties in the calculations, and the potential errors, the results should be viewed mainly as an argument that it would not be entirely unexpected that collision induced processes could be fully operational at the relevant pressures (40-760 torr).

Considering then the previous crossed beam studies of Gutman, the appearance of CH_3^+ could be ascribed to secondary collisions leading to CH_3 products as well as to dissociative ionization of $\text{C}_2\text{H}_3\text{O}$.

In our crossed beam experiment we have observed only $\text{H} + \text{CH}_2\text{CHO}$ product from the reaction of $\text{O}(^3\text{P}) + \text{ethylene}$. Ketene product must be a minor channel at best, and while $\text{CH}_3 + \text{CHO}$ product seems unlikely, the crossed beam results cannot rule out that it is comparable in cross section to vinoxy formation. Evidence for a potential energy barrier in the exit channel for C-H single bond cleavage was observed. The $^3\text{A}''(\sigma, \pi)$ and $^3\text{A}'(\pi, \pi)$ diradical intermediates have a lifetime comparable to their rotational period at 5.4 kcal/mole collision energy, prior to dissociation to $\text{H} + \text{CH}_2\text{CHO}$, but live somewhat less than that at 8.3 kcal/mole. The $^3\text{A}'(\sigma, \sigma')$ and $^3\text{A}''(\pi, \sigma)$ states are expected to form only reactants under collisionless conditions at collision energies less than 8 kcal/mole.

REFERENCES: CHAPTER III

1. I. Glassman, Combustion, Academic Press, New York (1977), p. 55.
2. R. A. Whitby, E. R. Altwicker, Atoms. Environ. 12, 1289 (1978).
3. I. Glassman, Combustion, Academic Press, New York (1977), p. 202.
4. J. T. Herron, R. E. Huie, J. Phys. Chem. Ref. Data 2, 467 (1973).
5. J. A. Kerr and E. Ratajczak, Third Supplementary Tables of Bimolecular Gas Reactions, Department of Chemistry, The University of Birmingham, England (1977).
6. R. J. Cvetanovic, Adv. in Photochem. 1, 115 (1963).
7. Huie and Herron, Progr. Reaction Kinet. 8, 1 (1975).
8. M. C. Lin in Potential Energy Surfaces, K. P. Lawley, Ed., Wiley, New York (1980), p. 136.
9. R. J. Cvetanovic, J. Chem. Phys. 23, 1375 (1955).
10. R. J. Cvetanovic, J. Chem. Phys. 33, 1063 (1960).
11. L. Elias, J. Chem. Phys. 38, 989 (1963).
12. J. M. Brown, B. A. Thrush, Trans. Faraday Soc. 63, 630 (1967).
13. H. Niki, E. E. Daby, B. Weinstock, 12th Symposium International on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania (1969), p. 277.
14. A. A. Westenberg, N. deHaas, 12th Symposium International on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania (1969), p. 289.
15. R. Atkinson, R. J. Cvetanovic, J. Chem. Phys. 55, 659 (1971).
16. R. Stuhl, H. Niki, J. Chem. Phys. 55, 3954 (1971).
17. R. E. Huie, J. T. Herron, D. D. Davis, J. Phys. Chem. 75, 3902 (1971).

18. D. D. Davis, R. E. Huie, J. T. Heron, M. J. Kurylo, W. Braun, J. Chem. Phys. 56, 4868 (1972).
19. R. Atkinson, R. J. Cvetanovic, J. Chem. Phys. 56, 432 (1972).
20. M. J. Kurylo, R. E. Huie, J. Chem. Phys. 58, 1258 (1973).
21. R. Atkinson, J. N. Pitts, Jr., J. Phys. Chem. 78, 1780 (1974).
22. R. Atkinson, J. N. Pitts, Jr., J. Chem. Phys. 67, 38 (1977).
23. M. D. Scheer, R. Klein, J. Phys. Chem. 73, 597 (1969).
24. R. Klein, M. D. Scheer, J. Phys. Chem. 73, 1598 (1969).
25. M. D. Scheer, R. Klein, J. Phys. Chem. 74, 2732 (1970).
26. R. J. Cvetanovic, J. Phys. Chem. 74, 2730 (1970).
27. J. R. Kanofsky, D. Gutman, Chem. Phys. Lett. 236 (1972).
28. J. R. Kanofsky, D. Lucas, D. Gutman, 14th Symposium International on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania (1971), p. 285.
29. F. J. Pruss, I. R. Slagle, D. Gutman, J. Phys. Chem. 78, 663 (1974).
30. B. Blumenberg, K. Hoyer mann, R. Sievert, 16th Symposium International on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania (1973).
31. K. O. McFadden, C. L. Currie, J. Chem. Phys. 58, 1213 (1973).
32. F. Huisken, D. Krajnovich, Z. Zhang, Y. R. Shen, Y. T. Lee, Sub to J. Chem. Phys.
33. R. F. W. Bader, M. E. Stephens, R. A. Gangi, Can. J. Chem. 55, 2755 (1977).
34. N. C. Baird, R. R. Gupta, K. F. Taylor, J. Amer. Chem. Soc. 101, 4531 (1979).

35. N. C. Baird, K. F. Taylor, *Can. J. Chem.* 58, 733 (1980).
36. B. Bigot, A. Sevin, A. Devaquet, *J. Amer. Chem. Soc.* 101, 1095, 1101 (1979).
37. K. Yamaguchi, S. Yabushita, T. Fueno, S. Kato, K. Morokuma, *Chem. Phys. Lett.* 70, 27 (1980).
38. D. J. Bogan, *J. Phys. Chem.* 81, 2509 (1977).
39. E. Stehhagen, S. Abrahamsson, F. W. McLafferty, Eds., *Atlas of Mass Spectral Data*, Wiley Interscience, New York (1969).
40. M. Dupuis, J. J. Wendoloski, T. Takada, W. A. Lester, Jr., *J. Chem. Phys.* 76, 481 (1982).
41. S. W. Benson, *Thermochemical Kinetics*, Wiley Interscience, New York (1976).
42. J. O. Hirschfelder, C. F. Curtiss, H. C. Bird, *Molecular Theory of Gases and Liquids*, Wiley Interscience, New York (1954).
43. Levine and Bern, *Molecular Reaction Dynamics*, Oxford, New York (1974).
44. K. Kleinermanns, A. C. Luntz, *J. Phys. Chem.* 85, 1966 (1981).
45. G. Inoue, H. Akimoto, *J. Chem. Phys.* 74, 425 (1981).
46. H. E. Hunziker, H. Knepe, and H. R. Wendt, *J. of Photochemistry* 17, 389 (1981).
47. M. Dupuis, J. J. Wendoloski, W. A. Lester, Jr., *J. Chem. Phys.* 76, 488 (1982).
48. H. M. Frey, G. J. Kennedy, *J. Chem. Soc. Faraday Trans. I* 73, 164 (1977).
49. Y. T. Lee, 14th Informal Conference on Photochemistry, Newport Beach, California (April 1980).

50. S. W. Benson, H. E. O'Neal, Kinetic Data on Gas Phase Unimolecular Reactions, NSRDS-NBS21, National Bureau of Standards, Washington, D.C. (1970).
51. G. W. Castellan, Physical Chemistry, Addison Wesley, Reading, Massachusetts (Second Edition, 1971).
52. Unpublished results of D. Gutman.

FIGURE CAPTIONS: CHAPTER III

1. $O + \text{ethylene}$ energy level diagram. Heats of formation at 300° .
2. Mass 42, CH_2CHO product, angular distribution at 8.3 kcal/mole.
3. Mass 42, CH_2CHO product, angular distribution at 5.4 kcal/mole.
4. Mass 42 (CH_2CHO) and 27 (C_2H_4) angular distributions at 8.3 kcal/mole. Below, mass 15 and 29 angular distributions. Curves shown with the 15 and 29 distributions are the distributions predicted in the absence of $\text{CH}_3 + \text{CHO}$ primary product.
5. Mass 42 (CH_2CHO) and 27 (C_2H_4) angular distributions at 5.4 kcal/mole. Below, mass 15 and 29 angular distributions. Curves shown with the 15 and 29 distributions are the distributions predicted in the absence of $\text{CH}_3 + \text{CHO}$ primary product.
6. Assuming equal cross sections, relative kinematic effects on detection efficiencies, 5.4 kcal/mole.
7. CH_2CHO product time of flight at 5.4 kcal/mole.
8. CH_2CHO product center of mass translational energy distribution, 5.4 kcal/mole. (Solid line best fit, cross hatched area experimental error, dotted line statistical calculation.)
9. CH_2CHO product time of flight at 8.3 kcal/mole.
10. CH_2CHO product center of mass angular distribution, 8.3 kcal/mole.
11. CH_2CHO product center of mass translational energy distribution, 8.3 kcal/mole. (Solid line best fit, cross hatched area experimental error, dotted line statistical calculation.)
12. Expanded $O(^3P) + \text{ethylene}$ energy level diagram.

FIGURE 3-1

FIGURE 3-2

FIGURE 3-3

XBL 8211-3286

FIGURE 3-4

XBL 8211-3283

FIGURE 3-5

XBL 8211-3285

FIGURE 3-6

FIGURE 3-7

FIGURE 3-8

XBL 8211-3232

FIGURE 3-9

FIGURE 3-10

FIGURE 3-11

XBL 8211-3234

FIGURE 3-12

IV. PRIMARY PRODUCTS OF THE REACTIONS OF $O(^3P)$ WITH SUBSTITUTED ETHYLENES

1. INTRODUCTION

In this chapter, the results of crossed beams experiments studying the reactions of $O(^3P)$ with substituted ethylenes are presented. In particular, here we focus on a portion of the experimental results; primary product identification in the reactions of $O(^3P)$ with methyl-ethylene, bromoethylene, 1,1 and 1,2 dichloroethylene.

In the reaction of $O(^3P)$ with ethylene, initial addition of $O(^3P)$ to form a 1,3 triplet diradical, is followed by C-H single bond cleavage, to form the only primary product, vinoxy radical. 1,2 C-C hydrogen migrations, followed by C-C bond cleavage, and three or four center molecular elimination of products are, apparently, not significant primary product forming routes.

Several questions can be addressed by the study of $O(^3P)$ -substituted ethylene reactions. One carbon in a singly substituted ethylene (CH_2CHX) has two different single bonds, C-H and C-X, almost certainly of different strengths. To what extent does a competition take place between C-H and C-X single bond cleavage en route to products? 1,2 C-C hydrogen and alkyl group migrations are not expected on a triplet surface. However, some heavier groups (Heavy here refers specifically to the halogens. It is certainly the electronic structure, not the mass of the group which is important. Phenyl groups, and

other substituents whose electronic structures are generically more similar to the third, fourth, or fifth row elements, than the first row elements, would also be included. Alkyl groups would not be included.), including some halogens, are believed to make facile 1,2 C-C migrations on a triplet surface. Does the presence of a halogen substituent manifest itself in a new product forming route, addition of oxygen, 1,2 C-C halogen migration, followed by C-C bond cleavage to form CH_2X and CHO ? Finally, does a halogen substituent expedite 1,2 C-C hydrogen or alkyl group migrations?

We have addressed these questions (as well as associated dynamical questions) by studying the reactions of $\text{O}(^3\text{P})$ with some substituted ethylenes in crossed molecular beams experiments. Here, primary product identification is presented.

2. PRODUCTS OF THE REACTION OF $\text{O}(^3\text{P})$ WITH PROPYLENE

The previously accepted products of this reaction¹ were $\text{HCO} + \text{C}_2\text{H}_5$, and $\text{CH}_3 + \text{CH}_3\text{CO}$ (major routes), $\text{H}_2\text{CO} + \text{C}_2\text{H}_4$, $\text{C}_3\text{H}_4\text{O} + \text{H}_2$, and $\text{H}_6\text{C}_3\text{O} + \text{h}\nu$ (minor routes). These products represent the same mechanisms previously thought to lead to primary products in $\text{O}(^3\text{P}) + \text{ethylene}$: $\text{HCO} + \text{C}_2\text{H}_5$ would result from the addition of oxygen to the perhydro carbon of propylene, 1,2 C-C hydrogen migration, or addition to the methylated carbon, 1,2 C-C methyl migration, and subsequent C-C bond cleavage; $\text{CH}_3 + \text{CH}_3\text{CO}$ would result from the addition of oxygen to the methylated carbon, 1,2 C-C hydrogen migration and C-C bond cleavage; $\text{C}_3\text{H}_4\text{O} + \text{H}_2$ and $\text{H}_2\text{CO} + \text{C}_2\text{H}_4$, would result from three or four center eliminations of H_2 and C_2H_4 respectively. (Addition of oxygen to the

perhydro carbon and immediate C-C bond cleavage would also lead to $\text{CH}_2\text{O} + \text{C}_2\text{H}_4$.)

Figure 1 shows the mass 56 angular distribution we obtained by crossing a beam of propylene ($v_0 = 6.39 \times 10^4$ cm/sec, speed ratio = 4.5) with a beam of $\text{O}(^3\text{P})$ ($v_0 = 21.1 \times 10^4$ cm/sec, speed ratio = 6.1) at roughly 7.1 kcal/mole collision energy. The distribution is identical to that we observed for $m/e = 57$, although more intense. These masses correspond to masses 42 and 43 in the reaction of $\text{O}(^3\text{P}) + \text{ethylene}$, and prove that, in fact, C-H single bond cleavage, leading to CH_3CHCHO or $\text{CH}_2\text{C}(\text{CH}_3)\text{O}$, methyl substituted vinoxy, is an important primary product. (Our evidence for C-H single bond cleavage is even stronger in this case than in $\text{O} + \text{C}_2\text{H}_4$, as fragmentation of $\text{C}_3\text{H}_5\text{O}$ in the ionizer is much less extensive than CH_2CHO , $57/56 = .16 \pm .02$).

$\text{CH}_3 + \text{CH}_2\text{CHO}$ would be formed if addition of oxygen at the methylated carbon is followed by C- CH_3 single bond cleavage. The parent mass of CH_2CHO is 43, and CH_2CHO fragments extensively when ionized. The parent mass of propylene is 42, and produces such intense elastically scattered signals at masses 42 and 43, that observation of a mass 42 or 43 reactively scattered angular distribution is unlikely. However, a search for $\text{CH}_3 + \text{CH}_2\text{CHO}$ products is still possible. Our $\text{O}(^3\text{P}) + \text{ethylene}$ experiment demonstrated that mass 29 is an important daughter ion of vinoxy, but is a relatively less important daughter ion of propylene. Thus, the mass 29 angular distribution could be expected to reveal both an elastically scattered contribution and a reactively scattered contribution if CH_2CHO is formed as a primary product. However, methyl substituted vinoxy will also fragment to $m/e = 29$, so

even in the absence of CH_2CHO product an elastic and reactive contribution to the mass 29 angular distribution is expected. Just as in the search for CH_3 and/or CHO in the $\text{O}(^3\text{P}) + \text{ethylene}$ experiment, a predicted mass 29 distribution, in the absence of CH_2CHO ($+\text{CH}_3$) product, can be obtained by scaling the mass 56 (methylvinoxy only) and mass 39 (elastically scattered propylene only) angular distributions to account for all the observed intensity at 50° , near the center of mass. In Figure 2, the mass 56 (methylvinoxy) and mass 39 (propylene) distributions are shown again. Below them is the mass 29 angular distribution and a curve representing the mass 29 angular distribution anticipated in the absence of $\text{CH}_2\text{CHO} + \text{CH}_3$ products. In this case, the predicted distribution clearly fails to account for the observed wide angle intensity. A second reactive contribution to the mass 29 angular distribution is confirmed, and is almost certainly a daughter ion of CH_2CHO . Luntz² and Hunziger³ have, in fact, reported spectroscopic observations of CH_2CHO from the reaction of $\text{O}(^3\text{P})$ with propylene.

A crude estimate for the vinyloxy/methylvinyloxy branching ratio can be obtained from our experiment, and we find $\sigma_{(\text{H} + \text{methylvinyloxy})} / \sigma_{(\text{methyl} + \text{vinyloxy})} = .1$.

Our experiment has demonstrated that C-H and C- CH_3 single bond cleavages leading to vinyloxy, and methylvinyloxy, following the initial addition of oxygen to propylene are important (if not the exclusive) primary product forming routes. No evidence for 1,2 C-C hydrogen or methyl migrations or three or four center molecular elimination of products was observed.

3. PRODUCTS OF THE REACTION OF $O(^3P)$ WITH VINYL BROMIDE

A complete report of our study of the reaction of $O(^3P)$ with vinyl bromide is reprinted as an appendix to this chapter. Three primary products are reported, $H + \text{bromovinoxy}$, $Br + \text{vinoxy}$, representing single bond cleavages (as in ethylene and propylene), and $CH_2Br + CHO$. $CH_2Br + CHO$ can only be formed via a 1,2 C-C migration in the oxygen-vinyl bromide triplet diradical intermediate. Oxygen addition at the brominated carbon could be followed by 1,2 bromine migration, or oxygen addition at the perhydro carbon could be followed by 1,2 C-C hydrogen migration, prior to C-C bond cleavage to form $CH_2Br + CHO$. The bromine migration is certainly the most likely possibility, but the identity of the migrating atom could not be experimentally determined.

4. PRODUCTS OF THE REACTIONS OF $O(^3P)$ WITH 1,1 AND 1,2 DICHLOROETHYLENE

The studies of $O(^3P) + 1,1$ and $1,2$ dichloroethylene were undertaken with two specific objectives in mind. First, the $O(^3P) + \text{vinyl bromide}$ results demonstrated that 1,2 C-C migrations were taking place en route to products. Most probably, bromine migrates, but the possibility that hydrogen migrations become facile in the presence of bromine could not be ruled out. Assuming that an analogous product forming route is important in the reaction of $O(^3P)$ with 1,1 dichloroethylene, primary product identification would determine exactly which atom (if indeed, both do not) migrates prior to C-C bond cleavage. That is, the addition of $O(^3P)$ to the perhydro carbon can be followed

only by either C-H single bond cleavage or H migration (with C-C bond cleavage) to form $\text{CHCl}_2 + \text{CHO}$. Addition of oxygen to the chlorinated carbon can only be followed by either C-Cl single bond cleavage or 1,2 chlorine migration to form $\text{CH}_2\text{Cl} + \text{CClO}$.

Figure 3 presents angular distributions observed in the $\text{O}(^3\text{P}) + 1,1$ dichloroethylene experiment. The mass 110 angular distribution is the angular distribution of dichlorovinoxy, demonstrating that addition to the perhydro carbon is still followed by C-H single bond cleavage. The mass 76 angular distribution clearly contains two components, an ionizer crack of dichlorovinoxy, and a second reactive contribution from chlorovinoxy, demonstrating that addition of oxygen to the chlorinated carbon is followed by C-Cl single bond cleavage. Finally, we show the mass 51 angular distribution. Although the signal to noise is very low, there is not doubt that this represents a third primary reaction product. Mass 51 ions can come only from CH_2Cl , not CHCl_2 , so Cl is identified as the migrating group, prior to C-C bond cleavage.

Our second objective in these studies was an assessment of the extent to which it is the weaker of the two single bonds that breaks when an ethylenic carbon is attacked. That is, each carbon in 1,2 dichloroethylene has a relatively strong (C-H ~ 108 kcal/mole) and weak (C-Cl ~ 91 kcal/mole) single bond.⁴ If rupture of the weakest single bond dominates to a great extent, then $\text{Cl} + \text{C}_2\text{H}_2\text{OCl}$ and $\text{CHCl}_2 + \text{CClO}$ would be the only products formed.

We have only a negative, though highly suggestive, result for this reaction. Unlike all other $O(^3P) +$ unsaturated hydrocarbon reactions we have studied, the intense signal associated with C-H single bond cleavage was absent, suggesting that, in fact, C-H single bond cleavage is not an important product forming route---that cleavage of the weakest single bond on a ethylenic carbon dominates cleavage of the stronger single bond to a great extent.

5. SUMMARY

Our $O(^3P) +$ substituted ethylenes primary product identification results can be briefly summarized with the following simple mechanism. $O(^3P)$ will add to either ethylenic carbon, forming a 1,3 triplet diradical. A (substituted) vinoxy radical can then be formed by cleavage of one of the single bonds to that carbon; in cases where the two single bonds have different strengths, the weakest single bond breaks preferentially. If a "heavy" group X ("heavy" as earlier) is originally bonded to the carbon that oxygen attacks, a competition between C-X cleavage, and 1,2 C-C X migration with subsequent C-C bond cleavage is expected.

REFERENCES: CHAPTER IV

1. J. R. Kanofsky, D. Gutman, Chem. Phys. Lett. 15, 236 (1972).
2. K. Kleinermanns, A. C. Luntz, J. Phys. Chem. 85, 1966 (1981).
3. H. E. Hunziker, H. Knepe, H. R. Wendt, J. of Photochemistry 17, 389 (1981).
4. S. W. Benson, Thermochemical Kinetics, Wiley Interscience, New York (1976).

FIGURE CAPTIONS: CHAPTER IV

1. Mass 56 (methylvinoxy) angular distribution. Below, methylvinoxy center of mass translational energy distribution.
2. Mass 56 (methylvinoxy), mass 39 (elastically scattered propylene), and mass 29 angular distributions. Solid line with the mass 29 data is the distribution anticipated in the absence of CH_2CHO product.
3. Mass 110 (dichlorovinoxy), mass 76 (chlorovinoxy) and mass 51 (CH_2Cl) angular distributions.

XBL 818-11321

FIGURE 4-1

XBL 818-11325

FIGURE 4-2

FIGURE 4-3

APPENDIX

CROSSED MOLECULAR BEAMS STUDIES OF THE REACTION
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ABSTRACT

The reaction of $O(^3P)$ with C_2H_3Br has been studied in a crossed molecular beam experiment with rotatable mass spectrometric detector. Three major reaction routes were identified giving products $H + C_2H_2BrO$, $CH_2Br + CHO$ and $Br + C_2H_3O$. Relative product yields were measured at two collision energies, 7.4 kcal/mole and 12.4 kcal/mole. The product translational energy distributions were determined for each reaction and are compared to statistical calculations. The center of mass angular distributions of the products indicate that the hydrogen elimination and the C-C bond cleavage occur from dissociation of a complex with a lifetime greater than a rotational period while the Br atom elimination is somewhat faster.

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INTRODUCTION

The reactions of oxygen atoms with olefins and halogenated olefins have been studied extensively,¹ because these reactions are important in combustion processes and in atmospheric chemistry. Although the rate constants of many of these reactions have been accurately determined,² the reaction mechanisms are not very well understood. Secondary reactions and problems associated with the identification of vibrationally excited radical products have made primary product identification difficult in many earlier experimental investigations.

Recently, experiments carried out under single- or near single-collision conditions have avoided the complication of secondary reactions, but mass spectrometric identification of primary products has not always given reliable results. In the ionization of vibrationally excited radical molecules, it is quite common to obtain only fragment ions even at low photon and electron energies and to detect no parent ions at all due to their lack of stability.

In our recent crossed molecular beams studies of oxygen atoms with several unsaturated hydrocarbons, benzene,⁴ ethylene,⁵ and acetylene⁶ it has been demonstrated that the problems associated with the fragmentation of products in the mass spectrometer can be overcome if the experimental measurements of angular and velocity distributions of products are carried out with sufficiently high resolution by monitoring all the ions arising from reactively scattered neutrals in a mass spectrometer. Because signals measured at ions produced from an identical product molecule must have the same angular and velocity distributions, by

matching the angular and velocity distribution of signal measured at various masses, and using the kinematic constraints of energy and momentum conservation, the primary reaction products have been unambiguously determined.

The reaction mechanism of $O(^3P) + C_2H_3Br$ has been investigated previously by Gutman and his coworkers.⁷ They used a crossed molecular beam apparatus employing photoionization mass spectrometry at a fixed angle to identify the reaction products. Among the energetically feasible channels listed below, they identified three reactive channels, (1), (2), and (3):

and reported a branching ratio of 29%, 51% and 20% respectively. Implicit in reaction (1) and (3) is a mechanism involving the migration of H or Br atoms followed by C-C bond rupture while reaction (2) requires a three or four center elimination of HBr. These mechanisms are not entirely convincing, because the simple substitution of a H atom or Br atom by the $O(^3P)$ atom is exothermic and the exit channel potential energy barriers for C-H and C-Br bond ruptures⁸ are not expected to be higher than those of 1,2 hydrogen migration in the triplet intermediate⁹ and of the molecular elimination processes.¹⁰ As was seen in the reaction of

$O(^3P)$ with C_6H_6 , C_2H_2 and C_2H_4 , the substitution reactions (4) and (5) are likely to compete effectively with the other possible channels in the reactions of oxygen atoms with vinyl bromide.

In this paper, we report crossed molecular beams studies of the reaction of $O(^3P)$ and C_2H_3Br . The reaction mechanism, especially the competition between the substitution reactions replacing H and Br atoms and the migration of Br atom or H atom in the reaction complex prior to C-C bond rupture, is carefully examined.

EXPERIMENTAL

The crossed molecular beam apparatus with a rotatable mass spectrometric detector used in this experiment was the high resolution version of the previously described, smaller machine.¹¹ In addition to the greater velocity resolution, the angular range of the detector has been increased more than 40%.¹² Two beams which are doubly differentially pumped are crossed at 90° in a well-defined interaction region inside a scattering chamber which has a pressure of $\sim 1 \times 10^{-7}$ torr. The detector, a triply-differentially pumped electron-impact ionization mass spectrometer, is rotated about the interaction region in the plane defined by the two colliding beams in order to obtain the product angular distribution. The product velocity distributions are determined by chopping the beam with a rotating disk and measuring the flight time to the detector.

The seeded, supersonic atomic oxygen beams used in these studies were generated by a high pressure, radio frequency discharge beam source which has been described elsewhere.¹³ The reaction was studied at two collision energies. The higher collision energy, 12.4 kcal/mole was obtained with a 5% O₂ in helium gas mixture discharged at 200 torr and with 250 watts of rf power which gave oxygen atoms with a peak velocity of 2.7×10^5 cm/s and a FWHM velocity spread of 25%. For the lower collision energy, 7.4 kcal/mole, 5% O₂ in neon was discharged at 500 torr and with 250 watts of rf power giving a peak velocity of 2.0×10^5 cm/s and a FWHM velocity spread of 20%. The oxygen atom beams have been found to contain a small amount of O(¹D).¹³ About 80% of the O₂ molecules are dissociated in the helium-oxygen beam.

The vinyl bromide beam was generated by expansion of C_2H_3Br gas from a quartz nozzle at a stagnation pressure of 180 torr maintained by immersing the C_2H_3Br reservoir in an ice bath. The nozzle was heated to 390°K in order to prevent the formation of C_2H_3Br clusters during the expansion. The peak velocity was measured to be 5.8×10^4 with a FWHM spread of 30%. Laboratory angular distributions of product were taken by repeated scans of 300 second counts at each angle. The C_2H_3Br beam was modulated at 150 Hz with a tuning fork chopper, and the signal which is proportional to product number density was obtained by subtracting the chopper-closed count from the chopper-open count. In addition, in order to eliminate any modulated background caused by effusion of C_2H_3Br molecules from the differentially pumped beam collimation chamber located between the beam source and the main chamber, the data were taken with the oxygen beam both flagged and unflagged at each laboratory angle. The final signal was obtained by subtracting the flagged data from the unflagged data. Product velocity distributions for some of the mass numbers were measured at various angles by the cross correlation time of flight method. Counting times varied depending upon the laboratory angle and product mass under investigation with several hours often being necessary to obtain a good velocity distribution.

RESULTS AND ANALYSIS

A. Product Identification

For the $O + C_2H_3Br$ reaction, just as for other reactions of oxygen atoms with unsaturated hydrocarbons, the identification of product molecules by mass spectroscopy is complicated by the fragmentation of primary products in the ionization process. Measurements of product angular distributions were made at $m/e = 123, 122, 121, 120, 109, 106, 95$ and 42. These are the mass numbers which give a high enough signal to noise ratio to provide meaningful angular distributions in less than 60 minutes per angle. The particular relationships between the possible products and daughter fragments in the ionizer are as follows:

The mass numbers shown in parentheses take both bromine isotopes ^{79}Br , ^{81}Br into account but not minor hydrogen and carbon isotopes. The angular distribution of products measured at $m/e = 120$ and collision energy, $(E_c) = 12.4$ kcal/mole is shown in Fig. 1A. Angular distributions of $m/e = 123, 122, 121$ are all superimposable on that of $m/e = 120$ and are strongly peaked at the center of mass (CM) angle, indicating

that one of the primary products is C_2H_2BrO which on ionization yields both $C_2H_2BrO^+$ and C_2HBrO^+ . It is expected that this product will fragment extensively during the ionization process to yield many other ions with identical angular distributions. Angular and velocity distributions measured at these mass numbers should contain the unmistakable contribution from the C_2H_2BrO product. The fragmentation of this species was investigated by counting signal at the CM angle for many of the probable fragments. A large signal at mass 29, HCO^+ was observed while none was seen at mass 109, $BrCO^+$. This suggests that the species at mass 123 is $CHBrCHO$, not CH_2CBrO .

Two features of the mass 95 angular distribution shown in Fig. 1-B are easily recognized. The strong signal near the vinyl bromide beam arises from elastically scattered C_2H_3Br which yields CH_2Br^+ in the ionizer, and the peak at the center of mass angle results from fragmentation of the C_2H_2BrO product. These contributions to the total signal are shown in Fig. 1-B, together with the signal remaining after correction for these sources, the open circles, which are widely distributed from -25 to 130° . The source of the remaining signal must be the primary reaction product CH_2Br , because no other possible products can give $m/e = 95$. While the elastic scattering can be subtracted accurately by knowing the angular distribution of C_2H_3Br , the exact fragmentation pattern of C_2H_2BrO is unknown. Consequently, the intensity of CH_2Br product around the center of mass is quite uncertain. Further verification that the CH_2Br is indeed a primary product is seen in Fig. 2 in which the velocity spectra for mass 95 and

mass 120 at the same angle are compared. At mass 95 the CH_2Br product is seen as a separate peak distinctly faster than the larger peak due to $\text{C}_2\text{H}_2\text{BrO}$ which is identical in shape to that measured at mass 120.

The signal at mass 42 ($\text{C}_2\text{H}_2\text{O}^+$) is shown in Fig. 1-C and clearly results from a combination of fragmentation of the $\text{C}_2\text{H}_2\text{BrO}$ product and a third primary product because its distribution extends broadly over the laboratory angular range and fragmentation of the second channel, CH_2Br , cannot give daughter ions at mass 42. The peak at the center of mass angle results from fragmentation of the $\text{C}_2\text{H}_2\text{BrO}$ to give $\text{C}_2\text{H}_2\text{O}^+$.

In Fig. 3 the velocity spectra of mass 42 is compared with that of mass 95 at $\theta = 70^\circ$ to show that although the angular distributions are similarly very broad, the signal at mass 42 has a distinctly faster distribution. The identity of the primary product which yields the fast mass 42 signal can not be definitively established because both reaction (2) and (5) will yield products which ionize to give mass 42. We believe that the source of the mass 42 signal is bromine atom elimination, reaction (5), as will be discussed below. The product $\text{C}_2\text{H}_3\text{O}$ is known to fragment extensively in the ionizer to give $\text{C}_2\text{H}_2\text{O}^+$ as the major ion.¹⁴ Proof that reaction (5) is occurring would require measurement of the mass 43 ion but its intensity was below our detection capabilities.

No direct evidence for CH_3 elimination from the collision complex to give COBr was found although our sensitivity to mass 109 product is reduced by severe elastic scattering of ^{13}C containing $\text{C}_2\text{H}_3\text{Br}$ and we cannot therefore completely rule out the possibility. Taking account of this limited detection ability we estimate that if reaction (1) is

present, it constitutes less than 10% of the overall reaction. In Fig. 4 the angular distributions of the product C_2H_2BrO , CH_2Br and C_2H_3O resulting from the $O + C_2H_3Br$ reaction at the lower collision energy (7.4 kcal/mole) are shown. The qualitative similarity of these data to those at the higher collision energy indicates that no major changes in the reaction mechanism have occurred with the change in collision energy.

B. Relative Yield of Reactive Channels

In the angular distribution of mass 95, corrected for elastic scattering, the intensity of signal at angle 60° results wholly from reaction (3), CH_2Br product, while at the center of mass angle, most of the signal results from fragmentation of C_2H_2BrO product formed in reaction (4). The branching ratio for reaction (3) and (4) cannot be obtained directly from this data because the fragmentation pattern of the products are not known, but a change in the ratio with collision energy is easily seen from a change in the relative intensity of signal at the two angles. In fact, the ratio $I_{95}(60^\circ)/I_{95}(C.M.)$ changes from ~ 0.30 at 7.4 kcal/mole to ~ 0.12 at 12.4 kcal/mole collision energy. Thus, with increase in collision energy, the migration channel becomes less important relative to the H atom channel. Applying the same analysis to the mass 42 angular distribution, we find $I_{42}(70^\circ)/I_{42}(C.M.)$ changes from ~ 0.60 at the low energy to 0.24 at the higher energy. The behavior of mass 42 exactly parallels that of mass 95, both of these decrease by the same

amount relative to the mass 120 product and, by extension, the ratio of mass 95 to mass 42 remains fairly constant with the change in collision energy.

In order to obtain information about the relative cross sections of the various channels, the ionization cross sections of the polyatomic products are assumed to be roughly proportional to the square roots of the polarizabilities.¹⁵ While this is a reasonable assumption, the principal uncertainty in relating the detected intensity relates to the actual yield of that product arising from the unknown fragmentation pattern of the products. The fragmentation pattern of the C_2H_2BrO product was investigated by measuring the product intensity at the most probable fragments, at the center of mass angle. The resulting fragmentation pattern was as follows, mass 123, 121 = 0.6%, mass 122, 120 = 2.6%, mass 95, 93 = 18.2%, mass 94, 92 = 9.1%, mass 42 = 7.9% and mass 29 = 31%. Fragmentation of the C_2H_3O species has already been investigated in the $O + C_2H_4$ reaction and approximately 50% of the total ions have mass 42. The CH_2Br species was estimated to yield 25% mass 95 ions. After accounting for kinematic effects and products angular and velocity distributions on the relative detection efficiency we obtain an estimate of the branching ratio shown in Table 1.

C. The Product Energy and Angular Distribution

The measured laboratory angular and velocity data were used to obtain the product translational energy distribution $P(E)$ and center of mass

angular distribution $T(\theta)$ by an iterative procedure which assumed $P(E)$ and $T(\theta)$ to be uncoupled. The data for mass 120 and mass 95 were fit well with an isotropic $T(\theta)$, while the mass 42 product was preferentially scattered forward with respect to the incident oxygen direction. The measured $P(E')$ of the three reactive channels are shown as solid lines in Fig. 5 and Fig. 6.

The $P(E)$ for the mass 120 product is found to have a mean at about 50% of the available energy and the maximum energy observed is consistent with the estimated ΔH of -20 kcal/mole.¹⁶ The mass 95 product also exhibits a large fraction, $\sim 50\%$, of the available energy in translation. The maximum energy is higher than that observed for the 120 product, in agreement with greater exothermicity expected for the C-C cleavage, $\Delta H = -30$ kcal/mole.

The mass 42 product is found to have much less energy in translation than the other two products, approximately 17% if the exothermicity for the Br atom substitution is 48 kcal/mole. Also shown in Fig. 5 and 6 are statistical phase space calculations¹⁷ of the $P(E)$ for the three reactions. The calculation assumes that the collision cross section is governed by long range forces and that no potential energy barrier exists in the exit channel. All vibrational modes are assumed to be active in energy sharing. These phase space calculations predict far less energy in translation than is observed for the H atom elimination and for the carbon-carbon bond rupture but the agreement between theory and experiment is quite good for the mass 42 product.

By estimating the geometry of the O-vinyl bromide complex we calculate that in the energy range of our experiment the rotational period

should be $\tau_{\text{rot}} = 2.0 \pm 1.0$ ps, if the average impact parameter is 1.8 Å. RRKM calculations for the three channels were used to give a rough idea of the expected lifetime. The average lifetimes of the collision complex which is formed by adding an oxygen atom to the non-halogenated carbon atom and which leads to the reaction (4) is estimated to be 4–6 psec. The complex formed by adding an oxygen atom to the halogenated carbon atoms and leading to reactions (4) and (5), on the other hand, is estimated to have an average lifetime of less than 0.1 psec, if the migration of Br atom is fast and the rate of decomposition is solely determined by the energetics and the properties of the critical configuration.

DISCUSSION

Some of the features of the reaction of $O(^3P)$ with vinyl bromide are analogous to those of $O(^3P) + C_2H_4$. The energetic relationships of reactants, intermediates, and products formed by hydrogen substitution are similar, however the presence of the weakly bound halogen atom provides additional features in the reaction mechanism which are not found in the reaction with ethylene. An energy level diagram for this reaction is shown in Fig. 7. Previous to this work, the substitution of the H or Br atom by the oxygen atom was not thought to occur in this reaction. Our experimental results, however suggest that two of the three major reaction channels are simple bond ruptures from the reaction intermediate yielding H atoms and Br atoms, reactions (4) and (5).

Similar to the reaction $O + C_2H_4$, the $O(^3P)$ approaches C_2H_3Br on a triplet surface which may result in formation of a triplet biradical complex. Whereas with ethylene there are two possible low lying intermediate states^{18,19} which are nonconvertible by an internal rotation, with vinyl bromide, four analogous complexes may be formed depending on the carbon to which the oxygen attaches. Attachment of the oxygen to the carbon with two hydrogens leads to formation of an $^3A'$ or an $^3A''$ species. The $^3A''$ corresponds to a triplet where the two unpaired electrons reside in two atomic p orbitals, one on the oxygen, the other on the far carbon, both pointed out of the CCO plane. For the $^3A'$ state the p orbital on O with a single electron lies in the CCO plane. The $^3A'$ should be nonreactive at our collision energy because it correlates to the excited state $CHBrCHO$ product. The $^3A''$ can yield only H atoms

unless migration of the hydrogen over a large barrier occurs. The heights of the barriers to atomic migrations in general between carbon atoms on triplet surfaces are not well known but recent theoretical studies have found these barriers for H atom migration to be very high^{16,18} in contrast to the negligible barrier for the same process on a singlet surface.

Upon addition of the oxygen atom to the bromine-containing carbon, again two species may be formed, $^3A'$ and $^3A''$. Atomic elimination of H or Br from the $^3A'$ leads to electronically excited products, probably not energetically feasible. The only energetically allowed reaction of the $^3A'$ species is migration of the bromine atom followed by C-C bond scission. The $^3A''$ species may undergo either H atom or Br atom detachment as well as Br atom migration. The loss of H atom would result in formation of CH_2CBrO while the observed mass 123 product is identified as $CHBrCHO$ as discussed above. In both cases the barrier to H atom migration is prohibitively large. The highly exothermic (~48 kcal/mole) Br atom substitution would be expected to be the dominant reaction for this species.

Other possible reactions include the three centered elimination of H_2 or HBr from any of the species. We observe no H_2 elimination but our data cannot definitely rule out the HBr channel. The barrier to three center elimination of HX from some species is known to be large,¹⁰ however we know of no measurements of the barrier for HX addition to a triplet species.

The simplest explanation for our experimental results is that reaction occurs with attack on the CH_2 end of the molecule leading through the $^3\text{A}''$ to H atom elimination while attack on the CHBr end yields Br atoms from the $^3\text{A}''$ intermediate or CH_2Br after Br migration from the $^3\text{A}'$ species. The fact that reactions (1) and (5), which both involve the attack of oxygen atom on the CHBr end, show different lifetimes of the complex, as seen in the presence or absence of forward backward symmetry in the angular distributions, supports the idea that these two reactions do not go through the same reaction intermediate. Our results suggest that higher collision energy is relatively more effective for the H atom channel, where attack is on the carbon far away from the center of mass. The centrifugal barrier in the entrance channels will be greater for this channel with nominally larger impact parameters. As such, more of the collision energy will be tied up as rotational energy. Higher collision energies will be more effective in overcoming the barrier and should enhance the reaction probability relative to attack at the brominated carbon. The other two channels involve attack of the $0(^3\text{p})$ near the center of mass of vinyl bromide and both will be affected similarly by a change in E_c if the exit barriers for these two channels are not significant compared to the excess energy available, and the electronic branching ratio of forming $^3\text{A}'$ and $^3\text{A}''$ states does not depend strongly on collision energy. Thus no major change in relative rates of the Br atom loss and Br migration channels with collision energy are expected, and none is observed.

The product translational energy distributions for the H atom elimination and for the migration channels are broad with a mean energy greatly exceeding a statistical average. The Br atom elimination channel on the other hand has a $P(E')$ in good agreement with the statistical calculation. This difference in behavior can be attributed to the presence or absence of a potential barrier in the exit channel rather than a reflection of the extent of energy randomization. Experimental studies by Parsons et al.²⁰ and classical trajectory studies by Hase²¹ have shown that in the elimination of a hydrogen atom from the C_2H_4F radical the $P(E')$ is broadened and increased in a manner similar to what we observe here. It is important to note that the reverse of reaction (4) is not a typical radical-radical reaction with no barrier but is the addition of the H atom to an unsaturated carbon, a process known to have a barrier of several kcal/mole. Likewise the reverse of reaction (3) is the addition of CH_2Br to CHO on the triplet surface only. In contrast the Br atom addition to an unsaturated carbon occurs without activation energy, hence reaction (5) has no barrier in the exit channel such that the translational energy of products does reflect the energy distribution in reaction coordinate.

The C.M. angular distributions of the product from the H atom channel and from the migration channel are isotropic indicating that the reaction intermediate lives longer than a rotational period and that there is no strong correlation between the entrance and exit channel orbital angular momenta. The RRKM calculations of the lifetime for the H atom channel indicate that the complex should live several rotational periods before

dissociation. Calculation for the C-C bond cleavage indicate a much shorter lifetime, in conflict with our observation of isotropic product. It is possible that the migration of Br atom to the adjacent carbon is the rate limiting step, however because of uncertainties in the transition state, the RRKM calculated lifetime is not considered sufficiently reliable to justify drawing conclusions from this discrepancy. The bromine atom channel $T(\theta)$ is not forward backward symmetric, hence this reactions occurs in a time shorter than a rotational period. The difference in behavior is reasonable in view of the much larger exothermicity of the Br atom channel which makes the existence of a complex on this surface questionable and the agreement of the statistical calculation of translational energy distribution to that observed in the experiment should not be taken as an evidence of complete energy randomization before decomposition. The model proposed above would have the three channels be non-competitive, thus there is no conflict between the observed relative yields and lifetimes inferred from the angular distribution.

CONCLUSION

The reaction of $O(^3P)$ with C_2H_3Br is seen to proceed by three major routes, hydrogen atom elimination, bromine atom elimination and C-C bond cleavage after bromine atom migration. An explanation for this behavior is found by considering the individual triplet potential energy

surfaces on which reaction can occur. The three reactions are thought to be non competitive, except in the formation of three distinct intermediate states in the approach of reagents, the course of the reaction having been decided in the entrance channel.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

REFERENCES

1. M. C. Lin, in Potential Energy Surfaces, K. P. Lawley, Editor (J. P. Wiley and Sons, 1980) p.136.
2. J. T. Herron, R. E. Huse, J. Phys. Chem. Ref. Data 2, 467 (1973).
3. B. Blumenberg, K. Hoyerman, R. Sievert, Proc. 16th Internat. Symp. Combust. 1976 (The Combustion Institute, 1977) p.841.
4. S. J. Sibener, R. J. Buss, P. Casavecchia, T. Hirooka, Y. T. Lee, J. Chem. Phys. 72, 4341 (1980).
5. R. J. Buss, R. J. Baseman, Guozhong He, Y. T. Lee, J. of Photochem. 17, 389 (1981).
6. R. J. Buss, R. J. Baseman, Guozhong He, R. S. Tse, Y. T. Lee, to be published.
7. I. R. Slagle, D. Gutman, J. R. Gilbert, Chem. Phys. Lett. 26, 111 (1974).
8. The reverse reactions, addition of H or Br to olefinic carbon atoms are known to proceed with only a small (several kcal/mole) activation energy. See V. N. Kondratiev, Rate Constants of Gas Phase Reactions, Office of Standard Reference Data NBS 1972, p.31 and p.108.
9. H. F. Schaefer III, Acc. Chem. Res. 12, 288 (1979).
10. 3 or 4 center molecular eliminations are known to encounter larger barriers in singlet species. See Aa. S. Sudbo, D. J. Krajnovich, P. A. Schulz, Y. R. Shen and Y. T. Lee, in Multiple-Photon Excitation and Dissociation of Polyatomic Molecules, C. D. Cantrell, Editor (Springer-Verlag, 1979). We expect similarly large barriers to accompany eliminations from triplets.

11. Y. T. Lee, J. D. McDonald, P. R. LeBreton and D. R. Herschbach, Rev. Sci. Instrum. 40, 1402 (1969).
12. R. K. Sparks, Ph.D. Thesis, University of California, Berkeley, 1979.
13. S. J. Sibener, R. J. Buss, C. Y. Ng, Y. T. Lee, Rev. Sci. Instrum. 51, 167 (1980).
14. R. J. Buss, R. J. Baseman, Guozhong He, Y. T. Lee, J. Photochem. 17, 389 (1981) and unpublished results on the photodissociation of ethyl vinyl ether by D. J. Krajnovich, F. Huiskens, Z. Zhang, Y. R. Shen and Y. T. Lee.
15. R. E. Center and A. Mandl, J. Chem. Phys. 57, 4104 (1972).
16. L. B. Harding, J. Phys. Chem. 85, 10 (1981).
17. J. C. Light, Dis. Farad. Soc. 44, 14 (1967). P. Pechukas, J. C. Light, C. Rankin, J. Chem. Phys. 44, 794 (1966).
18. M. Dupuis, J. J. Wendoloski, T. Takada and W. A. Lester, Jr., J. Chem. Phys. 76, 481 (1982).
19. H. E. Hunziker, H. Kneppke and H. R. Wendt, J. Photochem. 17, 389 (1981).
20. J. M. Parsons and Y. T. Lee, J. Chem. Phys. 56, 4658 (1972).
21. W. L. Hase, K. C. Bhalla, J. Chem. Phys. 75, 2807 (1981).

Table 1. Branching Ratio

Product Collision Energy	H + C ₂ H ₂ BrO	CH ₂ Br + CHO	Br + C ₂ H ₃ O
12.4 kcal/mole	14 ± 6 %	25 ± 10 %	61 ± 10 %
7.4 kcal/mole	6 ± 5 %	29 ± 10 %	65 ± 10 %

FIGURE CAPTIONS

- Fig. 1. Angular distribution of product from the reaction $O + C_2H_3Br$ at 12.4 kcal/mole collision energy. A. C_2H_2BrO product. B. CH_2Br product showing subtraction of contributions from elastic scattering of C_2H_3Br and fragmentation of C_2H_2BrO . C. C_2H_3O product with subtraction of contribution from fragmentation of C_2H_2BrO .
- Fig. 2. Time of flight spectra for mass 95 and mass 120 products, at $\theta = 45^\circ$.
- Fig. 3. Time of flight spectra for mass 42 and mass 95 products, at $\theta = 70^\circ$.
- Fig. 4. Angular distribution of product at 7.4 kcal/mole collision energy. A. C_2H_2BrO product. B. CH_2Br product showing subtraction of contributions from elastic scattering of C_2H_3Br and fragmentation of C_2H_2BrO . C. C_2H_3O product with subtraction of contributions from fragmentation of C_2H_2BrO .
- Fig. 5. Translational energy distribution of the product from the reaction $O + C_2H_3Br$ at 12.4 kcal/mole collision energy. A. C_2H_2BrO product. B. CH_2Br product. C. C_2H_3O product. — Experimental. - - - Phase space calculation. Uncertainty of experimental results are indicated by shaded areas.

Fig. 6. Translational energy distribution of the product from the reaction $O + C_2H_3Br$ at 7.4 kcal/mole collision energy. A. C_2H_2BrO product. B. CH_2Br product. C. C_2H_3O product. — Experimental — . — . — . Phase space calculation. Uncertainty of experimental results are indicated by shaded areas.

Fig. 7. Energy level diagram for the reaction $O + C_2H_3Br$.

XBL 8110-12301

FIGURE 4-A-1

XBL 815-9968

FIGURE 4-A-2

XBL 815-9967

FIGURE 4-A-3

FIGURE 4-A-4

XBL 818-11322

XBL 8110-11984

FIGURE 4-A-5

FIGURE 4-A-6

XBL 8110-11983

FIGURE 4-A-7

V. THE REACTION OF $O(^3P)$ WITH ACETYLENE

1. INTRODUCTION

Acetylene and ethylene are the two simplest prototypical unsaturated hydrocarbons, and are similar in many respects. While the chemistries of the double and triple bonds show some important differences,¹ in general, they are very similar, since the dominating feature of acetylene and ethylene is the relatively loosely held pi electron cloud forming the multiple bonds in both molecules. In particular, the multiple C-C bonds make acetylene and ethylene vulnerable to electrophilic attack. Since the reactions of $O(^3P)$ atoms with unsaturated hydrocarbons are electrophilic in nature, it is quite reasonable to assume that the mechanism for the reaction of $O(^3P)$ with acetylene would be the same as that for the reaction of $O(^3P)$ with ethylene. Assuming that the generic similarities between ethylene and acetylene will dominate their respective reactions with $O(^3P)$, then the $O(^3P)$ -acetylene reaction can be used as a test of the $O(^3P)$ -ethylene reaction mechanism, that is, a test of the predictive nature of the mechanism. In particular, the extension of the $O(^3P) + \text{ethylene}$ results to the $O(^3P) + \text{acetylene}$ reaction clearly predicts an initial addition of oxygen to one carbon, forming a 1,3 triplet diradical, which subsequently would dissociate through either C-H or C-O single bond cleavage leading to ketyl radical and hydrogen

atom products, or reformed reactants respectively. Another lesson of the $O(^3P)$ -ethylene reaction would seem to be that the addition of oxygen to acetylene would not likely be followed either by (1) a 1,2 C-C hydrogen migration (to form an excited ketene) and subsequent C-C bond cleavage (to form $CO + CH_2$) or subsequent three center elimination of H_2 (+ C_2O) or (2) a four centered elimination of H_2 (+ C_2O) from the initially formed diradical.

We have noted that ethylene is believed to be an important participant in some combustion and atmospheric systems. One striking difference between ethylene and acetylene is the fact that there is no doubt that acetylene is of paramount importance in many hydrocarbon combustion systems.² Acetylene itself, of course, is commonly used as a fuel. Oxygen-acetylene mixtures are known for their wide detonation and flammability limits and oxygen-acetylene flames are characterized by unusually high temperatures.³ In general, acetylenes are believed to be important intermediates leading to the soot, luminosity and ion yields in hydrocarbon flames.² The reaction of $O(^3P)$ itself with acetylene may be the major path of acetylene consumption in flames.^{4,5,6} For this reason, many of the previous studies of hydrocarbon flames have significant implications for the elementary $O(^3P)$ -acetylene reaction; particularly those dealing with radical chains, chemiluminescence, and chemi-ionization in the oxygen acetylene flame.

In this chapter, then, the focus is on the reaction of $O(^3P)$ + acetylene vis a vis the reaction of $O(^3P)$ + ethylene. To begin, we review the $O(^3P)$ -acetylene thermochemistry.

2. ENERGISTICS

The nominally important thermochemistry of the chemical species expected to be important, based on the $O(^3P) + \text{ethylene}$ reaction, is presented in Figure 1. Oxygen initially adds to the electron rich carbon framework and can make any of four 1,3 triplet diradicals, generically $\cdot O - C = C\cdot$, just as in the reaction of $O(^3P)$ and ethylene. The origins of the four different configurations are slightly different in this case. Each carbon remains essentially sp_2 hybridized, so two configurations (the lower two) arise from a geometry

oxygen unpaired spin out of the plane, another (the lowest energy of the four) with the unpaired spin in the CCO plane and the oxygen lone pair out of the CCO plane. In each case the unpaired spin on the terminal carbon lies in the CCO plane. A second corresponding set of (higher energy) triplets have a geometry where the terminal $\cdot CH$ group

estimate of the heat of formation of these 1,3 ($^3A'$) diradicals (the separation in energy of these (at least the two lowest) should be relatively small, as the O-ethylene calculations verify) can be obtained⁷ by (1) using the known enthalpy of formation of the ethenyl (C_2H_3) radical (-69 kcal/mole) to obtain a group ΔH_f value of 63 kcal/mole for the $\cdot C_d(H)$ group and by (2) adjusting Benson's group ΔH_f value of -9 kcal/mole for $C_d(C\cdot)(H)$ to -19 kcal/mole for $C_d(O\cdot)(H)$ (based on the differences between $C-(O\cdot)(C)(H)_2$ and $C-(C\cdot)(C)(H)_2$) and

$(C-(O^{\bullet})(C)_3$ and $C-(C^{\bullet})(C)_3$). This method gives 82 kcal/mole for the ΔH_f of $^{\bullet}C \equiv C - O^{\bullet}$, ~ 30 kcal/mole below the reactants' level, implying exactly the same stabilization for the 1,3 $O(^3P)$ -acetylene diradical as the best estimates of the 1,3 $O(^3P)$ -ethylene diradical's stabilization relative to $O(^3P) + \text{ethylene}$.

Five different primary products have been proposed for the $O(^3P)$ -acetylene reaction. The only stable closed shell product that has been suggested is ketene. Ketene has been observed in high pressure gas phase experiments,⁸ and in low temperature matrix studies,⁹ where frequent collisions can stabilize an energy rich ketene-like intermediate (if, for example, 1,2 C-C hydrogen migration were important); but the unimolecular decay of ground state ketene, with ~ 120 kcal/mole internal excitation, or the lowest triplet state of ketene, with ~ 60 kcal/mole internal excitation in a collisionless environment, is undoubted.

The abstraction of a hydrogen atom by $O(^3P)$ to form OH and C_2H has been suggested as a primary product forming route in some high temperature studies, but is more than 15 kcal/mole endothermic, and need not be considered further here, since our experimental results were obtained at collision energies of 10 kcal/mole or less.

Two of the remaining possible sets of products are analogous to those previously thought to be the major routes in $O(^3P) + \text{ethylene}$. First, $CO + CH_2$: Addition of oxygen to a carbon, followed by 1,2 C-C hydrogen migration, and subsequent C-C bond cleavage would lead to $CO + CH_2$ ($CHO + CH_3$ in the $O(^3P) + \text{ethylene}$ reaction). However, it is quite clear that there is a large (~ 50 kcal/mole) potential energy

barrier to the formation of a triplet ketene (which would decompose to $\text{CO} + \text{CH}_2$) by a 1,2 C-C hydrogen migration on the triplet surface. Given the stability of the 1,3 diradical intermediate, ~ 30 kcal/mole, and no more than 10 kcal/mole collision energy, passage over the barrier from the 1,3 triplet diradical to triplet ketene is highly unlikely. Second, $\text{H}_2 + \text{C}_2\text{O}$: Either a four center elimination of H_2 from the 1,3 diradical, or a three centered elimination of H_2 from a triplet ketene would be required to form $\text{H}_2 + \text{C}_2\text{O}$ (analogous to $\text{H}_2 + \text{ketene}$ product in $\text{O}(^3\text{P}) + \text{ethylene}$). We expect that a very large ~ 50 kcal/mole potential energy barrier should accompany the three or four center molecular elimination, and as just mentioned, a large potential energy barrier is expected to prohibit access to triplet ketene itself (where the three center elimination would be considered). It seems, then, that although both of these products have been frequently suggested as primary products, significant potential energy barriers should prohibit their formation from the 1,3 triplet A' oxyacetylene diradical.

The final possible primary products shown are $\text{H} + \text{ketyl radical}$. The lowest $^3\text{A}'$ diradical should, through C-H single bond cleavage, lead to the ground state of ketyl radical. The next highest 1,3 triplet diradical would lead by C-H single bond cleavage to an excited ketyl radical. If we use 1 eV as a guess for the ketyl excitation energy (corresponding to the vinoxy radical excitation) then the excited ketyl would be accessible at collision energies greater than ~ 5 kcal/mole. A small potential energy barrier is shown in the C-H single bond cleavage exit channels, as we have come to expect for the

elimination of hydrogen atoms from $O(^3P)$ -unsaturated hydrocarbon triplet intermediates.

3. PREVIOUS RESULTS

Most of the previous studies of the $O(^3P)$ -acetylene reaction that we are concerned with, can be placed into one of three groups: (1) purely kinetic studies, (2) flame studies with implications for the isolated $O(^3P)$ -acetylene reaction or (3) studies directed at determining the primary $O(^3P)$ -acetylene reaction products and detailed reaction mechanism. First we review the kinetic studies.

The various kinetic studies of $O(^3P) + \text{acetylene}$ have been in remarkably good agreement, even though a wide variety of techniques have been used to make $O(^3P)$ atoms and to follow the course of the reaction.

In 1965 Sullivan and Warneck¹⁰ used a microwave discharge (with O_2 in helium mixtures to make oxygen atoms directly, or by discharging N_2 and then titrating the resulting N atoms with NO) to make $O(^3P)$ atoms in a fast flow system, detected products mass spectrometrically, and reported the first absolute rate constant for $O(^3P) + \text{acetylene}$, 1.5×10^{-13} molecule/cc sec.

Arrington et al.,¹¹ also used a nitrogen discharge with NO titration and a fast flow system with mass spectrometric (photometric as well) detection, but attempted to obtain Arrhenius parameters for the reaction by measuring the rate at room temperature and, by cooling their flow system with dry ice, at -77°C . They saw little difference in the rate at the two temperatures and concluded that the activation

energy for the reaction was less than 1 kcal/mole. Saunders and Heicklein¹² then used the mercury sensitized decomposition of N_2 to make $O(^3P)$ in the presence of acetylene-fluoro-olefin mixtures to obtain relative rates and activation energies for the $O(^3P)$ -acetylene and $O(^3P) + \text{fluoro-olefin}$ reactions. Their results showed that the activation energy for $O(^3P) + \text{acetylene}$ was 2.6 kcal/mole greater than their reference (fluoro-olefin) reactions. This experiment established a non-zero activation energy for $O(^3P) + \text{acetylene}$.

Several groups have used esr detection of oxygen atoms (made either by oxygen discharge or by N_2 discharge/NO titration), hydrogen atoms, and hydroxyl radicals in fast flow systems to obtain absolute rate constants. These experiments include the work of Brown and Thrush,¹³ Westenberg and deHaas¹⁴ (230°–450°C), and Bradley and Tse.¹⁵

Other reports of the $O(^3P)$ -acetylene rate include the measurements of James and Glass,¹⁶ time resolved CH^* chemiluminescence in a fast flow system from 273°–729°; Stuhl and Niki,¹⁷ NO_2^* chemiluminescence intensity following the titration of $O(^3P)$ with NO; Gaedtke et al.,⁸ $CH_2 + CO$ and C_2H_2O product yields at pressures up to 1000 atm; Vandooren and Tiggelen,¹⁸ molecular beam sampling and mass spectrometric analysis of the low pressure oxyacetylene flame, 700°–1430°K; and finally Westenberg and deHaas,¹⁹ flash photolysis-resonance fluorescence and chemiluminescence decays.

This entire set of rate measurements spans only a factor of 2, from $.9 \times 10^{-13}$ to 1.8×10^{-13} cc/mole sec, in the room temperature rate constant, illustrating the excellent agreement mentioned earlier. In 1973, Huie and Herron²⁰ recommended $1.4 \times 10^{-13} \exp(-3000/RT)$ cc/mole sec for the range 200°–700°.

Now we turn our attention to the relevant flame studies. Oxygen-acetylene flame studies have dated from le Chatelier's first measurements of the oxyacetylene flame burning velocity in²¹ 1895.

More recently, Robertson and Matsen²² observed the infrared spectrum of ketene in a heated flow study of acetylene self-combustion in 1956. This was the first observation of ketene in an oxygen-acetylene system and suggested that ketene or ketene-like intermediates might be important in the oxygen-acetylene reaction. Later, Miller²³ proposed that excited ketene was present in the oxygen-acetylene flame (and was an important intermediate in the formation of the negative ions in the flame) based on his observations of negative ions in the flame.

Relatively high energy processes have frequently been studied in the oxygen-acetylene flame, visible or ultraviolet chemiluminescence and chemi-ionization in particular. Various authors then have tried to interpret their results in terms of the elementary processes leading to the observed high energy phenomena. The first paper by Hand in 1962,²⁴ describing the vacuum ultraviolet chemiluminescence from the oxygen-acetylene flame, is a typical example. The fourth positive bands of CO were identified by Hand, and based on the energetics involved, the electronically excited CO was supposed to arise from the reaction of electronically excited CH with $O(^3P)$. The electronically excited CH was proposed to have been the result of the reaction of O_2 with C_2H , C_2H being the primary product of the reaction of $O(^3P)$ + acetylene. In this way, $C_2H + OH$ was established as a likely primary $O(^3P)$ + acetylene reaction product.

Becker and Bayes^{25,26} also studied the emission from CO in oxygen-acetylene flames. They were able to identify the triplet and Herman bands as well as the fourth positive bands of CO (with v' up to 6, 202 kcal/mole excitation). However, they also observed identical emission from the flame when carbon suboxide was substituted for acetylene. The presence of the emission in the nonhydrogen containing system excluded the possibility that any hydrogen containing species was an important precursor to the emission, in contrast to Hand's proposal. Rather than $O + CH^*$, they proposed $O + C_2O \rightarrow CO(A) + CO(X)$ as the probable source of the excited CO. One of the possible sources suggested for C_2O was $O(^3P) + C_2H_2 \rightarrow C_2O + H_2$, establishing another possible primary product. Later, Kinbara and Noda²⁷ flash photolyzed mixtures of O_2 , NO_2 , and acetylene, as well as using the mixtures in microwave discharges to study hydrocarbon oxidation. Their observations of emission from C_2 , CH, and OH as well as their ion current measurements were interpreted in terms of, and supported, the Becker and Bayes $O(^3P) + C_2H_2 \rightarrow C_2O + H_2$ mechanism.

In 1963, Fenimore and Jones⁴ studied the destruction of acetylene in flames with oxygen by measuring the rates of acetylene and oxygen loss and the CO appearance rate. In addition to establishing that acetylene was consumed by $O(^3P)$ in the flame, Fenimore and Jones made two other important suggestions. One, that the differences between saturated hydrocarbon flames and unsaturated hydrocarbon flames might be the result of a direct attack by oxygen on carbon in the unsaturated flames, and two, that the primary $O(^3P) +$ acetylene reaction might proceed through an excited ketene to form $CH_2 + CO$ or to form $H + HC_2O$ primary products.

Finally, Eberius, Hoyer mann, and Wagner³ measured product concentration profiles within premixed flames. Among the products reported were CO and H, both conceivably primary products.

This brief review of previous oxygen-acetylene flame studies demonstrates that the flame studies themselves indicated that, in fact, any or all of the conceivable $O(^3P)$ + acetylene primary product forming routes operate in the oxyacetylene flame. In the main, however, these systems are so complicated, and the observables frequently so far removed from the primary products, that confidence in deductions about the primary $O(^3P)$ -acetylene process is hard to build. More sophisticated experiments in cleaner systems, were really required to address the elementary $O(^3P)$ -acetylene reaction.

Many of the groups involved in the determination of the primary products of $O(^3P)$ + ethylene were also involved in parallel studies of $O(^3P)$ + acetylene. Low temperature matrix isolated flash photolysis, shock tube experiments, final product analysis, chemiluminescence identification, kinetic parameters, detection of radical intermediates, and high intensity crossed beam results have all been interpreted in terms of primary reaction products. One important difference in the development of the accepted reaction mechanisms, however, was that the substitution for hydrogen by oxygen was recognized very early on in $O(^3P)$ + acetylene studies.

In 1962, Haller and Pimentel⁹ photolyzed N_2O in solid argon with acetylene, at 20°K, and were able to observe the infrared spectrum of ketene in the process. They proposed a two step mechanism for the reaction, addition to form a 1,3 diradical, then 1,2 C-C hydrogen

migration to form ketene. While ketene was established as a primary $O(^3P)$ reaction product in this experiment, it was uncertain as to whether processes leading to ketene were enhanced by matrix effects, specifically whether collisions might be important in intersystem crossing, and access, to ground state ketene.

In a series of oxygen-acetylene shock tube experiments,^{28,29,30} Kistiakowsky and co-workers studied the temporal behavior of the total ion current and vacuum ultraviolet chemiluminescence, and mass spectrometrically determined product concentrations. The group's results were interpreted in terms of the chain branching reaction $O(^3P) + C_2H_2 \rightarrow OH + C_2H$ (Hand's suggestion). Stubbeman and Gardiner³¹ did another shock tube study and reported measurements of both visible and ultraviolet chemiluminescence as well as OH radical concentrations. While Stubbeman and Gardiner did include $C_2H + OH$ as possible products from $O(^3P) + \text{acetylene}$ they also suggested that the reactions $O(^3P) + C_2H_2 \rightarrow CO + CH_2$ and/or $CH + CHO$ might be important.

Several groups have relied on product analysis in fast flow systems, etc., to assess the relative importance of the various possible primary products. Arrington's experiment¹¹ revealed significant CO, H_2 , and H product yields. No CH_2 or H_2O , however, were observed. The absence of H_2O implied that few hydroxyl radicals were formed, further implying that $C_2H + OH$ were not very important primary products. In 1969, Williamson and Bayes³² used the mercury sensitized decomposition of N_2O to generate $O(^3P)$ in the presence of acetylene in a static system prior to product analysis. CO product yields were measured, the presence of CH_2 was confirmed by observing

C_3H_4 product, and $CO + CH_2$ were advanced as primary reaction products. However, the maximum CO yield could not account for all of the oxygen atoms consumed in the reaction, so $CO + CH_2$ was not the only primary product. (The $CO + CH_2$ yield was estimated to be 12-25 percent.) Molecular hydrogen was observed as a product, and it was argued that H_2 most likely originated from hydrogen atoms, formed as primary products in the reaction $O + C_2H_2 \rightarrow H + HC_2O$. Williamson and Bayes also believed that $H_2 + C_2O$ were formed as primary products—in short all energetically possible reactions were suggested. In a later static experiment, Williamson³³ was able to assess the importance of the $H + HC_2O$ channel and estimated that 42 percent of the primary products were formed by that process. Gaedtke⁸ analyzed the final products formed in high pressure (up to 1000 atm) $O(^3P) +$ acetylene reactions, and reported evidence for $CH_2 + CO$ and ketene primary products, suggesting that ketene-like intermediates would be important in a collisionless environment.

In contrast to the shock tube (and flame) results, Jonathon, Marmo, and Padur³⁴ (a fast flow experiment) and Clough, Schwartz, and Thrush³⁵ (a spherical flow reactor) studied the CO vacuum ultraviolet emission and concluded that electronically excited CO^* was formed not from $O_2 + C_2H$ ($O + C_2H_2 \rightarrow OH + C_2H$), but from $O + CH_2$. The CH_2 itself was believed to be a primary reaction product. (Clough, Schwartz, and Thrush also suggested that $O + CH \rightarrow CO^* + H$ might be important.) Westenberg and deHaas,¹⁹ on the other hand, felt that their flash photolysis (resonance fluorescence) chemiluminescence decay studies were explained best by assuming that $C_2O + H_2$ were the primary products leading ultimately to CO emission.

James and Glass¹⁶ attempted to determine the relative importance of abstraction and addition processes by interpretation of their kinetic parameters. In particular, they argued that the lack of deviation from their Arrhenius plot below 729° was proof that the addition type reactions dominate any abstraction reaction. The addition products were assumed to be CH₂ + CO.

Fast flow experiments with esr or photoionization detection have been used to monitor radical concentrations during the course of the O(³P)-acetylene reaction. Brown and Thrush,¹³ and Westenberg and deHaas,¹⁴ detected high hydrogen atom concentrations with esr. Both groups, however, believed that the hydrogen atoms were formed in the reaction $O(^3P) + CH_2 \rightarrow 2H + CO$, CH₂ the dominant primary product of $O(^3P) + C_2H_2$. Jones and Bayes³⁶ detected CH₂ and HC₂O among other radicals (C₃H₃, C₃H₂, CHO), and obtained steady state concentrations for CH₂ and HC₂O, using photoionization techniques. An analysis of their data led to the branching ratios

In 1974, crossed beam techniques were applied to this system for the first time. In experiments identical to those discussed in the O(³P) + ethylene literature review, Kanofsky, Lucas, Pruss, and Gutman³⁷ identified CH₂ and HC₂O as major product signals. No branching ratios were reported. In later independent experiments Blumenberg et al.,³⁸ using both their crossed jet and concentric nozzle arrangement (with high resolution mass spectrometric detection) reported CH₂ + CO and H + HC₂O

products with a 20:1 branching ratio favoring $\text{CH}_2 + \text{CO}$. At the very highest pressures used in the Blumenberg experiment, ketene product was also observed.

Essentially the only information about the dynamics of the reaction currently available are the results of a CO laser resonance absorption experiment by Shaub et al.,³⁹ in 1980. Assuming for the moment that $\text{CO} + \text{CH}_2$ are primary $\text{O} + \text{C}_2\text{H}_2$ reaction products, as did Shaub, then in the reaction of $\text{O}(^3\text{P})$ with substituted acetylenes, RC_2H , the product forming route that would lead to $\text{CO} + :\text{CH}_2$ in $\text{O}(^3\text{P}) + \text{C}_2\text{H}_2$, leads to $\text{CO} + :\text{CRH}$. The $:\text{CRH}$ carbene was expected to isomerize by a 1,2 hydrogen migration to form the more stable corresponding alkene. Shaub attempted to determine whether this isomerization occurred to any appreciable extent during C-C bond cleavage by probing the CO product vibrational distribution. That is, were the isomerization to occur simultaneously with the C-C bond cleavage, a great deal more energy would be available for CO vibrational distribution than if the carbene were formed and then isomerized. The CO vibrational distributions were identical to those calculated on a statistical basis assuming that the carbene was formed.

One major theoretical work on $\text{O}(^3\text{P}) + \text{acetylene}$ has appeared, inspired in part by our experiments. These results will be discussed later.

To summarize the previous results, there are four possible exothermic primary products: $\text{C}_2\text{H}_2\text{O}$, $\text{H} + \text{HC}_2\text{O}$, $\text{CO} + \text{CH}_2$, and $\text{H}_2 + \text{C}_2\text{O}$. Direct evidence in nearly collisionless environments has been reported to support $\text{H} + \text{HC}_2\text{O}$ and $\text{CO} + \text{CH}_2$ formation. Many reports of indirect

evidence for $C_2O + H_2$ as well as for $H + HC_2O$ and $CO + CH_2$ have appeared, from flame and more simple studies. The $CO + CH_2 : H + HC_2O$ branching ratios reported have varied from 20:1 to 1:8. In general it has been agreed that the C_2O route is relatively minor, based mainly on the low CO photon²⁶ yields $\sim 10^{-4}$. The only reports of ketene product have been associated with condensed phase or very high pressure gas phase experiments, never in collisionless environments. Abstraction to form $OH + C_2H$ has been suggested repeatedly, but only in high temperature (shock tube or flame) environments.

4. EXPERIMENTAL

We have now studied this reaction on three separate occasions, on two different machines. Initially we studied the reaction using the 25" universal crossed beams machine. Two hundred watts of RF power was discharged through 200 torr of a 5 percent O_2 in helium mixture prior to expanding through a .007" nozzle to produce an $O(^3P)$ beam with a $v_0 = 23.2 \times 10^4$ cm/sec and a speed ratio of 5.89. The acetylene beam was a neat beam, formed by expanding 300 torr of room temperature acetylene through a .004" nozzle. This beam had a v_0 of 9.94×10^4 cm/sec and a speed ratio of 7.64. The skimming and collimation of both of these beams was identical to that reported for the 25" machine $O(^3P) + \text{toluene}$ and $O(^3P) + \text{ethylene}$ experiments. The nominal collision energy for this experiment was 7.9 kcal/mole.

In this experiment the mass 41 and 40 angular distributions were obtained, as well as 12 microsecond per channel cross correlation time of flight distributions of the mass 41 signal at nine different

laboratory angles. The mass 41 angular distribution below represents at least six 60 second counts per angle, with a peak intensity of ~6500 counts/second at 35° , near the center of mass. No more than 1 hour of counting was required for the mass 41 TOF distributions at any angle. The high mass 28 and 14 background in our detector made it impossible for us to look for CO or CH₂ product at that time.

At a later date we returned to the $O(^3P) + \text{acetylene}$ reaction with the 35" crossed beams machine. Two hundred watts of RF power was discharged through 150 torr of a 5 percent O₂ in helium mixture prior to expansion through a .007" nozzle and skimming and collimation exactly as described for the 35" $O(^3P) + \text{ethylene}$ experiment. The resulting $O(^3P)$ beam had a v_0 of 25.96×10^4 cm/sec and a speed ratio of 5.9. 435 torr of neat acetylene was passed through a dry ice acetone trap to minimize the acetone in the beam prior to expansion at room temperature through a .005" nozzle. Collimation and skimming of this acetylene beam were the same as for the ethylene beam in the 35" $O(^3P) + \text{ethylene}$ experiment. This beam had a v_0 of 8.33×10^4 cm/sec and a speed ratio of 7.6. The collision energy for this experiment was 9.2 kcal/mole. The mass 41 angular distribution was obtained again at this time, requiring at least six 50 second counts per laboratory angle to obtain signal to noise of 50 at the peak of the distribution, ~1800 counts per second signal. The observed distribution was identical to the one previously obtained in shape, but was shifted towards the oxygen beam due to the change in the canonical center of mass angle. The mass 28 angular distribution was also measured at this time. The distribution shown below represents at least fifteen 100 second counts

per laboratory angle, with a peak counting rate of ~400 counts per second of mass 28 reactive signal. A small correction to the observed distribution was made to account for some elastically scattered mass 28 coming from residual acetone in the acetylene beam. (The mass 43 angular distribution was measured from 5° to 15° away from the acetylene beam. The same distribution was also obtained for the mass 28 signal. Assuming that nearly all of the mass 28 is elastically scattered at 5° from the beam, the 43 distribution was scaled to match the 28 5° from the beam, and the 43 distribution was subtracted from the 28 to obtain a distribution representing, nominally, only reactively scattered mass 28. However, it is unlikely that much more than half the 28 at 275° is elastically scattered, so this scheme must be regarded as a crude approximation at best. Even so, it substantially effects the mass 28 intensity at only two laboratory angles and errors associated with the subtraction are hardly critical in any respect.)

Finally, we obtained the mass 41 and 28 distributions at a reduced collision energy, by discharging 170 watts of RF power through 200 torr of a 5 percent O_2 in neon mixture prior to expansion through a .007" nozzle to obtain an oxygen beam with a $v_0 = 15.5 \times 10^4$ cm/sec and a speed ratio of 4.2. This beam was crossed with a beam of acetylene (neat, passed through dry ice acetone trap) formed by expanding 300 torr of acetylene through a .005" nozzle maintained at ~400°K (to minimize polymer formation). A v_0 of 8.87×10^4 cm/sec and speed ratio of 4.3 were obtained. The nominal collision energy for this experiment was 4.0 kcal/mole. The mass 41 angular distribution

required at least five 100 second counts per angle, and represents ~350 counts per second at its peak. The mass 28 angular distribution required at least five 300 second counts per angle, with a peak intensity of ~150 counts per second. Due to the low signal to noise of the mass 28 distribution, no elastic correction was made, but errors incurred are expected to be small. Ten microsecond/channel cross correlation time of flight mass 41 distributions were obtained at eight different laboratory angles, requiring ~1 hour counting per angle. Attempts were made to obtain time of flight mass 28 distributions at both 9.2 and 4.0 kcal/mole, but the signal to noise was too low to obtain data in any reasonable counting time.

5. IDENTIFICATION OF PRIMARY REACTION PRODUCTS

At collision energies of 10 kcal/mole or less, we need consider only ketene, $H + HC_2O$, $CO + CH_2$, and $H_2 + C_2O$ as possible primary products. We observed little or no mass 42 reactively scattered signal, confirming that in a collisionless environment, no ketene product is formed. The mass 40 angular distributions are superimposable on the mass 41 angular distributions at 7.9 kcal/mole and 4.2 kcal/mole shown in Figures 2 and 3 (proving that both $m/e = 41$ and $m/e = 40$ have the same neutral parent) and are only ~1/4 as intense as the 41 (ruling out the possibility that $m/e = 41$ appears only as ^{13}C and ^{17}O isotopic impurities in a C_2O product), so the $m/e = 40$ signal is clearly an ionizer crack off, and the $m/e = 41$ signal is the parent ion of ketyl $HCCO (+H)$ primary product. Ketyl product is no surprise at all given our previous results--facile replacement of

hydrogen by oxygen in every other⁴⁰ $O(^3P)$ -unsaturated hydrocarbon reaction.

A startling fact, however, is revealed by the mass 28 mass angular distributions at 9.2 and 4.0 kcal/mole shown in Figures 4 and 5. These mass 28 angular distributions are clearly not superimposable on the 41, and unambiguously confirm that CO (+ CH₂) is a primary product of the reaction of $O(^3P)$ + C₂H₂. This, of course, implies a 1,2 hydrogen migration prior to C-C bond cleavage, in stark contrast to the $O(^3P)$ + ethylene results.

This important difference between the $O(^3P)$ + acetylene and $O(^3P)$ + ethylene reactions could be due to either of two possible general reasons; either there is a significant difference between the $O(^3P)$ -ethylene and $O(^3P)$ -acetylene intermediates, or some of the governing principles of the $O(^3P)$ + ethylene reaction mechanism (i.e., a large barrier to 1,2 C-C hydrogen migration) are not generally applicable. In fact, the former, and not the latter reasoning is appropriate.

Harding⁴¹ has done ab initio configuration interaction calculations with a polarization double z basis set on the reaction of $O(^3P)$ with acetylene. Harding's study included calculations of intermediate and product energies as well as barrier heights. The single most important part of his report, with respect to our product analysis, is the fact that there exists another $O(^3P)$ -acetylene triplet diradical, one with no counterpart in the oxygen ethylene system. That is, in the preceding discussion the intermediate ~30 kcal/mole stable with respect to the reactants was pictured as the 1,3 diradical formed analogous to

that formed in the reaction of $O(^3P) + \text{ethylene}$, $^3A'$. However, as Harding's calculations point out, a considerably more stable triplet diradical can be formed, $^3A''$, a carbene-like intermediate. Harding's calculations indicate that the $^3A'$ species should be ~ 13 kcal/mole stable with respect to the reactants (vs. the thermochemical estimate of 30 kcal/mole) while the $^3A''$ should be ~ 50 (thermochemical estimate ~ 47) kcal/mole stable with respect to reactants.

At the most elementary level, the difference in energy between the $^3A'$ and $^3A''$ species corresponds to the difference between a C-C and a C-O pi bond.

Harding's calculations give barriers of 37 and 53 kcal/mole for the C-H single bond cleavage, and 1,2 C-C hydrogen shift in the $^3A''$ intermediate. The 37 kcal barrier for C-H bond cleavage is 5 kcal above the $H + HCCO$ ground state, implying a barrier of ~ 5 kcal/mole for the reverse $H + \text{ketyl}$ reaction, as mentioned earlier. The 53 kcal/mole barrier for the 1,2 C-C hydrogen migration on the $^3A''$ surface is again in concert with our previous remarks.

The $^3A'$ intermediates, therefore, still cannot be expected to lead to $CO + CH_2$. Only $H + HC_2O$ can be formed from the $^3A'$ diradical. On the other hand, the $^3A''$ intermediate's stability, with respect to the reactants' level is great enough that even a ~ 60 kcal/mole barrier could be surmounted en route to products, so a competition between the

formation of $\text{CO} + \text{CH}_2$ and $\text{H} + \text{HC}_2\text{O}$ would be expected after $^3\text{A}''$ formation. This completed picture is illustrated in the revised energy level diagram, Figure 6. It should be noted that the $^3\text{A}''$ intermediate or $^3\text{A}''$ ketene (formed by 1,2 C-C hydrogen migration in the $^3\text{A}''$ intermediate) could also energetically surmount a ~ 50 kcal/mole barrier to the four or three center elimination of H_2 respectively, but we observed no evidence for C_2O product.

We have observed two different sets of primary products in $\text{O}(^3\text{P})$ + acetylene, $\text{H} + \text{ketyl}$ and $\text{CO} + \text{CH}_2$. $\text{H} + \text{ketyl}$ may arise from either $^3\text{A}'$ or $^3\text{A}''$ intermediates. The $^3\text{A}''$ intermediate alone can account for the $\text{CO} + \text{CH}_2$ forming route. While the $^3\text{A}'$ intermediate has an exact analog in the reaction of $\text{O}(^3\text{P})$ + ethylene, there is no analog to the $^3\text{A}''$ species. The ability to form the $^3\text{A}''$ species, with stability enhanced to the point that 1,2 C-C hydrogen migrations are possible, is attributed to the extra pi electrons present in the acetylene system.

6. CENTER OF MASS PRODUCT ANGULAR AND TRANSLATIONAL ENERGY DISTRIBUTIONS

A. $\text{H} + \text{HC}_2\text{O}$

The fits shown to the 7.9 kcal/mole HC_2O angular distribution (Figure 2) and time of flight distributions (Figure 7) were obtained with the center of mass translational distribution ($P(E')$) and center of mass angular distribution ($T(\theta')$) shown in Figures 8 and 9. The center of mass angular distribution is forward-backward symmetric, with a slight preference for sideways scattering ($T(\theta^*) = T(180^\circ) = .86$,

$T(90^\circ) = 1.$). The translational energy distribution is quite broad, peaking at ~ 10 kcal/mole, and represents, an average of 10.4 kcal/mole deposited into translation. The angular distribution alone is fit best by an isotropic $T(\theta')$ and a $P(E')$ shifted to slightly higher energies than the one shown in Figure 8.

The time of flight data alone, on the other hand, is fit best by an angular distribution that is skewed slightly backwards and sideways with respect to the initial oxygen direction ($T(\theta^\circ) = .5$, $T(120^\circ) = 1.$, $T(180^\circ) = .8$) and a $P(E')$ shifted to slightly lower energies than the one shown in Figure 8. The error limits in the figures illustrate the range of $P(E')$ and $T(\theta')$ required for the best angular and time of flight fits. The intensity in the extremes of the angular distribution, and in the 10° time of flight distribution, not accounted for by the calculation, is believed to be due to either the presence of a high translational energy tail (not represented accurately in the calculation) or a small amount of $O(^1D)$ in the $O(^3P)$ beam (as in the $O(^3P) + \text{ethylene}$ results). Only a very small fraction of the observed intensities are not accounted for in the calculation, and the fits are quite good. (These same $P(E')$ and $T(\theta')$ also fit the mass 41 angular distribution at 9 kcal/mole very well.)

The mass 41 angular (Figure 3) and time of flight distributions (Figure 10) at 4.0 kcal/mole are fit best by an isotropic center of mass angular distribution and the broad $P(E')$ shown in Figures 11 and 12. This $P(E')$ also peaks at ~ 10 kcal/mole, and represents an average of ~ 10.8 kcal/mole deposited into translation. The errors in these distributions were estimated by evaluating the effects of slight

changes in the best fit $P(E')$ and $T(\theta')$ on the calculated angular distribution only.

At 4.0, 7.9, and 9.0 kcal/mole a broad translational energy distribution fits the C_2HO product angular and time of flight distributions well. Some slight sideways peaking achieves the best overall fits to the data at 7.9 and 9.0 kcal/mole, but isotropic scattering does the best job at 4.0 kcal/mole.

B. $CO + CH_2$

It is obvious from the shape of the mass 28 angular distribution at 9.2 kcal/mole that the distribution has two components. One is clearly an ionizer crack of the HC_2O product, the other is, of course, the actual CO primary product angular distribution. In order to obtain center of mass translational energy and angular distributions for CO product, a method is required to separate the two contributions to the observed laboratory angular distribution (thereby obtaining the lab distribution of CO product alone). Ideally, the two contributions at any laboratory angle could be separated, and their relative intensities measured, by the time of flight experiment. However, we were unable to obtain mass 28 time of flight data with reasonable signal to noise. Here then, the range of possible CO center of mass product angular and translational energy distributions is explored by assuming that different fractions of the mass 28 signal comes from HC_2O , and determining what center of mass distributions are required to reproduce the various possible lab distributions.

Two possible CO laboratory angular distributions were considered at 9.0 kcal/mole. The first was obtained as the result of scaling the mass 41 distribution to .5 of the mass 28 distribution at 25° and subtracting the mass 41 distribution from the mass 28 distribution. The second was obtained by scaling the 41 to match the 28 at 25° prior to subtraction. (The mass 41 intensity was ~1850 counts per second and the mass 28 intensity was ~400 counts per second at 35°. The first subtraction scheme implies that the 28/41 ion ratio for ketyl was ~.11, while the second scheme implies 28/41 (from ketyl) was ~.22.) These two distributions are shown in Figure 13.

The center of mass angular and translational energy distributions which fit the CO data best are shown in Figures 14 and 15. The calculated center of mass CO product flux corresponding to the first CO lab distribution is shown in Figure 16.

Both center of mass angular distributions are forward-backward symmetric, and peak strongly at 0° and 180° ($T(0^\circ) = T(180^\circ) = 4T(90^\circ)$). This strong forward-backward peaking is almost certainly a manifestation of correlation between the initial (l) and final (l') orbital angular momenta in the reaction. That is, frequently when a collision complex dissociates into two massive particles (versus say the elimination of a hydrogen atom), l goes predominately to l', and the dissociation is confined to the plane perpendicular to l (= j, the complex's rotational angular momentum, assuming that j, the initial rotational angular momentum, is negligible). This results in strong peaking on the relative velocity vector, since given an initial relative velocity v, all orientations of l will lead to measured

intensity at 0° and 180° , in the plane defined by the two beams' initial velocity vectors. It is unlikely that the CO angular distribution would have such sharp features as the second subtraction scheme indicates. The structure in the $T(\theta')$ near 90° used to fit that distribution is related to the very sharp structure, and no physical significance should be attached to it.

The best fit $P(E')$ for the first distribution peaks at ~ 1.2 kcal/mole and represents an average of ~ 16 kcal/mole, while, the best fit $P(E'')$ for the second distribution peaks at 5.8 kcal/mole, representing an average of 14.4 kcal/mole deposited into relative translation.

The same procedure was used to obtain three possible CO laboratory angular distributions at 4.0 kcal/mole. The mass 28 intensity at 40° in this experiment was ~ 150 counts/sec and the mass 41 intensity at 40° was ~ 350 counts/second. The first subtraction scheme scaled the 41 to .25 of the mass 28 at 40° (giving a 28/41 ratio of .11 for ketyl), a second scaled the 41 to .5 of the mass 28 (a 28/41 ratio of .22 for ketyl), and a third matched the 41 and 28 at 40° (a 28/41 ratio of .42 for ketyl). These three distributions are shown in Figure 17. As was mentioned earlier, some of the mass 28 signal near the acetylene beam comes from elastically scattered acetone, and no correction for this has been made in the 28 data presented. As a result, the fits to the 28 are consistently lacking in intensity within $\sim 20^\circ$ of the acetylene beam, and little attention was paid to this feature during the fitting process.

The center of mass angular and translational energy distributions which fit the three possible CO angular distributions are shown in Figures 18 and 19. All three center of mass angular distributions shown peak sharply at 0° and 180° . The extent of the 0° and 180° peaking relative to the intensity at 90° is directly determined by the extent of the 41 subtraction—as more signal is attributed to the HC_2O channel, the structure in the center of mass angular distribution becomes more severe. Again, almost certainly the correlation between l and l' is responsible for the shape of the distribution. It should be noted that the fits to the data near the acetylene beam can be improved by skewing the center of mass distribution to favor backward (with respect to oxygen) scattering, $T(0^\circ) = .75 T(180^\circ)$, but with essentially the same ratio, $T(180^\circ)/T(90^\circ)$. However, this almost certainly reflects the contribution to the 28 from the elastically scattered acetone and is not considered further.

The center of mass translational energy distributions are shown in Figure 19. All three are very similar. The distributions that fit the first and third subtraction schemes peak at ~ 12 kcal/mole and represent an average of 17.3 kcal/mole going into translation. The $P(E')$ that fits the second subtraction scheme best is shifted to slightly higher energies.

We see that at both 4.0 and 9.2 kcal/mole the CO product is characterized by a forward-backward symmetric center of mass angular distribution that peaks strongly at 0° and 180° (angular momentum effects). Roughly 16 kcal/mole is deposited into translation for this channel, at both 4.0 and 9.2 kcal/mole.

7. RELATIVE CROSS SECTIONS

In calculating the relative cross sections for $H + \text{ketyl}$ and $CO + CH_2$, we consider only the kinematic factors (k), the polarizabilities of the detected particles (α), the fraction of the total ions from a neutral product appearing at the detected mass (f), the actual cross sections (σ), and the observed intensities, so as before

$$\frac{\text{obs inten}_{(HC_2O)}}{\text{obs inten}_{(CO)}} = \frac{k_{HC_2O}}{k_{CO}} \cdot \frac{(\alpha_{HC_2O})^{1/2}}{(\alpha_{CO})^{1/2}} \cdot \frac{f_{HC_2O}}{f_{CO}} \cdot \frac{\sigma_{HC_2O}}{\sigma_{CO}}$$

In the 9.0 kcal experiment the mass 41 intensity 20° from the oxygen beam was 1700 counts/sec, and 1160 counts/sec at 15° . The 28 intensity was 400 counts/sec at 20° and 330 counts/sec at 15° . In the first subtraction considered, this corresponds to ~ 220 counts/sec of CO product at 20° and in the second scheme, ~ 85 counts/sec of CO product at 15° . The best fit kinematic factors were .33 at 20° , and .20 at 15° for the hydrogen elimination, and .037 at 20° (for the first subtraction), and .024 at 15° (for the second subtraction) for the CO elimination. The polarizability of ketyl and CO were estimated to be 32. and 19.5×10^{-35} cc respectively, by summing atomic polarizabilities. Finally, all the CO ions were assumed to appear at mass 28, and the fraction of mass 41 ions from ketyl was estimated to be .3 (roughly one-third of the ions from ketene are parent ions).

Using these values with the first subtraction scheme, $\sigma_{CO}/\sigma_{HC_2O} = .44$, and with the second subtraction scheme, $\sigma_{CO}/\sigma_{HC_2O} = .23$. It would appear that a reasonable estimate for $\sigma_{CO}/\sigma_{HC_2O}$ at 9.0 kcal/mole is .3.

The low energy experiment qualitatively indicates a difference in the branching ratio. The ratio of the mass 41 signals at 9.2 and 4.0 kcal/mole is ~ 5 while the 28 intensity falls by only a factor of ~ 2.5 . This implies that as the collision energy decreases $\sigma_{\text{CO}}/\sigma_{\text{HC}_2\text{O}}$ increases. An even more striking qualitative indication is the mass 28 angular distribution itself. At 9.2 kcal/mole it clearly contains a significant contribution from ketyl dissociative ionization, while at 4.0 kcal/mole no relatively sharp feature from ketyl is apparent. Assuming that the fragmentation of ketyl is roughly constant in the two experiments (conceivably as the internal excitation of ketyl changes, its fragmentation in the ionizer will change) then the absence of a sharp feature at 4.0 kcal/mole also implies that ketyl is relatively less important at 4.0 (than at 9.2) kcal/mole.

In the 4.0 kcal/mole experiment the mass 41 intensity 30° away from the beam was 250 counts/second, and the mass 28 intensity 30° away from the beam was ~ 150 counts/second. In the first, second, and third subtraction schemes this corresponds to 124, 98, and 45 counts/second of actual CO product at 30° respectively. The kinematic factor from the best fit hydrogen elimination analysis at 30° is .17, and the three kinematic factors from the CO analyses are $.012 \pm .001$ at 30° . Repeating the calculation done for the high energy experiment (α , f the same) we obtain $\sigma_{\text{CO}}/\sigma_{\text{HC}_2\text{O}} \sim 3, 2, \text{ and } 1$ for the first, second, and third subtraction schemes respectively.

Our experimental results indicate that the relative cross sections for $\text{CH}_2 + \text{CO}$ and $\text{H} + \text{HC}_2\text{O}$ go from $\sigma_{\text{CO}}/\sigma_{\text{HC}_2\text{O}} \sim .3$ at 9.2 kcal/mole to ~ 2 at 4.0 kcal/mole.

8. STATISTICAL CALCULATIONS: COMPARISON TO EXPERIMENT

Statistical models of several different processes can be compared with our experimental results. In particular, we are interested in the decay of the $^3A'$ intermediate to $H + HC_2O$, the decay of the $^3A''$ intermediate to $H + HC_2O$, the isomerization of the $^3A''$ intermediate to $^3A''$ ketene, and, finally, the decay of $^3A''$ ketene to $^3CH_2 + CO$. All four of these processes were modeled by RRKM-AM⁴² and phase space calculations.⁴³

A. MODELS

Table 1 lists most of the parameters used in the $^3A'' \rightarrow H + ^2A''$ HCCO calculations. Harding's geometries for the $^3A''$ intermediate, transition state, and $^2A''$ product were used, as well as his 37 kcal/mole barrier for C-H bond rupture and 18 kcal/mole exothermicity. The vibrational frequencies of the $^3A''$ intermediate and HCCO product were estimated by analogy with stable molecules. The transition state frequencies were chosen to correspond to a ΔS of activation for the reaction of $\sim .4$ gibb. (The decomposition of ethyl radical (to $H + C_2H_4$) has a high pressure A factor of $10^{13.4}$, which corresponds to an entropy of activation of $.4$ gibb. The geometric and energetic changes in the $^3A''$ intermediate should be very similar to those undergone by the ethyl radical, and, hence, the choice of $.4$ gibb for the energy of activation.) C_6 entrance and exit channel constants (1023 and 481 kcal A^6) were estimated by using known values for the polarizabilities of H, O, and C_2H_2 (4 , 8 , and 33×10^{-25} cc), using band additives and a contribution calculated for a C 2p electron to

estimate the polarizability of HCCO (38×10^{-25} cc), and the relation between C_6 constants and polarizabilities given by Hirschfelder.⁴⁴

The same model of the $^3A''$ intermediate was used in calculations describing the isomerization to $^3A''$ ketene (Table 2). Harding's geometry for the transition state, and Harding's barrier to 1,2 hydrogen migration (53 kcal/mole) were used. Other calculations were also done with different barrier heights (30-53 kcal/mole). In this case, an in plane CH bend was selected as the reaction coordinate. The A factor for 1,2 hydrogen migration in ethyl radical is believed to be a factor of ten lower than the A factor for hydrogen elimination, reflecting the very tight nature of the cyclic transition state. In light of this, the transition state frequencies were chosen to give a ΔS of activation equal to -3.4 gibbs, implying an A factor of $10^{12.5}$ (vs. $10^{13.4}$ for the $^3A''$ hydrogen elimination).

Table 3 lists most of the parameters used in calculations modeling the dissociation of $^3A''$ ketene to CO + 3CH_2 . The energy of the $^3A''$ ketene was given by Harding (20 kcal/mole below the $^3A''$ OCHCH) and the transition state was assumed to be 12 kcal/mole above that level (implying a 5 kcal/mole barrier for the addition of 3CH_2 to CO). The frequencies for $^3A''$ ketene were taken to be the same as for 1A_1 ketene, except for the C-C stretch which was reduced to 1000 cm^{-1} . The geometry of $^3A''$ ketene was slightly modified from that suggested by Dykstra.⁴⁵ Transition state vibrational frequencies were chosen to reproduce an A factor of $10^{15.1}$ ($\Delta S = 8.6$ gibbs) (typical for the elimination of a relatively heavy particle), and the transition state geometry used a $2\text{ \AA}$ C-C bond length. An exit channel C_6 constant for

this channel (1284 kcal A⁶) was estimated using the known polarizability of CO, and using atomic polarizabilities to estimate the polarizability of CH₂.

Finally, the decomposition of the ³A'OCHCH to H + ²A"OCCH was modeled (Table 4). The thermochemical estimate was used for the ³A' heat of formation, and dissociation to a level 17 kcal/mole above that, 5 kcal above the asymptotic H + OCCH level was considered. A geometry analogous to that suggested for ²A' CH₂CHO⁴⁶ was used for the ³A' diradical, and the same transition state geometry used in the ³A" decomposition was used for this transition state. Using the same transition state vibrational frequencies as well, and estimates of vibrational frequencies for the ³A' state based on known molecules, a ΔS[‡] of 2.2 gibbs is predicted. This ΔS[‡] implies an A factor of 10^{13.7}, which seems quite reasonable, so no changes in parameters describing the transition state in the ³A" decay were made to describe the ³A' dissociation.

B. STATISTICAL RESULTS

Generally, we are interested in the lifetimes and translational energy distributions predicted by the statistical calculations. Interest in the calculated lifetimes (rate constants) is two-fold; (1) we may be able to interpret asymmetry in the center of mass angular distribution in terms of lifetimes that are shorter than complex rotational periods, and (2) in the case of competitive dissociation channels, calculations will predict branching ratios.

RRKM-AM and phase space calculations of the product translational energy distributions are shown with the experimental distributions in Figures 8, 11, 14, and 19. The calculated distributions for ketyl radical are much narrower than the experimental ones; peaking at 3 and 4 kcal/mole, with averages of 5.8 and 6.5 kcal/mole at collision energies of 5 and 9 kcal/mole respectively, compared to the experimental average of 10.8 and 10.4 kcal/mole.

The calculations also predict less energy than that observed in translation for $\text{CO} + \text{CH}_2$ products--predicted averages of 10.8 and 12.5 kcal/mole versus the experimental values of 17 and 15 kcal/mole.

A potential energy barrier is expected in the exit channel for both $\text{CH}_2 + \text{CO}$ and $\text{H} + \text{HCCO}$ products. It is most likely that the extra energy appears in translation as a result of these exit channel effects. (The lifetime calculations indicate that the most rapid dissociation to $\text{CO} + \text{CH}_2$ or $\text{H} + \text{HCCO}$ takes place in a time frame at least as long as a 300 cm^{-1} vibrational period, so a statistical energy distribution at the top of the barrier could certainly be expected.)

In order to discuss the center of mass angular distributions, an estimate of a typical $\text{O}(^3\text{P})$ -acetylene complex's rotational period is required. Setting $1/2(I\omega^2) = (\hbar^2/8\pi^2 I)[J(J+1)]$ with $J = 2\pi\nu b/h$, $I = 47.11 \text{ amu } \text{\AA}^2$, and estimating an average impact parameter, b , to be $2 \text{ \AA}$ at 5 kcal/mole and $2.2 \text{ \AA}$ at 9 kcal/mole, then a typical rotational period at 5 kcal/mole is .73 picoseconds and .47 picoseconds at 10 kcal/mole.

The lifetime of the $^3A''$ intermediate with respect to hydrogen elimination is calculated to be 4.5 picoseconds at 5 kcal/mole and 2.5 picoseconds at 9 kcal/mole. In each case, roughly 5 rotational periods. The lifetime assuming that the $^3A''$ isomerizes to the $^3A''$ ketene is 38 nanoseconds at 5 kcal/mole ($\sim 5 \times 10^4$ rotational periods) and 7.2 nanoseconds ($\sim 1 \times 10^4$ rotational periods) at 9 kcal/mole, assuming a 53 kcal/mole barrier to the 1,2 C-C hydrogen migration. (The subsequent dissociation of $^3A''$ ketene to CO + CH₂ is very rapid--RRKM-AM calculated lifetimes of $\sim 5 \times 10^{-4}$ picoseconds at 5 and 9 kcal/mole.)

Clearly then, the calculations predict that the CO + CH₂ angular distribution should be forward-backward symmetric, and the experimental results confirm this. The ketyl angular distribution should also probably show forward-backward symmetry based on the lifetime calculations, as the experiment also confirms.

The ketyl center of mass angular distribution is forward-backward symmetric, but not quite isotropic at 7.9 kcal/mole. The elimination of a hydrogen atom is not expected to convert much of the complex's angular momentum into product orbital angular momentum. Little correlation between l and l' is expected. It is possible, then, that the slight deviation from isotropy in the center of mass angular distribution represents sub-rotational period dissociation to H + HCCO--in particular, attack of the oxygen at one of the two carbon atoms and elimination of a hydrogen near its equilibrium geometry, on the average, at right angles to the oxygen's velocity. The $^3A''$ lifetime calculations seem to rule out this possibility. However, the

calculated lifetimes of the $^3A'$ diradical are .13 picoseconds at 5 kcal/mole and .085 picoseconds at 9 kcal/mole, $\sim$.2 rotational periods in each case. While this line of reasoning is hardly conclusive, it is suggestive, and the possibility that both the $^3A'$ and $^3A''$ intermediates are formed and lead to $H + HCCO$ cannot be ruled out.

Both energy and entropy considerations favor $H + HCCO$ over $CH_2 + CO$ from the $^3A''$ intermediate; the barrier to 1,2 C-C hydrogen migration is greater than the barrier to C-H single bond cleavage, and the A factor favors hydrogen elimination over hydrogen migration by 10 to 1. We have two measurements to consider in light of the statistical calculations, (1) the measured absolute branching ratios, and (2) the change in branching ratio with collision energy. Our measurements of the change in branching ratio with collision energy are probably the more accurate of the two, since the errors in estimated factors (ion detection efficiencies, fraction of ions formed at a given mass, etc.) will cancel when calculate the ratio of branching ratios at two given energies.

With a 53 kcal/mole barrier to 1,2 hydrogen migration, a 37 kcal/mole barrier to elimination, and only 55 to 60 kcal/mole energy available, slight increases in the collision energy will have a much greater effect on the rate of $CO + CH_2$ formation than on the $H + HCCO$ formation. In fact, the RRKM-AM calculations show that (using the same A factors for all barrier heights) as long as the barrier to 1,2 C-C hydrogen migration is greater than 41 kcal/mole, then the $(CO + CH_2)/(H + HCCO)$ ratio should go up as the collision energy goes from 4 to 9 kcal/mole. Our experiment shows qualitatively the opposite trend, that

CO becomes more important as we lower the collision energy. However, this does not mean that the behavior of the $^3A''$ is contrary to that described above. The CO may in fact become a relatively more important decay route for the $^3A''$ as the collision energy increases, but another source of HCCO may be growing faster, so the total HCCO/CO ratio may increase with collision energy. In particular, if the cross section for $H + HCCO$ from the $^3A'$ intermediate increases rapidly with collision energy then it could compensate for the relative decrease in $H + HCCO$ from the $^3A''$ intermediate. Furthermore, as was noted earlier, the first excited state of the ketyl radical may not be accessible at 4 kcal/mole collision energy but may be accessible at 9 kcal/mole. If the slightly higher energy $^3A'$ intermediate is non-reactive at 4 kcal/mole, but can form excited ketyl at 9 kcal/mole (or if a $^3A''$ intermediate can dissociate to excited ketyl), then a whole new avenue to ketyl will have opened up and could make the total branching ratio favor ketyl as the collision energy increases.

There are, then, two possible explanations for the qualitative difference between our experiment and calculations describing the $^3A''$ intermediate as far as the dependence of branching ratio on collision energy. Both rely on significant reactive contributions (leading to $H + HCCO$) from the $^3A'$ intermediates.

Finally, we consider the measured and calculated branching ratios themselves. Considering the $^3A''$ intermediates alone, then as mentioned above, both energetics and entropics heavily favor $H + HCCO$ products. With a 53 kcal/mole barrier to 1,2 hydrogen migration, a 37 kcal barrier to hydrogen elimination and a difference of 10

(favoring hydrogen elimination) in A factor, the calculated branching ratio is $\sim 1.5 \times 10^{-4}$ at 4 kcal/mole and 5×10^{-4} at 9 kcal/mole (the experimental value was $\sim .3$ at 9 kcal/mole). With a barrier to migration of 42 kcal/mole the calculated branching ratios are $\sim 1 \times 10^{-2}$ at both 4 and 9 kcal/mole. To obtain a branching ratio of .1, the barrier to hydrogen migration must be ~ 31 kcal/mole. (It should be noted that with that low of a barrier, as the collision energy increases from 4 to 9 kcal/mole the branching ratio σ_H/σ_{CO} also increases, as our experiment indicates.) However, it is extremely unlikely that the barrier could be that low. More likely, the barrier to 1,2 hydrogen migration may be in the 45-50 kcal/mole range and the barrier to hydrogen elimination may be several kcal/mole greater than the 37 used in the calculations. If the barriers are assumed to be 44 and 40 kcal/mole respectively, then the branching ratio is $\sim .015$ at both 4 and 9 kcal/mole. Even with these barriers the calculated and experimental values differ by a factor of ~ 20 . The high pressure A factors may not differ by an order of magnitude but certainly the ratio of A factors should not be off by more than a factor of 2.

The difference between experimental and calculation could be due to processes not considered in the calculation. We have already suggested that the $^3A'$ intermediates play an important role in the reaction, but the $^3A'$ can only lead to $H + HCCO$, not $CH_2 + CO$, so if anything, the reaction products coming from the $^3A'$ intermediate should make the experimental branching ratio $\sigma_{HC_2O}/\sigma_{CO}$ greater than, not less than, that calculated considering only the $^3A''$ intermediate.

Entrance channel effects could be important within the $^3A''$ intermediates. Two different $^3A''$ intermediates could be formed (if C-C rotation is not completely free), a "cis" and a "trans" structure (similar to the geometrically different forms of the $^3A'$ intermediate). In the "trans" structure the hydrogen atom on the carbon

that is attacked by oxygen can migrate to the in plane half-filled sp_2 orbital on the other carbon. In the "cis" structure the most accessible half-filled orbital is the out of plane orbital. It is conceivable then, that if rotation about the C-C bond is not free, and that these two different $^3A''$ states exist, then they may have different preferences for elimination and migration. However, it would seem that both would be free to eliminate hydrogen atoms, while one would have great difficulty in supporting 1,2 hydrogen migration, and this would again lead to a cross section ratio favoring hydrogen elimination more than that calculated.

It is difficult then, to explain the differences between the measured and calculated cross section ratios beyond attributing the differences to the admittedly large experimental errors involved in estimating relative cross sections from the reactive scattering distributions, especially in cases (CO product) where signal to noise is extremely low.

9. SUMMARY

We have presented evidence for two sets of primary products in the reaction of $O(^3P)$ with acetylene; $H + HCCO$ and $^3CH_2 + CO$. A triplet diradical intermediate $^3A'$ analogous to that formed in the reaction of $O(^3P)$ with ethylene can lead to $H + HCCO$ but not $^3CH_2 + CO$, exactly as in the reaction of $O(^3P) +$ ethylene. A second intermediate, a triplet carbene $^3A''$, which has no counterpart in $O(^3P) +$ ethylene, is considerably more stable than the $^3A'$ intermediate and can lead to $H + HCCO$ or by 1,2 C-C hydrogen migration ultimately to $^3CH_2 + CO$. This is a major difference in the $O(^3P)$ -acetylene and $O(^3P)$ -ethylene reaction mechanism. $H + HCCO$ certainly dominates $CH_2 + CO$ at 9 kcal/mole collision energy but at 4 kcal/mole the experiment indicates that the two channels may be of comparable importance--this observation is difficult to reconcile with the general picture of the reaction. Finally, evidence for small potential energy barriers in the exit channels for C-H and C-C bond cleavage was observed in both products' translational energy distributions.

REFERENCES: CHAPTER V

1. R. T. Morrison, R. N. Boyd, Organic Chemistry, Allyn and Bacon, Boston (1973).
2. A. Williams, D. B. Smith, Chem. Rev. 70, 267 (1970).
3. K. H. Eberius, K. Hoyer mann, H. G. Wagner, 14th Symposium International on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania (1973), p. 147.
4. C. P. Fenimore, G. W. Jones, J. Chem. Phys. 39, 1514 (1963).
5. W. C. Gardiner, Jr., J. Chem. Phys. 40, 2410 (1964).
6. C. P. Fenimore, J. Chem. Phys. 40, 2411 (1964).
7. S. W. Benson, Thermochemical Kinetics, Wiley Interscience, New York (1976).
8. H. Gaedtke, K. Glanzev, H. Hippler, K. Luther, J. Troe, 14th Symposium International on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania (1973), p. 295.
9. I. Haller, G. C. Pimental, J. Amer. Chem. Soc. 84, 2855 (1962).
10. J. O. Sullivan, P. Warneck, J. Phys. Chem. 69, 1749 (1965).
11. C. A. Arrington, W. Brennen, G. P. Glass, J. U. Michael, H. Niki, J. Chem. Phys. 43, 525 (1965).
12. D. Saunders, J. Heicklen, J. Phys. Chem. 70, 1950 (1966).
13. J. M. Brown, B. A. Thrush, Trans. Farad. Soc. 63, 630 (1967).
14. A. A. Westenberg, N. deHaas, J. Phys. Chem. 73, 1181 (1969).
15. J. N. Bradley, R. Tse, Trans. Farad. Soc. 65, 2685 (1969).
16. G. S. James, G. P. Glass, J. Chem. Phys. 50, 2268 (1969).
17. F. Stuhl, H. Niki, J. Chem. Phys. 55, 3954 (1971).

18. J. Vandooren, P. J. Van Tiggelen, 16th Symposium International on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania (1976), p. 1133.
19. A. A. Westenberg, N. deHaas, J. Chem. Phys. 66, 4900 (1977).
20. J. T. Heron, R. E. Huie, J. Phys. Chem. Ref. Data 2, 467 (1973).
21. H. le Chatelier, C. R. Acad. Sci., Paris 121, 1144 (1895).
22. W. W. Robertson, F. A. Matsen, Comb. and Flame 1, 94 (1956).
23. W. J. Miller, H. F. Calcote, J. Chem. Phys. 41, 4001 (1964).
24. C. W. Hand, J. Chem. Phys. 36, 2521 (1962).
25. K. H. Becker, K. D. Bayes, J. Chem. Phys. 45, 396 (1966).
26. K. H. Becker, K. D. Bayes, J. Chem. Phys. 48, 653 (1968).
27. T. Kinbara, K. Noda, 14th Symposium International on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania (1973), p. 321.
28. C. W. Hand, G. B. Kistiakowsky, J. Chem. Phys. 37, 1239 (1962).
29. G. B. Kistiakowsky, L. W. Richards, J. Chem. Phys. 36, 1707 (1962).
30. G. P. Glass, G. B. Kistiakowsky, J. U. Michael, H. Niki, 10th Symposium International on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania (1965), p. 513.
31. R. F. Stubbeman, W. C. Gardiner, Jr., J. Phys. Chem. 68, 3169 (1964).
32. D. G. Williamson, K. D. Bayes, J. Phys. Chem. 73, 1232 (1969).
33. D. G. Williamson, J. Phys. Chem. 75, 4053 (1971).
34. N. Jonathon, F. P. Marmo, J. P. Padur, J. Chem. Phys. 42, 1463 (1965).
35. P. N. Clough, S. E. Schwartz, B. A. Thrush, Proc. Roy. Soc. A317, 575 (1970).

36. I. T. N. Jones, K. D. Bayes, 14th Symposium International on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania (1973), p. 277.
37. J. R. Kanofsky, D. Lucas, F. Pruss, D. Gutman, J. Phys. Chem. 78, 311 (1974).
38. B. Blumenberg, K. Hoyerman, R. Sievert, 16th Symposium International on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania (1976), p. 841.
39. W. M. Shaub, T. L. Burks, M. C. Lin, Chemical Physics 45, 455 (1980).
40. With the possible exception of $O(^3P) + 1,2$ dichloroethylene.
41. L. B. Harding, J. Phys. Chem. 85, 10 (1981), and private communications.
42. P. J. Robinson, K. A. Holbrook, Unimolecular Reactions, Wiley Interscience, London (1972).
43. J. C. Light, Dis. Faraday Society 44, 14 (1967).
44. J. O. Hirschfelder, C. F. Curtiss, H. C. Bird, Molecular Theory of Gases and Liquids, Wiley Interscience, New York (1954).
45. C. E. Dykstra et al., J. Amer. Chem. Soc. 98, 2689 (1976).
46. M. Dupuis, J. J. Wendoloski, W. A. Lester, Jr., J. Chem. Phys. 76, 488 (1982).

TABLE 1. $3A'' \text{ OCHCH} \rightarrow 2A'' \text{ OCCH} + \text{H}$

	$3A'' \text{ OCHCH}$	Transition State	$2A'' \text{ OCCH}$
<u>Moments of Inertia</u> (amu Å ²)	47.11, 39.48, 7.62	51.94, 46.15, 5.79	46.93, 46.35, .584
<u>Vibrational Frequencies</u> (cm ⁻¹)	3100 CH stretch 3100 CH stretch 1700 CO stretch 1400 CH bend 1300 CH bend 1150 CH bend 1000 CC stretch 500 CCO bend 200 torsion	- (reaction coord.) 3100 1700 1300 400 400 1300 600 400	- 3000 1700 1150 - - 1550 700 800
<u>Critical Energy</u> (kcal/mole)	37		
<u>Molecular Energy</u> (kcal/mole)	54-60		
<u>ΔH</u> (kcal/mole)	18		

TABLE 2. $3A''$ OCHCH $\rightarrow$ $3A''$ CH₂CO

	$3A''$ OCHCH	Transition State	Product $3A''$ CH ₂ CO
<u>Moments of Inertia</u> (amu Å ²)	47.11, 39.48, 7.62	49.96, 46.07, 3.89	51.77, 47.58, 4.19
<u>Vibrational Frequencies</u> (cm ⁻¹)	3100 CH stretch 3100 CH stretch 1700 CO stretch 1400 CH bend 1300 CH bend 1150 CH bend 1000 CC stretch 500 OCC bend 200 int. rot.	3100 2100 1700 1400 1300 - (reaction coord.) 1000 1200 1200	3100 3100 2160 1450 1150 1100 1000 800 500
<u>Critical Energy</u>	53 (30 to 55)		
<u>Molecular Energy</u>	54-60		

TABLE 3. $3A'' \text{ CH}_2\text{CO} \rightarrow 3\text{CH}_2 + \text{CO}$

	$3A'' \text{ CH}_2\text{CO}$	Transition State	Product $3\text{CH}_2 + \text{CO}$
<u>Moments of Inertia</u> ($\text{amu } \text{\AA}^2$)	51.77, 47.58, 4.19	81.86, 79.50, 2.35	
<u>Vibrational Frequencies</u> (cm^{-1})	3166 ν_1 CH	3166	3000
	3081 ν_5 CH	3081	2968
	2162 ν_2 CO	2170	2170
	1400 ν_3 CH ₂	1400	1444
	1000 ν_4 CC	- (reaction coord.)	-
	1000 ν_6 CH ₂	250	-
	788 ν_8 CH ₂	200	-
	588 ν_9 CCO	150	-
	528 ν_7 CCO	125	-
<u>Critical Energy</u> (kcal/mole)	12		
<u>Molecular Energy</u> (kcal/mole)	74-80		

TABLE 4. 3A' OCHCH $\rightarrow$ 2A'' OCCH + H

	3A' OCHCH	Transition State	Product 2A'' OCCH + H
<u>Moments of Inertia</u> (amu Å ²)	50.48, 44.82, 5.66	51.94, 46.15, 5.79	
<u>Vibrational Frequencies</u>	3100 CH stretch	-(reaction coord.)	-
	3100 CH stretch	3100	3000
	1650 CH stretch	1300	1650
	1450 CH bend	1300	1150
	1200 CO stretch	1700	1700
	1150 CH bend	400	-
	1150 CH bend	400	-
	500 CCO bend	600	700
	500 CCO bend	400	800
<u>Critical Energy</u> (kcal/mole)	17		
<u>Molecular Energy</u> (kcal/mole)	34-40		
<u>ΔH</u> (kcal/mole)	18		

FIGURE CAPTIONS: CHAPTER V

1. Energy level diagram for $O(^3P) + \text{acetylene}$.
2. Mass 41, HCCO product, angular distribution at 7.9 kcal/mole collision energy.
3. Mass 41, HCCO product, angular distribution at 4.0 kcal/mole collision energy.
4. Mass 28 angular distribution at 9.2 kcal/mole collision energy. Mass 41 distribution shown below (not to scale).
5. Mass 28 angular distribution at 4.0 kcal/mole collision energy. Mass 41 distribution shown below (not to scale).
6. Revised energy level diagram for $O(^3P) + \text{acetylene}$.
7. Mass 41, HCCO product, time of flight distributions at 7.9 kcal/mole collision energy.
8. HCCO product center of mass translational energy distribution at 7.9 kcal/mole. Solid line best fit, cross hatched area experimental error, dotted line statistical calculations.
9. HCCO product center of mass angular distribution at 7.9 kcal/mole. Solid line best fit, cross hatched area experimental error.
10. Mass 41, HCCO product, time of flight distributions at 4.0 kcal/mole collision energy.
11. HCCO product center of mass translational energy distribution at 4.0 kcal/mole. Solid line best fit, cross hatched area experimental error, dotted line statistical calculations.
12. HCCO product center of mass angular distribution at 4.0 kcal/mole. Solid line best fit, cross hatched area experimental error.

13. Possible CO product laboratory angular distributions at 9.2 kcal/mole collision energy.
14. CO product center of mass translational energy distributions at 9.2 kcal/mole for subtraction schemes 1 and 2. Dotted line statistical calculation.
15. CO product center of mass angular distributions at 9.2 kcal/mole collision energy for subtraction schemes 1 and 2.
16. Center of mass CO product flux for subtraction scheme 1.
17. Possible CO product laboratory angular distributions at 4.0 kcal/mole collision energy.
18. CO product center of mass angular distributions at 4.0 kcal/mole collision energy for subtraction schemes 1, 2, and 3.
19. CO product center of mass translational energy distributions at 4.0 kcal/mole for subtraction schemes 1, 2, and 3. Dotted line statistical calculation.

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FIGURE 5-1

FIGURE 5-2

FIGURE 5-3

FIGURE 5-4

XBL 8211-3275

FIGURE 5-5

XBL 8211-3244

FIGURE 5-6

FIGURE 5-7

XBL 8211-3230

FIGURE 5-8

XBL 8211-3280

FIGURE 5-9

FIGURE 5-10

FIGURE 5-11

FIGURE 5-12

FIGURE 5-13

XBL 8211-3281

FIGURE 5-14

FIGURE 5-15

CENTER OF MASS FLUX

FIGURE 5-16

FIGURE 5-17

FIGURE 5-18

FIGURE 5-19

VI. THE REACTION OF $O(^1D)$ WITH HD

1. INTRODUCTION

The reactions of $O(^1D)$ atoms have attracted as much or more attention as the reactions of $O(^3P)$ atoms recently. While $O(^1D)$ may be an important participant in some combustion or laser systems,¹ the primary focus has been on the important role $O(^1D)$ plays in the upper atmosphere, specifically with respect to ozone chemistry.² $O(^1D)$ results from the photodissociation of O_3 , as well as O_2 , and to a lesser extent N_2O and NO_2 , in the stratosphere, and also ultimately consumes ozone, by first reacting with hydrogen (or other species) to form OH, which consumes significant quantities of O_3 in the atmosphere.

The chemistries of $O(^1D)$ and $O(^3P)$ show some striking differences. $O(^3P)$ may abstract atoms, and is known to add to unsaturated systems. While $O(^1D)$ may also abstract atoms and add to unsaturated systems, the $O(^1D)$ atom may insert into single bonds,^{3,4} presenting a whole new reactive mechanism. These differences are paralleled by other isoelectronic systems, most notably singlet and triplet methylene. In this chapter, we focus on the competition between abstraction and insertion, and the associated dynamics in the prototypical $O(^1D) + HD$ reaction.

There is no question about the chemical identity of the products of $O(^1D) + H_2$. Formation of $OH + H$ is 43 kcal/mole exothermic and no other products are possible in a single collision experiment. In the reaction of $O(^1D) + HD$, $H + OD$ products are 44.2 kcal/mole exothermic and $D + OH$ products are 42.6 kcal exothermic. The adiabatic reaction leading from ground state reactants to ground electronic state products takes place on the X^1A_1 surface of H_2O^5 , so if an insertion type mechanism occurs, the system has access to the deep H_2O (HOH) ground state well, -160 kcal/mole below the reactants' level. No such well is believed to exist for any nearly end on-abstraction type mechanism.⁶ Either mechanism, of course, could account for the $OH + H$ products. More detailed, a priori, considerations of the insertion and abstraction mechanisms give clues as to how the relative importance of the two possible mechanisms, and their dynamics, may be ascertained. If $O(^1D)$ inserts into H_2 , and samples the H_2O ground state well, a relatively long unimolecular lifetime might result, the two OH bonds would be equivalent, and product energy distributions, neglecting any subtle dynamical effects would be statistical. On the other hand, if abstraction type processes are important, one might expect a more localized interaction of the $O(^1D)$ with just one H atom, a shorter lifetime, and conceivably significant OH product vibrational excitation similar to the reaction of $F + H_2$.⁷

The results of crossed molecular beams scattering experiments provide information that can help to determine which of these mechanisms is dominant. The products' center of mass angular distribution can lead to complex lifetime information, and can also help to dis-

tinguish insertion and abstraction mechanisms by its symmetry. Measurements of the products' translational energy distributions can be interpreted in terms of whether the excess product energy is in fact statistically distributed.

To this end, a crossed molecular beams study of the $O(^1D) + H_2$ reaction was completed recently in our laboratory.⁸ This experiment was done at 2.4 kcal/mole collision energy. A forward-backward symmetric center of mass angular distribution, peaking at 0° and 180° fit the data well. A translational energy distribution slightly colder than, but essentially statistical in nature was observed (in agreement with other measurements). Any HHO structure, an abstraction channel, would almost certainly have a sub-rotational (complex) lifetime and result in OH product being backward scattered. The forward-backward symmetry observed at 2.4 kcal indicated that insertion must be the dominant reaction mechanism. Lifetime information from the center of mass angular distribution is lost however, for the insertion of $O(^1D)$ into a homonuclear diatomic, since as long as the two OH (fractional or whole) bonds are equivalent, then forward or backward scattered OH is equally likely.

To further our understanding of the mechanism of OH product formation in the reaction of $O(^1D) + H_2$ we have now studied the reaction of $O(^1D) + HD$.

This $O(^1D) + HD$ experiment was carried out at 3.4 kcal/mole collision energy. Along with the center of mass angular and velocity distributions, the OH to OD product ratio provides another indication of the relative importance of insertion and abstraction. Within the

Born Oppenheimer approximation, abstraction by end-on attack would almost certainly result in equal abundancies of OH and OD product. (This result is expected as long as the rotational motion of the HD is slower than the relative velocity between HD and O. If the rotational motion is very fast compared to the relative velocity, since the hydrogen is further away from the HD center of mass than the deuterium, the oxygen atom will effectively see only the H atom--the H atom screens the deuterium atom--and OH product would be favored.) If a relatively long-lived insertion complex is formed, OD product would be favored due to zero point energy differences.

If insertion does dominate, the center of mass angular distribution will reveal lifetime information in this reaction, unlike $O + H_2$. A sub-rotational complex lifetime would be revealed in differences between the OH and OD distributions.

Before proceeding to a discussion of this experiment and its results, we briefly review some of the other experiments performed previously on this system.

2. PREVIOUS RESULTS

Many groups have made measurements of the $O(^1D)$ deactivation rate during the last twenty years. For the most part, the absolute rate measurements that have been made detected the $O(^1D)$ concentration as a function of time. A composite rate is obtained when the $O(^1D)$ concentration is measured in systems where $O(^1D)$ can be both physically and chemically deactivated. Fortunately, very early on, it was discovered that in the reaction of $O(^1D)$ with H_2 , the electronically

adiabatic process, forming $\text{OH} + \text{H}$ dominates (by nearly 1000 to 1) the spin forbidden physical deactivation,^{9,10} so rate measurements based on $\text{O}(^1\text{D})$ concentrations in the $\text{O}(^1\text{D}) + \text{H}_2$ system have accurately reflected the rate of $\text{OH} + \text{H}$ formation. Another simplifying feature of the $\text{O}(^1\text{D}) + \text{H}_2$ kinetics, noted first by DeMore in 1967,¹¹ in a flash photolysis study of $\text{O}_3\text{-H}_2$ mixtures in liquid argon, is the absence of an activation energy for the reaction. A constant (pre-exponential) factor is all that is needed to characterize the reaction rate.

Previous kinetic rate experiments can be grouped into those that measure the $\text{O}(^1\text{D})$ concentration directly as a function of time, and those that measure it indirectly, for example by measuring the amount of $\text{O}(^1\text{D})$ precursor remaining after a given photolysis time. Invariably $\text{O}(^1\text{D})$ is generated photolytically. The most common method is by exciting (say with 266 nm quadrupoled YAG) the Hartley band of ozone, although O_2 and CO_2 have also been photolyzed in the uv to form $\text{O}(^1\text{D})$.¹²

Snelling and Bair^{13,14} have measured the rates of $\text{O}(^1\text{D})$ deactivation by N_2 , Xe, Ar, and O_2^* , as well as the rate of reaction with O_3 by measuring the extent of O_3 decomposition in their experiments. Noxon,¹² Gilpin,¹⁵ Clark,¹⁶ and Davidson¹⁷ have all made absolute deactivation, or reaction rate measurements, by monitoring time resolved $\text{O}(^1\text{D}) \rightarrow \text{O}(^3\text{P})$ 630 nm radiation during the reaction. Davidson's measurement of the $\text{O} + \text{H}_2$ rate constant is the most recent using this technique, and gives 1.3×10^{-10} cc/mole sec at 298°. Husain et al.,^{18,19,20} have performed the most comprehensive series of absolute reaction and deactivation rate measurements, using time resolved resonant $\text{O}(3^1\text{D}_2) \leftarrow \text{O}(2^1\text{D}_2)$ absorption at 115.2 nm. Schofield²¹ has presented a rather recent

critical review of these rate measurements and recommends the value 1.2×10^{-10} cc/mole sec for the reaction of $O(^1D) + H_2$ over the 204° – $352^\circ K$ temperature range.

While rate constants were being measured, other experiments were devised to obtain dynamical information about the $O(^1D) + H_2$ reaction, and the manifestations of these dynamics on the product energy distributions. In the early 1960s, McGrath and Norrish,²² and Basco and Norrish²³ were able to determine significant vibrational excitation (up to $v = 2$), in OH produced from the flash photolysis of H_2-O_3 mixtures. Callear et al.,¹ in fact observed stimulated infrared emission after flash photolyzing H_2-O_3 mixtures. Basco and Norrish assumed that the reaction of $O(^1D)$ with H_2 led to the vibrationally excited OH, but could not eliminate the possibility that the source was $H + O_3 \rightarrow OH + O_2$. DeMore's 1967 experiment¹¹ was also addressed in part to the question of insertion vs. abstraction. At 87° in liquid argon, enough H_2O was observed to provide an estimate of the relative importance of the two channels. DeMore suggested that abstraction might lead to as much as 60 percent of the reaction forming OH. The ability of $O(^1D)$ to both insert into single C-H bonds, and (if collisionally de-excited) form alcohols, and abstract H atoms in simple alkanes was demonstrated by Lin et al., in 1973,²⁴ as well as by Cvetanovic's work.² In 1975 Stief,⁹ in a flash photolysis-resonance fluorescence experiment, was able to confirm the belief that physical deactivation of $O(^1D)$ by H_2 is unimportant compared to chemical (reactive) deactivation forming $H + OH$.

Most recently Luntz,²⁵ Smith,²⁶ and Smith and Butler²⁷ have used laser induced fluorescence of the OH formed in the $O(^1D) + H_2$ reaction to probe the internal energy distribution of the products. These studies agree on an essentially statistical OH vibrational distribution, while they find highly nonstatistical OH rotational distributions. There is significantly more energy in OH rotation than that expected on a statistical basis, the populations inverted, with a maximum in K-25.

As far as previous experiments go then, there is essential agreement on a ~0 activation energy. OH product vibrations are populated very nearly statistically, OH rotations are considerably hotter than statistical and, finally, apparently both insertion and abstraction mechanisms are operative.

Current understanding of the reaction of $O(^1D) + H_2$ has been significantly enhanced by several detailed theoretical studies. Tully^{10,28} was able to use a statistical model to calculate the reaction rate constant within experimental errors, but had to assume that two surfaces contributed to reaction product, vide infra. In addition, Tully's statistical calculations predicted that deactivation of $O(^1D)$ by H_2 would be 99.9 percent chemical in nature, supporting Stief's results.

Gangi and Bader,²⁹ Whitlock et al.,^{5,30} and Schinke and Lester⁶ have all constructed potential energy surfaces for the water molecule. Whitlock, Sorbie, and Lester, in addition, have performed classical $O(^1D) + H_2$ trajectory studies using those surfaces in order to rationalize the features observed in the reaction, and have obtained a detailed picture of the reaction mechanism.

Of the five different entrance channels for $O(^1D) + H_2$, only the lowest two correlate to ground state $OH + H$ products. One path is via the X^1A_1 surface of water, the other goes by way of the first excited 1B_1 state of water. That state is more than 170 kcal/mole above ground state water, nearly 10 kcal above the reactants' level, and it is not necessary to consider scattering on that surface for collision energies of less than 5 kcal/mole. (That only one of the five possible surfaces should be considered in the reaction, is an objection raised to Tully's rate constant calculation.)

Gangi and Bader's surface included significant barriers for both insertion and abstraction, a ~9 kcal/mole insertion barrier in C_{2v} , and a 24 kcal/mole abstraction barrier for $C_{\infty v}$ approach, which were not present on the other surfaces, and which seem unphysical in view of the small or zero activation energy for the reaction, and is not considered further.

Whitlock et al., used the diatomics in molecules formulation to calculate two 1A_1 surfaces for H_2O . Their surface I included a 1.3 kcal/mole barrier to C_{2v} insertion, which they regarded as inappropriate in view of the existing experimental evidence. Their surface II was a modification of surface I which had no barrier to C_{2v} insertion, as well as a ~1 kcal/mole barrier to $C_{\infty v}$ abstraction. The Sorbie and Murrell surface is an empirical construction, with no energetic barriers for insertion or abstraction. The path for insertion on this surface is much more attractive than on the Whitlock surface. Lester has noted that, while the Sorbie surface describes equilibrium 1A_1 H_2O exceptionally well, the abstraction path on the

Sorbie surface passes through a deep well, and an exit channel barrier, which is probably qualitatively in error. Finally, Schinke and Lester developed an analytic fit to their ab initio first order CI 1A_1 H_2O surface. Trajectories were considered on their original surface I, with no barrier to insertion and a ~ 1 kcal barrier to abstraction (like Whitlock II), a surface II, which was a modification that included a .7 kcal/mole barrier to insertion (like Whitlock I), and a third, attractive surface, with no barriers either for insertion or abstraction (like Sorbie and Murrell). The energetics of the asymptotic limits were in error on the Schinke-Lester surface; OH product could be excited to $v = 5$ as opposed to the thermodynamic limit of $v = 4$.

The initial conditions for the Whitlock and Schinke-Lester trajectories were $v = 0$ and $J = 1$ for H_2 , the most probable values at room temperature, and the collision energies were varied from .5 to 6 and 5 kcal/mole respectively. Sorbie used a Boltzmann distribution of initial internal states corresponding to temperatures between 200° and 600° , and collision energies from .23 to .92 kcal/mole.

For the most part, the major dynamical features predicted by the various trajectory calculations are similar. While the models agree that the reactive cross sections do decrease with increasing collision energy, Lester points out that the total cross section, and rate constants, are very sensitive to the long range parts of the potential for highly exothermic, extremely attractive surfaces with no entrance channel potential energy barriers. So it's not too surprising that the different calculations do not agree exactly on the total cross sections.

All three calculations agree that the final product vibrational distribution is essentially statistical, while the rotational distribution is inverted, quite a bit hotter than statistical, and rather narrow. Sorbie finds that ~ 25 percent of the reaction exothermicity goes into rotation and ~ 45 percent into vibration, nearly independent of temperature. Lester finds a variation away from the statistical vibrational distribution as the collision energy increases. This is consistent with Whitlock's studies. Whitlock was able to divide the trajectories into insertion or abstraction types (on the basis of the maximum potential energy during a trajectory; achieving a potential energy corresponding to the formation of at least 1.5 OH bonds qualified a trajectory as insertion) and examine the final energy distributions for each group, as well as for all the trajectories. Abstractions were typified as resulting in low rotational and high vibrational energy release, corresponding to the simple small impact parameter, nearly end-on attack model. Vibrations were statistical for products of insertion-type reactions. Generally the H_2O bend was highly excited during the insertion process and the large bending excitation was effectively channeled into OH rotational energy. Since both Whitlock's and Lester's surfaces included barriers for abstraction and not insertion, the ratio of abstraction to insertion would be expected to increase, and deviations from hot rotations and statistical vibrations begin, as the collision energy increases, as Lester reported. On Whitlock's surface, insertion represents 80 percent of the reactive trajectories at .5 kcal/mole and 75 percent at 6 kcal/mole.

All three calculations indicated that the H_2O intermediate formed in the insertion process is vibrationally long-lived, with typical lifetimes of 5×10^{-14} seconds.

Finally, Schinke-Lester, Sorbie and Murrell, and the initial report of Whitlock, predicted a forward-backward symmetric differential cross section at low collision energies, peaking at 0° and 180° . As expected, due to the increasing importance of abstraction as the collision energy increases, Lester saw some asymmetry, favoring back-scattering at his highest collision energy, 5 kcal/mole. Whitlock's original report predicted only a sharpening of the 0° and 180° peaks with collision energy, and retention of forward-backward symmetry. Whitlock's more recent results show significant forward peaking at low (~ 0.5 kcal/mole) collision energy and forward-backward symmetry is obtained as the collision energy is raised to ~ 5 kcal/mole. To explain the low energy asymmetry, Whitlock proposed an osculating complex model of the reaction at low collision energies. As the collision energy increases the lifetime does not change much, but the rotational period becomes shorter, so the lifetime relative to rotation becomes long enough to produce forward-backward symmetry.

Even for a sub-rotational decay, a symmetric insertion mechanism must lead to forward-backward symmetric differential cross sections, when the insertion is into a homonuclear diatomic (symmetric implying equivalent interaction between the oxygen and each hydrogen). The forward peaking calculated by Whitlock at low collision energy suggests a type of insertion more akin to a "stripping" of one hydrogen by the oxygen. That is, while the oxygen attacks between the

two hydrogens, the interaction is asymmetric to the point that one hydrogen is carried away with the oxygen before a truly statistical-type symmetric complex is formed. Whitlock did not discuss the increased importance of backscattering at the higher collision energies in terms of increasing abstraction participation.

Then to summarize the previous results, it appears that there are two mechanistically different routes to OH product: insertion, characterized by a relatively long lifetime (at least several OH stretching periods), statistical product vibrational energy distributions, hot product rotations, and an essentially forward-backward symmetric center of mass differential cross section peaking at 0° and 180° ; and abstraction, with a small entrance channel barrier, little rotational excitation, hot vibrations, a shorter lifetime than that typical for insertion and, probably, an anisotropic backward-peaking center of mass differential cross section. Insertion should dominate at low collision energies, but abstraction should gain in relative importance as the collision energy increases.

3. EXPERIMENTAL

This experiment was performed on the 35 inch universal crossed molecular beams machine.³² We believe that $O(^1D)$ production is maximized in the O_2/He discharge,³³ as the cross section for quenching of $O(^1D)$ to $O(^3P)$ is least for He among He, Ne, and Ar, so a 5 percent O_2 in helium mixture was used in the atomic oxygen source. A liquid nitrogen trap was installed in the gas delivery line to minimize any water in the source. 190 watts of radio frequency power was discharged through

the mixture prior to expansion through a .007" nozzle and .032" x .55" long conical boron nitride skimmer. The beam finally passed through a .060" x .120" rectangular slit in the differential pumping wall prior to entering the main scattering chamber. The oxygen beam obtained had a v_0 of 2.45×10^5 cm/sec and a speed ratio of 6.45.

Seven hundred torr of neat HD³⁴ expanded through a .003" nozzle in a tungsten oven after passing through another liquid nitrogen trap to eliminate any impurities remaining after the HD synthesis. The beam was skimmed by a .045" diameter x .254" long thoriated tungsten skimmer, mounted .55" away from the nozzle (nozzle skimmer distance .3") and passed through a .038" x .075" rectangular defining slit, mounted on the reducer, ~.050" from the skimmer, prior to passing through a final slit on the differential pumping wall, .085" x .165". The HD beam had a v_0 of 2.19×10^5 cm/sec and a speed ratio of 8.44. The nominal collision energy for these two beams was 3.4 kcal/mole.

The mass 17 intensity was ~210 counts per second and the mass 18 intensity was nearly 530 counts/second 17.5° away from the oxygen beam. The mass 17 and 18 angular distributions obtained are the result of at least six 100 second counts at each angle. Both mass 17 and 18 angular distributions displayed an unexpected very intense, rapidly rising feature close to the oxygen beam, suggesting that some species issuing from the oxygen source was elastically scattered and fragmented to give mass 17 and 18 ions. It was immediately noted that the natural abundance of ^{18}O was sufficiently large to make a noticeable contribution. However, ^{18}O would not contribute to the mass 17 distribution, as the mass spectrometric resolution was orders of magnitude above what would be

required to allow sufficient 18 to leak through. The most likely other explanation was water entering into the gas line. Considerable effort was put into eliminating water from the system, but the elastic features remained in the 17 and 18 distributions.

A method for correcting the observed distributions for the elastic contamination was used as follows. Repeated measurements of the mass 18 to mass 16 intensity were made in the absence of mass 18 OD product--either by crossing a beam of He or H₂ with the oxygen beam, or by observing the beam itself. These measurements gave 18/16 = .00482 ± .00001, a little more than twice what was expected from ¹⁸O alone (.002), in the absence of reactive mass 18 signal. A companion measurement of the mass 17/mass 16 ratio was obtained by crossing the oxygen beam with a helium beam, and gave 17/16 = .0022 ± .00022 in the absence of reactive mass 17 signal. Assuming water to be the sole source of extra 18 and 17, these ratios imply a fragmentation ratio for water of .0028/.0022 ~1.3, smaller than that reported,³⁵ but any water coming out of the discharge source is coming out at ~700°C mass average temperature, and the fragmentation pattern could easily be perturbed. Moreover, water in the beam source could be expected to dissociate to H + OH. OH would be produced in this fashion, as well as in the subsequent H + O₂ reaction in the source. These other sources of OH would make the apparent 17/18 fragmentation ratio of water greater than the literature value as well.

Next, the mass 18/16 and mass 17/16 intensity ratios were measured carefully with the HD beam on, 10° from the oxygen beam: 18/16 = .0089 ± .0001 and 17/16 = .0034 ± .0001. By combining these two sets of

ratios, 64.7 percent of the mass 17 and 54.2 percent of the mass 18 signals at 350° were identified as elastically scattered signal.

At least two different neutral species contributed to the mass 18 elastic signal, ^{18}O and probably water. The mass 17 elastic signal consisted then, probably of water fragments and conceivably some OH radicals as well. However, in order to correct the observed distributions, the assumption was made that the mass 16 angular distribution, nominally elastically scattered ^{16}O only, would adequately represent the elastic angular distributions of all those species contributing elastic intensity at mass 17 and 18. The mass 16 angular distribution was measured, and was scaled to account for 64.7 percent and 54.2 percent of the mass 17 and 18 intensities 10° from the oxygen beam. The distributions obtained by subtracting the scaled 16 from the observed 17 and 18 are shown in Figures 1 and 2 as the OH and OD product angular distribution from $\text{O}(^1\text{D}) + \text{HD} \rightarrow \text{H} + \text{OD}$ or $\text{D} + \text{OH}$.

Nine microsecond/channel cross correlation time of flight distributions of mass 17 and 18 product were obtained at six different laboratory angles. Three features appeared in the distributions that were obtained, other than the actual product time of flight. Frequently in the cross correlation experiment a non-uniform baseline was observed, believed to be due either to vibrations of the detector caused by the spinning cross correlation wheel, or to slight non-uniformities in the slotted structure of the wheel. In any event, scattered product signal frequently coincided with a non-uniform baseline, and baseline subtractions can introduce uncertainties in the data. Second, although the ion deflecting field removes almost all of the ions generated by

the oxygen atom source, some very fast particles (ion exchanged neutrals) do still exit the source and make it into the detector; producing (at angles $\leq 15^\circ$ from the oxygen beam) a very intense (~ 20 times the peak reactive intensity) and sharp signal at very short flight times. An effective method for removing both of these contributions was found to be obtaining TOF distributions with both beams on, and then with the HD beam off, scaling only for counting times, if necessary, and then subtracting the two distributions. In all cases an excellent baseline was achieved, although the signal to noise in the difference distribution suffered. The third nonreactive contribution, expected after the discussion of the angular distribution's appearance, is an elastically scattered contribution. Mass 16 TOF was also obtained with HD both on and off, and then, was scaled so that the integral of the 16 TOF was the same fraction of the 17 or 18 integrated TOF that the mass 16 elastic signal was, in the angular distribution at the given angle. The mass 17 and 18 TOF data shown are the result of this three-fold subtraction procedure.

Mass 17 and mass 18 TOF required between $.6(20^\circ)$ and $3.6(-10^\circ)$ hours with the HD beam on and identical counting times with the HD beam off. The mass 16 distributions generally required no more than $.6$ hour at any angle. Thus, while the signal to noise is undesirably low at some angles, particularly for the mass 17 signal, (in order to fully account for undesired contributions) the distributions shown represent more than eight hours counting at some angles.

4. CENTER OF MASS PRODUCT ANGULAR AND TRANSLATIONAL ENERGY DISTRIBUTIONS

A. OD PRODUCT

The best fit to the OD laboratory angular distribution is obtained with the $P(E')$ and $T(\theta')$ labeled "A" in Figures 5 and 6. While these distributions do an excellent job of reproducing the angular distribution and most of the TOF distributions, a bimodal structure is indicated for the TOF distribution at 80° , nearly at the center of mass, by the calculation, which is not obvious in the data. The relative minimum in the 80° calculated time of flight is near the center of mass velocity and is due to the very low intensity of the $P(E')$ for $E' < 1.5$ kcal/mole. This same feature of the $P(E')$, however, is necessary to provide for the sharp minimum at $\sim 80^\circ$ in the OD angular distribution.

For comparison, a second $P(E')$ labeled "B" in Figure 5 is provided. This $P(E')$ has increased intensity in the 0-1.5 kcal/mole region, and as the calculations shown indicate, removes the bimodal structure from the 80° TOF. However, the increased low energy intensity blows up the angular distribution at 80° , and skews it such that a poor fit to the angular distribution is obtained. It is reasonable then, to take these two translational energy distributions as our experimental limits, but distribution "A" generally fits the data better than "B." Distributions "A" and "B" represent an average of ~ 18.6 and 14.4 kcal/mole deposited into translation respectively.

Errors in the $T(\theta')$ were estimated by using the "A" $P(E')$ (which gave the best fit to the angular distribution) and varying the $T(\theta')$ to see what ranges in $T(\theta')$ would provide reasonable fits to the

angular distribution. The two other $T(\theta')$ shown in Figure 6 produce fits very similar to the best fit from 50° to 72.5° and from 105° to 110° . In the range surrounding the center of mass angle, the best fit calculation is bracketed by calculations using the "A" $P(E')$ and the "C" and "D" $T(\theta')$, roughly one standard deviation apart. Thus the "C" and "D" $T(\theta')$ are chosen as our error limits. The cross section ratio for backward to forward scattering for these distributions is given by $\int_0^{30} \sin\theta T(\theta') d\theta / \int_{50}^{180} \sin\theta T(\theta') d\theta$, and is 1.40 for "A," 1.62 for "B," and 1.19 for "C."

B. OH PRODUCT

The time of flight data for the OH product has very low signal to noise after the subtractions discussed earlier, and it is difficult to extract very much information from them. The $P(E')$ and $T(\theta')$ labeled "A" in Figures 7 and 8 produce the best fit to the angular distribution. However, the calculated time of flight distributions using these $P(E')$ and $T(\theta')$ are clearly slow at 60° and narrow at 75° . The overall best fits to the OH TOF are achieved with the $T(\theta')$ and $P(E')$ labeled "B" in Figures 7 and 8. Just as in the OD analysis, these best fits to the TOF are achieved at the expense of unacceptably high intensity at the center of mass angle, and skewing of the calculated angular distribution. A third and final set of $P(E')$ and $T(\theta')$ are shown as compromise values, labeled "C."

The three $P(E')$ are very similar, indicating 14.2(A), 15.84(B), and 14.4(C) kcal/mole deposited into translation (on average) respectively. While the shapes of the $T(\theta')$ are somewhat different, the

integrated cross section ratios, backward to forward, do not vary greatly and are 1.31(C), 1.25(B), and .98(A).

To summarize the experimental product center of mass angular and translational distributions, we may say (1) there is more energy deposited into translation for the OD product than for the OH product, the best fit to the OD angular distribution representing ~18 kcal/mole, the best fit to the OH angular distribution representing ~15 kcal/mole, and (2) both products are scattered preferentially ~1.3 to 1.0 backwards with respect to the incident oxygen velocity. The center of mass angular distributions also suggest that the OH product is slightly less backward scattered than the OD product.

5. RELATIVE CROSS SECTIONS

This experiment, unlike several of the others discussed earlier, does permit an accurate estimation of the relative cross sections for OH and OD product. This is because we expect there to be very little, if any, difference in the various factors affecting the relative detection efficiency of the two products, polarizability, ion counting efficiency, fragmentation pattern, etc. Thus we have only to consider the observed intensities and the kinematic factors arrived at from the data fitting process. Using, in all cases, the calculated distributions, at 17.5° the kinematic factor for OD formation is .27, from the best fit angular distribution calculation. Kinematic factors at that angle vary only $\pm .02$ for the other distributions presented. The kinematic factor from the calculation that gives the best fit to the OH angular distribution at 17.5° is .14 (.12 for the two other sets

($P(E')$ $T(\theta')$) presented). The actual ratio of observed intensities at 17.5° is $\pm .36$. These values lead to $\sigma_{OH} / \sigma_{OD} = .70 \pm .05$, the error estimated from the slight differences in the possible $P(E')$ and $T(\theta')$ presented.

6. STATISTICAL CALCULATIONS

RRKM-AM^{36,37} and phase space³⁸ calculations for the decomposition of HOD to D + OH and to H + OD were performed to obtain statistical estimates of the complex's lifetime, translational energy distributions and product branching ratios.

In the RRKM-AM calculation, the equilibrium structure of HOD was chosen to represent the structure of the activated molecule. The transition state was modeled using Benson's³⁹ suggestion that for a simple bond fission, at the transition state, the breaking bond is stretched to ~ 2.8 times its equilibrium distance (from .96 to 2.7 Å). Since the product OH or OD frequency is nearly that of the same OH or OD stretch in HOD, only the HOD bending frequency was different from its equilibrium value in the transition state model, and depended on the A factor for decomposition (vide infra). C_6 constants were estimated from atomic polarizabilities,⁴⁰ 232 kcal Å⁶ for O + HD, 166 kcal Å⁶ for H + OD or D + OH. Equilibrium HOD, OH or OD properties were used for any other required parameters.

The phase space and RRKM-AM calculations of the product translational energy distributions for OH and OD products are shown in Figures 5 and 7 with the experimental distributions. The average energy predicted for OD product is 18.1 kcal/mole and is 15.5 kcal/mole for

OH product. These values agree well with the experimental ones, and while their maxima are at slightly larger energies than the experimental best fits, these predicted distributions are functional very similar to the experimental best fit distribution. These calculated product translational energy distributions are, of course, independent of any model of the transition state (i.e., A factor).

A factors for the simple fission of a hydrogen atom are commonly $\sim 10^{14.5}$.³⁹ The A factor for the elimination of a deuterium atom would be larger due to mass effects (increased transition state moments of inertia). A range of values for the A factors were considered. For OH product, A factors of $10^{14.5}$, $10^{15.}$, and $10^{15.5}$, requiring transition state bending frequencies of 100, 63, and 10 cm^{-1} were considered. OD product was modeled with the same bending frequencies, but these implied lower A factors since the transition state moments of inertia were lower, $10^{14.4}$, $10^{14.9}$, and $10^{15.4}$.

Throughout this range of A factors, the branching ratio is essentially constant, $.72 \pm .01$. This ratio can be understood at an elementary level, essentially on the basis of the product's zero point vibrational energy, within the approximations of the Activated Complex Theory.⁴¹ Within the Activated Complex Theory, the rate constant for product formation is the product of a transmission factor, kT/h , and an equilibrium constant for the formation of activated complexes from reactants, $K^\ddagger$. This equilibrium constant can be expressed in terms of partition functions; the ratio of the complex's partition function (does not include the degree of freedom corresponding to the reaction coordinate) to the product of the reactant's partition

functions. A classical evaluation, within the Born Oppenheimer approximation, of that ratio gives $(k_{\text{OH}}/k_{\text{OD}}) = (m^{\text{OD}}/m^{\text{OH}})^{1/2}$, where m^{OD} and m^{OH} are the reduced masses corresponding to motion along the reaction coordinate. In the $\text{HOD} \rightarrow \text{OH} + \text{D}$ or $\text{OD} + \text{H}$ case, that ratio is .73 as the OD product is favored to the extent that the complex leading to OD product, with a 2721 cm^{-1} vibration represented in the transition state, has a higher density of states than a complex leading to OH product, with a 3735 cm^{-1} vibration. The success of these simple considerations is accentuated by the similarity of the Activated Complex Theory and RRKM-AM values for the branching ratio.

The RRKM-AM lifetimes are, of course, very sensitive to the A factor chosen to adapt the transition state model to. For A factors of $10^{15.5}$ and $10^{15.4}$ the lifetimes for decomposition are $\sim 2 \times 10^{-15}$ seconds, while for A factors of $10^{14.5}$ the lifetimes are $\sim 2 \times 10^{-14}$ seconds.

It is useful to keep in mind some estimates of the typical vibrational and rotational periods of a HOD complex. Typical 3000 cm^{-1} vibrations (OH stretch) have a $\sim .01$ picosecond period, the equilibrium HUD bend a .025 picosecond period. Assuming that long range forces of the Van der Waals type govern the entrance channel, the C_6 constant and collision energy can be used to estimate an average impact parameter of $1.85 \text{ \AA}$ for this reaction at 3.5 kcal/mole collision energy, and an average value of $L = \mu v b 2\pi/h = 25$. Setting $1/2 I \omega^2 = \{h^2/8\pi^2 I\}[L(L+1)]$, and using 2.56 cm^2 for the out of plane moment of inertia, gives an average rotational period of .10 picoseconds for the chemically activated HUD.

The statistical calculations predict, then, that HOD will live between .015 (highest A factor considered, OD product) and .210 (lowest A factor, OH product) rotational periods prior to decomposing. We recall that the classical trajectory calculations indicated lifetimes of $\sim 5 \times 10^{-14}$ seconds $\sim .5$ rotational periods. These calculations indicate that it is most likely the HOD will decompose prior to significant complex rotation, but on a time scale of several OH stretches.

It should be noted that all these considerations are due an insertion type mechanism only. Any end on-abstraction type mechanism would be expected to have a much shorter lifetime prior to decomposition, because of the absence of any appreciable potential well for complex formation.

7. REACTION MECHANISM

The original goal of this experiment was to probe the $O + H_2$ reaction mechanism in several ways. The previous crossed beams results, a forward-backward symmetric center of mass angular distribution indicated that an insertion mechanism dominated any abstraction, but lifetime information was unavailable for the decomposition of an adduct formed by insertion into a homonuclear diatomic.

If $O(^1D)$ inserts into HD and decays prior to complex rotation, then an anisotropic forward-backward asymmetric center of mass distribution is expected. On the average the O will insert midway between the H and D. Rotation in the plane is, however, about the center of

mass—in between the O and D atoms. The OH portion of the HOD then initially rotates forward with respect to the initial oxygen velocity, and sub-rotational decay results in OH forward scattered, OD backward scattered product. If the decay takes place after one or more rotational periods forward-backward symmetry would be expected as memory of the initial direction of attack is lost.

As before, any end on-abstraction product would be expected to be back scattered with respect to the oxygen atom initial velocity both for OH or OD product.

Thus, anisotropy in the center of mass angular distribution must be interpreted in terms of insertion vs. abstraction, and within the insertion mechanism, in terms of complex lifetime.

Then to review our results describing the reaction of $\text{O}(^1\text{D}) + \text{HD}$:

1. We have observed that both OH and OD are preferentially back-scattered. Both backscattered implies that the abstraction mechanism, apparently unimportant at 2.5 kcal/mole is becoming important at 3.5 kcal/mole collision energy. The OH product is apparently slightly less backscattered than the OD product. This implies that the HOD decay may after insertion, in fact, be taking place in a time slightly less than or comparable to a rotational period.
2. The branching ratio is indistinguishable from that predicted on statistical grounds for the HOD complex. This fact by itself would indicate that abstraction is still a minor route, since we would expect a 50-50 mix of OH and OD product if abstraction were the sole route, and a monotonic increase of $\sigma_{\text{OH}}/\sigma_{\text{OD}}$ from .72 to 1.0 as abstraction becomes relatively more important.

3. The translational energy distribution is, again, as in the $O + H_2$ experiment at 2.4 kcal/mole, essentially that expected for the statistical decay of an insertion complex. There may be some slight indication that translations are slightly cold, as in the $O + H_2$ study.
4. The statistical calculations, coupled with an estimate of the HOD rotational period (and the classical trajectory studies) indicate that, typically, HOD will have a several vibrational period (at least for the stretches) lifetime, but it is unlikely that the complex lives for much more than a single rotational period, if that, prior to decay.
5. The OH and OD angular distributions do not show any vibrational structure as in $F + H_2$, implying that there is significant rotational excitation in the OH and OD products.

While it is quite clear that the insertion is still very important, there is some evidence that abstraction also plays an important role. The exact magnitude of the abstraction contribution is difficult to discern. Moreover, the evidence in the center of mass angular distribution for the importance of the abstraction route depends sensitively on the validity of the subtraction schemes used to obtain the OH and OD product data, and conclusions based solely on those factors are less certain.

REFERENCES: CHAPTER VI

1. A. B. Callear, H. E. Van Den Bergh, Chem. Phys. Lett. 8, 17 (1971).
2. R. J. Cvetanovic, Can. J. Chem. 52, 1452 (1974).
3. H. Yamazaki, R. J. Cvetanovic, J. Chem. Phys. 40, 582 (1964).
4. G. Paraskevopoulou, R. J. Cvetanovic, J. Amer. Chem. Soc. 91, 7572 (1969).
5. P. A. Whitlock, J. T. Muckerman, E. R. Fisher, Research Institute for Engineering Science Report, Wayne State University (November 1976).
6. R. Schinke, W. A. Lester, Jr., J. Chem. Phys. 72, 3754 (1980).
7. Y. T. Lee, Ber. Bunsenges Phys. Chem. 86, 378 (1982).
8. R. J. Buss, P. Casavecchia, T. Hirooka, S. Sibener, Y. T. Lee, Chem. Phys. Lett. 82, 386 (1981).
9. L. J. Stief, W. A. Payne, R. B. Klemm, J. Chem. Phys. 62, 400 (1975).
10. J. C. Tully, J. Chem. Phys. 62, 1893 (1975).
11. W. B. Demore, J. Chem. Phys. 47, 2777 (1967).
12. J. F. Noxon, J. Chem. Phys. 52, 1852 (1970).
13. D. R. Snelling, E. J. Bair, J. Chem. Phys. 47, 228 (1967).
14. D. R. Snelling, E. J. Bair, J. Chem. Phys. 48, 5737 (1968).
15. R. Gilpin, H. I. Schiff, K. H. Welge, J. Chem. Phys. 55, 1087 (1971).
16. I. D. Clark, J. F. Noxon, J. Chem. Phys. 57, 1033 (1972).
17. J. A. Davidson, C. M. Sadowski, H. I. Schiff, G. E. Streit, C. J. Howard, D. A. Jennings, A. L. Schmeltkopf, J. Chem. Phys. 64, 57 (1976).

18. R. F. Heidner III, D. Husain, J. R. Wisenfeld, Chem. Phys. Lett. 530, (1972).
19. R. F. Heidner III, D. Husain, Int. J. Chem. Kin. 6, 77 (1974).
20. R. F. Heidner III, D. Husain, Int. J. Chem. Kin. 5, 819 (1973).
21. K. Schofield, J. Photochemistry 9, 55 (1978).
22. W. D. McGrath, R. G. W. Norrish, Proc. Royal Soc. 254A, 317 (1960).
23. N. Basco, R. G. W. Norrish, Proc. Royal Soc. 260A, 296 (1961).
24. C. L. Lin, W. B. Demore, J. Phys. Chem. 77, 863 (1973).
25. A. C. Luntz, R. Schinke, W. A. Lester, Jr., Hs. H. Gunthard, J. Chem. Phys. 70, 5908 (1979).
26. G. K. Smith, J. E. Butler, M. C. Lin, Chem. Phys. Lett. 65, 115 (1979).
27. G. K. Smith, J. E. Butler, J. Chem. Phys. 73, 2243 (1980).
28. J. C. Tully in Potential Energy Surfaces, K. P. Lawley, Ed., Adv. in Chem. Phys. 42, Wiley, New York (1980).
29. R. A. Gangi, R. F. W. Bader, J. Chem. Phys. 55, 5369 (1971).
30. P. A. Whitlock, J. T. Muckerman, E. R. Fisher, J. Chem. Phys. 76, 4468 (1982).
31. K. S. Sorbie, J. N. Murrell, Mol. Phys. 31, 905 (1976).
32. R. Sparks, Crossed Beams Studies of Full and Half Collisions, Ph.D. Thesis, University of California, Berkeley (1980).
33. S. J. Sibener, R. J. Buss, C. Y. Ng, Y. T. Lee, Rev. Sci. Instr. 51, 167 (1980).
34. Made by reacting D_2O with lithium aluminum hydride. We thank D. Neumark, A. Wodtke, and M. Valentine for the HD.

35. E. Stehagen, S. Abrahamsson, F. W. McLafferty, Eds., Atlas of Mass Spectral Data, Wiley Interscience, New York (1969).
36. P. J. Robinson, K. A. Holbrook, Unimolecular Reactions, Wiley Interscience, London (1972).
37. S. A. Safron, N. D. Weinstein, D. R. Herschbach, Chem. Phys. Lett. 12, 564 (1972).
38. J. C. Light, Disc. of Faraday Society 44, 14 (1967).
39. S. W. Benson, Thermochemical Kinetics, Wiley Interscience, New York (1976).
40. J. O. Hirschfelder, C. F. Curtiss, H. C. Bird, Molecular Theory of Gases and Liquids, Wiley Interscience, New York (1954).
41. R. E. Weston, Jr., H. A. Schwartz, Chemical Kinetics, Prentice-Hall, Inc., New Jersey (1972).

FIGURE CAPTIONS: CHAPTER VI

1. Mass 18, OD product, angular distribution. Solid line, fit obtained with $P(E')$ and $T(\theta')$ "A." Dashed line, fit obtained with $P(E')$ and $T(\theta')$ "B."
2. Mass 17, OH product, angular distribution. Solid line, fit obtained with $P(E')$ and $T(\theta')$ "C."
3. Mass 18, OD product, time of flight distributions. Solid line, fit obtained with $P(E')$ and $T(\theta')$ "A." Dashed line, fit obtained with $P(E')$ and $T(\theta')$ "B."
4. Mass 17, OH product, time of flight distributions. Solid line, fit obtained with $P(E')$ and $T(\theta')$ "C."
5. Center of mass OD product translational energy distributions "A" and "B" as in text. Dotted line statistical calculations.
6. Center of mass OD product angular distributions "A," "C," and "D" as in text.
7. Center of mass OH product translational energy distributions "A," "B," and "C" as in text. Dotted line statistical calculations.
8. Center of mass OH product angular distributions "A," "B," and "C" as in text.

FIGURE 6-1

XBL 8211-3305

FIGURE 6-2

3.5 KCAL/MOLE

FIGURE 6-3

FIGURE 6-4

XBL 8211-3309

FIGURE 6-5

XBL 8211-3310

FIGURE 6-6

FIGURE 6-7

XBL 8211-3311

FIGURE 6-8