DYNAMICS AND MECHANISMS OF HOT CHEMISTRY
STIMULATED BY RECOIL METHODS

Progress Report
for Period March 1, 1979 - February 29, 1980

Leonard D. Spicer

University of Utah
Salt Lake City, Utah 84112

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

November 1979

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *eb*

Prepared for

The United States Department of Energy

(Former Contract No EY-76-S-02-2190.*000)
UNDER CONTRACT NO. DE-AC02-76ER02190.A004

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Department of Energy
Chicago Operations and Regional Office
9800 South Cass Avenue
Argonne, Illinois 60439

May 14, 1980

Arthur D. Churm, Chief
Office of Patent Counsel, CORO

CONTRACT DE-AC02-76ER02190, UNIVERSITY OF UTAH

We are transmitting copies of ~~reports~~ submitted in accordance with our requirements under the subject contract.

Donnelly Lindholm
Contract Specialist
Acquisition and Assistance Unit

MASTER

AA: DL

Enclosures:

Progress Report No. ~~C90-2190-20~~ (DOE/ER02190-1)

cc: Technical Information Center, Oak Ridge, TN.
(THRU CN-OPC) w/Encl. and Form 427

7-AA-1
11/79

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, sub-contractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

ABSTRACT

A model for the kinetically controlled, nuclear recoil, chemical activation process is further developed to characterize the generation of excited cyclobutane and the collisional energy loss process from the excited molecule. The secondary excitation function for production of cyclobutane-t from the hot hydrogen replacement reaction with cyclobutane was estimated and reported. Using a stepladder model the average stepsizes for cascade deactivation by several bath gases have been determined.

Further progress on the interpretation of the dynamics which follow hot chlorine replacement reactions in small ring compounds has also been made. Comparison of the results with those observed for similar reactions involving chlorine cations is beginning to provide insight into mechanistic similarities and differences between neutral and carbonium ion intermediates. In particular the kinetics of rearrangement by hydrogen shifts in four carbon diradicals and their tendencies to close into three and four membered ring compounds are manifest in these results. In addition the electronic substituent effects of a chlorine atom on the carbon chain are observed.

A model for recoil atom dynamics has been extended to account for low energy reaction processes with and without dilution by non-reactive moderators. By comparing competitive low energy reaction yields as a function of moderator concentration, the proposition that thermal kinetics may be characterized in these systems without ever achieving a Boltzmann distribution of molecular energies is suggested and will be tested in subsequent work.

A new silylation reaction with sulfur dioxide was discovered. The process involves the direct attack of hexamethyldisilazane on sulfur dioxide leading eventually to 1,1,1-Trimethyl-N-sulfinyl silanamine. This represents a facile silylation in the absence of an acidic hydrogen and produces a synthetically and analytically useful silanamine.

PERSONNEL

Principal Investigator: Dr. Leonard D. Spicer, Professor.

Department of Chemistry, University of Utah.

The principal investigator has devoted 100% time during 2.0 summer months and at least 25% of his time during the remaining period to actively direct and perform research under this contract.

Post Doctoral Associate:

Dr. Dennis Bennett (June 1979 - February 1980) spent 100% time for six months and 80% time for 3 months 1) investigating the mechanism of and stoichiometry of silylation in the SO_2 -hexamethyldisilazane reaction, and 2) assisting in the mechanistic studies of strained cyclic, four carbon ions and excited neutral systems.

Graduate Students:

Mr. Leonard Ferro (March 1979 - February 1980) spent 100% time on studies of intermolecular and intramolecular energy transfer and mechanisms of rearrangement in excited small ring compounds in hot atom reaction system involving recoil chlorine.

Mr. Johnnie Chang (June 1979 - September 1979) spent 100% time developing a computer model to study recoil reaction dynamics.

Mr. Jan Vanderhoft (October 1979 - December 1979) spent 100% time on photochemical studies in sulfur systems.

Undergraduate Student:

Mr. Jon Davis (June 1979 - September 1979) spent 100% time characterizing

the products of photochemical reaction between SO_2 and alkanes and synthesizing authentic samples of silylized derivatives of those products.

RESEARCH RESULTS

During the past twelve month period significant results have been obtained in several areas of research supported by this program. Below are outlined the main findings of this work. A substantial part of this progress report is appended in the form of reprints and preprints of publications in which the reader may find a more detailed discussion of most of the topics studied.

General characteristics of highly excited molecular species and their energy transfer or heat conductance properties are extremely important in high temperature engineering applications such as those proposed in advanced power generating facilities. The recoil reaction technique often provides a unique method of producing such highly excited molecules for laboratory study. Therefore, more quantitative, detailed evaluation of the secondary processes experienced by nuclear recoil chemically activated molecules obtained in a variety of molecular environments has been undertaken. These studies have involved both calculations and experimental methods designed to characterize energetics and dynamics of hot molecules, and the results to date are described in the following sections. Of concurrent interest are parallel studies of excited carbonium ions formed in recoil reactions. Comparison of neutral and ion intermediates also shows potential for better characterization of common mechanisms and studies of such systems have been initiated.

Kinetic and mechanistic studies of the photochemically stimulated reactions between sulfur dioxide and hydrocarbons are also being carried out. In general these reactions are characterized by facile redox pathways and appear to occur readily both homogeneously in the gas phase and with molecules adsorbed on surfaces. The importance of these processes is manifest both in understanding atmospheric effects of sulfur dioxide pollution and also in planning strategy for the effective use of sulfur containing fuels. The redox processes on

surfaces may also prove to be a model for photocatalytic surface methods of producing hydrogen by reduction of water. Finally in an effort to stabilize photochemical reaction products by silylation a new, facile reaction with SO_2 which shows both synthetic and analytical promise has been discovered.

Chemical Activation by Kinetic Techniques: Collisional Energy Transfer from Excited Molecules.

The latest results which further define nuclear recoil chemical activation were published during the past year and reprints are appended. These studies represent the most complete characterization of the hot hydrogen replacement reaction in cyclobutane and subsequent collisional energy transfer processes to date and extend our understanding of the kinetic chemical activation process significantly. Included is the first quantitative, experimentally derived estimate of an excitation function for production of an excited product by reaction over the complete energy range of the cross section. The quantitative molecular energy transfer information also derived represents an extension of the operational method developed in this laboratory.¹

The primary advantage of chemical activation by recoil reactions is the kinetic control of the excitation process. Unlike thermochemical methods which are limited by the net free energy change of the reaction, kinetic stimulation is limited only by the initial relative kinetic energy of the colliding species and dynamical constraints on the reaction process. Thus extremely high excitation energies are potentially obtainable via the recoil reaction technique and indeed they have been produced in hot halogen and hot tritium atom reactions.

Briefly the overall process involved in the study of vibrationally excited molecules by the recoil reaction method can be modeled in the following way. The excitation spectrum of the nascent reaction product is obtained via a linear transformation of the reaction cross section as suggested by Bunker²

based on classical trajectory studies. The primary excitation function for hydrogen replacement reaction is given the functional form experimentally obtained by LeRoy *et al.*,³ scaled to experimentally determined integral reaction probabilities for cyclobutane reactant. The excited molecule is then characterized by RRKM theory explicitly taking into account rotational contributions which are found to be minimal in the cyclobutane system.

Two approaches to collisional energy degradation in the excited molecule have been employed. The first is based upon the strong collision approximation similar to that employed by Chou and Hase,⁴ but the master equation is considerably modified to explicitly account for mixed bath gases. This involves adjusting the energy distribution of the recoiling atom and incorporating effective collision frequencies based on energy transfer efficiencies for the various bath gases employed. If sufficient redundancy in the experimental data is present, as is the case with the well studied cyclobutane system, this technique provides a good value for the proportionality constant in the linear mapping of the energy distribution in the excited molecule. It also gives relative energy transfer efficiencies from vibrationally excited cyclobutane to non-reactive bath gases.

The second approach we have employed refines the picture of energy transfer by incorporating multistep deactivation processes. Thus the more fundamental property, the quanta of energy transferred from vibration upon collision as a function of the chemically activated collider and the individual bath gas studied, is obtained. Unlike classical chemical activation approaches this analysis is not dependent on precise data at low pressures in the cascade region, although such data assist considerably in narrowing the range of acceptable results. Indeed for nuclear recoil activation it has been found that the classical cascade turnup may not even be observed due to the broad

distribution of energies in the excited molecules.¹

We have also attempted to explore intramolecular energy transfer within molecules chemically activated to high energies by hot atom reaction. The hot reactions used to generate excited products are the chlorine for chlorine replacement reactions with 1-chloromethyl-cyclopropane and 1-chloroethyl cyclopropane. Initial results clearly show decomposition of the cyclopropyl ring, but the pressure dependence in two polyatomic bath gases SF_6 and CF_3Cl is not consistent with a normal unimolecular process. This has led us to speculate that ion reactions may be playing a role at least in the case of SF_6 diluent. Before proceeding further in the study of intramolecular processes, the contributions from alternate reaction mechanisms must be accounted for. In the next section we outline the mechanistic findings to date.

Mechanistic Studies of Energy Rich Intermediates.

Studies of chlorine atom and ion replacement reactions have progressed significantly during the past year but a complete and accurate mechanistic picture has yet to emerge. Here are outlined the main findings and our interpretation to date. The cases considered are chlorine atom reactions with chloromethylcyclopropane and chlorocyclobutane in the presence of freon moderator and chloride cation reactions with chlorocyclopropane in the presence of SF_6 moderator.

The most significant result for the chlorine atom replacement reaction is the observation that the chloromethylcyclopropane and chlorocyclobutane can be interconverted via the recoil reaction process. Thus large relative yields of labeled chlorocyclobutane are produced on reaction with chloromethylcyclopropane and vice-versa. In addition the labeled parent and the branched and straight chain butene isomers are formed. This has led us to

speculate that a common energy rich diradical is formed in both cases probably by the scission of a ring carbon-carbon bond following replacement. With the stabilizing effect of the chlorine atom, we feel the diradical lives long enough to rearrange by hydrogen shifts under kinetic control. The 1,3 and 1,4 diradical can also reclose in competition with hydrogen shifts and the 1,2 diradical is expected to rapidly lead to chlorobutene-1 when it is formed. Based on the preliminary data obtained it also appears that we will be able to make some estimate of the relative rates for interchange of diradicals and we are currently completing our studies with that objective in mind.

The carbonium ion system exhibits very similar behavior and in addition shows what looks like an additional reaction leading to a much larger yield of one product 2 methyl 3 chloro propene-1. We propose that this additional path comes from charge migration in the original replacement product to the ring. One of the important conclusions, however, that these results suggest is that the excited carbonium ion and neutral products behave similarly in most of their stabilizing rearrangements. We are currently preparing a manuscript for publication which identifies the similarities and differences in the context of the mechanistic organic chemistry literature on small ring compounds.

Recoil Trajectory Calculations

We have recently extended our earlier method for modeling the recoil reaction process⁵ to include low energy cross-sections for reactions like abstraction and addition. Our objective is to synthesize data in moderated systems in an effort to evaluate in detail the dynamics associated with the moderated nuclear recoil method for determining thermal rate constants. To date we have generated some relative reaction rate data in a single system.

The formalism incorporates a trajectory approach in which the fate of the hot atom is followed through successive collisions until reaction occurs. The average energy for non-thermal reaction is then calculated statistically on the basis of the energy distribution of reactive events for a large collection of recoil atoms having a broad distribution of initial energies. Recoil atoms which reach the average energy of the bath gas are partitioned amongst the various thermal reaction paths according to their rate constants at the temperature of the bath. The generality of the method is specifically dependent on the availability of information about the energy dependence of the cross sections for reactions of interest.

In general the average energy of reaction calculated for non-thermal reactions was found to be relatively independent of the composition of the system. In well scavenged systems of moderate reactivity at high energies, the increased density of potentially reactive low energy collisions found in highly moderated systems is almost quantitatively counteracted by the decreased collision fraction for the reactant, and the only major effect observed is a decrease in the absolute yields of hot reaction products. In other reactive systems, however, where there is extremely high reactivity or where a low threshold energy allows significant competition between reactant and scavengers, the situation is much less straightforward. It is in just such systems that the measurement of thermal rate constants have been reported.⁶ Clearly there is a need to broaden the approach developed to specifically characterize reactions such as abstraction and addition which have thermal or near thermal thresholds. Only then will a complete accounting of the total energy disposal and overall reactivity of typical systems be possible.

The initial results on including low energy processes have been obtained for reactions which are intended to represent abstraction and addition. Cross

sections were parameterized to generally represent these processes.³ Yields were calculated at 95% moderation as a function of concentration of two competitive reactants, one for abstraction and one for addition. Only those reactive events occurring during the recoil trajectory down to the average energy of the bath were included in this first effort. Non-reacted atoms were discarded. The inverse yield for abstraction was plotted against the inverse relative mole fraction for that reactant according to equation 5 of reference 6 and a linear relationship was found despite the fact that there were no truly thermal components to the yield results. This is despite the fact that equation 5 of reference 6 was derived from competitive thermal kinetics. The result is provocative and suggests that this method of thermal rate constant measurement may not depend on attainment of a Boltzmann distribution of collisions. We are currently extending this calculation specifically to explore this possibility.

Studies of the Photochemical Reactions Between Sulfur Dioxide and Aliphatic Hydrocarbons.

Photochemical reactions between SO_2 and aliphatic hydrocarbons are characterized by extremely complex kinetics and the formation of a variety of reactive and stable sulfur containing products. Preliminary investigations have indicated that the reactions tend to be free radical in nature and that they occur readily both homogeneously in the gas phase and heterogeneously with adsorbed reactant molecules. The unusual capability of SO_2 to undergo both oxidation and reduction in these systems provides a challenging mechanistic problem which may serve as a model for other photo-redox processes which occur in the gas phase and on surfaces.

We have spent much of the past year in a systematic program of product analysis of the results of the photochemical reactions in various hydrocarbons.

While direct analysis by gas chromatography or mass spectroscopy or a combination of the two, GC-MS, is possible for stable products like sulfones, sulfoxides, mercaptans sulfides, and disulfides, other more reactive, involatile products like sulfinic and sulfonic acids must be derivatized prior to analysis. We have approached this problem by attempting to silylize the product mixture directly. While direct silylation showed promise, the resultant combination of derivatized products was too complex to analyze completely even by GC-MS. Part of the difficulty came from the fact that residual SO_2 in the reaction mixture reacted directly with one component of the silylating reagent, hexamethyldisilazane (HMDS). This proved to be an unusual, interesting, and complex reaction and we devoted most of our efforts to understanding this reaction. A preprint of our initial studies is appended.

The reaction reported produces 1,1,1-Trimethyl-N-sulfinyl silanamine a potentially important synthetic precursor and analytical result because of its fluorescent properties. The detailed mechanism for reaction is indeed unusual for silylating reagents as it occurs in the absence of an acidic hydrogen. The common reagent trimethylchlorosilane is unreactive toward SO_2 . Rather we speculate that the observed reaction involves a Lewis acid-base mechanism. Also formed in the reaction are hexamethyldisiloxane and a white solid having a very high vapor pressure. We are currently determining the stoichiometry for the overall reaction and characterizing the unknown solid product.

Literature Cited

1. N. Nogar and L.D. Spicer, J. Chem. Phys., 66, 3624 (1977).
2. D.L. Bunker, J. Chem. Phys., 57, 332 (1972).
3. R.L. LeRoy, A.J. Yench, M. Menzinger, and R. Wolfgang, J. Chem. Phys., 58, 1741 (1973).
4. C.C. Chou and W.L. Hase, J. Phys. Chem., 78, 2309 (1974).

Literature Cited (continued)

5. L.D. Spicer, J. Chem. Soc. Faraday II, 74, 527 (1978).
6. S.H. Mo, E.R. Grant, F.E. Little, R.G. Manning, C.A. Mathis, G.S. Werre, and J.W. Root, A.C.S. Symposium Series, 66, 59 (1978).

New Publications and Manuscripts Submitted

- L.J. Ferro and L.D. Spicer, J. Chem. Phys., **69**, 4335 (1978).
"Characterization of the Unimolecular Behavior of Recoil Hot Reaction Products in Inert Bath Gases. Application to $\text{c-C}_4\text{H}_7\text{T}$ "
- M.B. Callahan and L.D. Spicer, J. Phys. Chem., **83**, 1013 (1979).
"Application of Multistep Deactivation Processes in the Interpretation of Intermolecular Energy Transfer Following Chemical Activation by Kinetic Techniques"
- J.F. Davis and L.D. Spicer
"Formation of 1,1,1-Trimethyl-N-sulfinyl-Silamine from the Direct Reaction of SO_2 with Hexamethyldisilazane"

Manuscripts in Preparation

- L.D. Spicer, Invited Book Chapter, ACS Advances in Chemistry.
"The Unique Role of Recoil Generated Radiotracers in Studies of Molecular Dynamics"
- L.J. Ferro and L.D. Spicer, Book Chapter, ACS Advances in Chemistry.
"Reactions of Recoil Chlorine in Highly Moderated Systems"
- L.J. Ferro and L.D. Spicer
"Mechanism and Dynamics of Recoil Chlorine Atoms and Ion Reactions in Four Carbon Ring Systems. Interconversion of Methylcyclopropyl Chloride and Chlorocyclobutane"

Talks Presented at Meetings

- L.D. Spicer, M.B. Callahan, and L.J. Ferro
"Characterization of Chemical Activation by Recoil Hot Atom Reactions for Studies of Excited Molecule Dynamics". Symposium on Studies of Chemical Properties by Nuclear Probes. National Meeting, ACS/CSJ Chemical Congress, Honolulu, Hawaii, March 1979 (Abs. Nucl. 44)
- L.D. Spicer
"Nuclear Recoil Chemical Activation" Tenth International Hot Atom Chemistry Symposium, Loughborough, England, September 1979 (Abs. 35)
- L.D. Spicer
"The Unique Role of Recoil Generated Radiotracers in Studies of Molecular Dynamics" Symposium on Recent Developments in Biological and Chemical Research with Short Lived Isotopes, National Meeting, ACS, Washington D.C., September 1979 (Abs. 68)

Talks Presented at Meetings (continued)

L.J. Ferro and L.D. Spicer

"Studies of Chlorine-38 Reactions in Systems Moderated with SF₆ and Freon" Symposium on Recent Developments in Biological and Chemical Research with Short Lived Isotopes, National Meeting, ACS, Washington, D.C., September 1979 (Ab. 72)