DOE/ER/13224--3¹⁹⁸⁶

KINETIC MEASUREMENTS ON ELEMENTARY FOSSIL FUEL COMBUSTION
REACTIONS OVER WIDE TEMPERATURE RANGES

Progress Report
For the Period May 1, 1984 - November 30, 1986

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December 1986

Prepared for

THE U.S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FG02-84ER13224

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ABSTRACT

The HTP (high-temperature photochemistry technique) has been used to study the reactions of ground state O atoms with C_2H_4 , C_2H_2 , H_2 and D_2 over the 300 to 1500 K temperature range. The results are described and discussed, as are the plans for study of the O + 1,3 butadiene and C_2H_6 reactions in the remainder of the present grant period.

I. INTRODUCTION AND SCOPE OF WORK

More efficient fossil utilization requires an improved data base on the kinetics of bimolecular reactions over wide temperature ranges. Particularly in the important 1000 - 1500 K range there is a lack of reliable data. The data available above 1000 K have most frequently been obtained in multireaction media, such as flames and shock tubes; in such environments, the ability to extract kinetic information on any particular reaction depends, to a variable degree, on assumptions regarding data for other reactions occurring simultaneously. By contrast, reliable measurement below 1000 K are often available from techniques for study of isolated elementary reactions, such as electrical discharge fast-flow reactors and flash-photolysis resonance fluorescence (FP-RF) apparatus. However, extrapolation of kinetic data from low to high temperatures is often unreliable, since different mechanisms may be involved. Theory, especially for exothermic and slightly endothermic reactions, is often not sufficiently advanced to accurately predict the variation of rate coefficients over large temperature ranges.¹

We have developed the HTP (high-temperature photochemistry) technique to allow isolated elementary reaction measurements for C/H/O species reactions above 1000 K. This technique, while similar in principle to FP-RF, is unique because of the construction of the reactor used, which allows operation to about 1800 K. The HTP facility, its operation and the data reduction procedures used have been described.^{2,3,4} Here we discuss results obtained since the inception of this grant. In this work we have concentrated on reactions of ground state oxygen atoms, usually produced via flash photolysis of CO₂; O₂ has been used as an additional photolyte for work below ~ 800 K.

II PROGRESS

In the first 15 months of this grant most of our efforts were dedicated to obtaining a fully operational HTP facility. Since then, i.e. during the second 15-month period, rapid progress has been made using this facility for kinetic measurement on a number of reactions of ground oxygen atoms. Three articles resulting from this work have already been accepted for publication and are reproduced as appendices to this report. Additionally, we have completed our measurements on the $O + H_2$ and $O + D_2$ reactions. A manuscript on that work is nearing completion; a short summary of it follows. Experiments on the $O + 1,3$ butadiene reaction have been initiated, see Section III.

Figure 1 summarizes our measurements for the reaction

and compares them to those from other experiments which isolated the reaction from secondary processes. Based on all these measurements we recommend

$$k_1(T) = 1.5 \times 10^{-12} \exp(-3540 \text{ K}/T) + 3.7 \times 10^{-10} \exp(-7450 \text{ K}/T) \\ \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (300 \text{ K} \leq T \leq 2500 \text{ K})$$

Also shown in Fig. 1 are the recent recommendations, based on critical reviews of the literature, by Cohen and Westberg⁸ and by Warnatz,⁹ respectively. Our work represents the first study of reaction (1) from 350 to 1420 K made in one apparatus.

Figure 2 summarizes our results for the reaction

For this reaction the only previous truly isolated reaction observations are the FP-RF measurements by Presser and Gordon⁵ over the range 420 to 470 K. Based on their and the present work we recommend

Figure 1. Summary of HTP experiments on the $O + H_2$ reaction. Literature data given are, respectively, from Presser and Gordon,⁵ Dubinsky and McKenney⁶ and Sutherland *et al.*⁷ The latter are indicated on the figure as BNL FP-RF (flash-photolysis resonance-fluorescence) and BNL FP-ST (flash-photolysis shock tube). The earlier recommendations are from Cohen and Westberg⁸ and Warnatz,⁹ respectively. The solid line represents the best fit to all data points shown.

Figure 2. Summary of HTP experiments on the $\text{O} + \text{D}_2$ reaction. Literature data given are, respectively, from Westenberg and deHaas,¹⁰ Presser and Gordon,⁵ Clyne and Thrush¹¹ and Pamidimukkala and Skinner.¹² The solid line represents the best fit to our data and those of Ref. 5.

$$k_2(T) = 1.4 \times 10^{-12} \exp(-4260 \text{ K}/T) + 2.9 \times 10^{-10} \exp(-7780 \text{ K}/T) \\ \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (390 \text{ K} < T < 1420 \text{ K})$$

which is shown as the solid line in Fig. 2. Results from the discharge-flow (DF) reactor work* of Westenberg and deHaas¹⁰ and Clyne and Thrush¹¹ are also included in the figure, as are the shock tube results of Pamidimukkala and Skinner¹² from 2100 to 2500 K. The apparently good agreement between extrapolations of the shock tube and our work, Fig. 2, suggests that $k_2(T)$ now is well-characterized from 390 to 2500 K. Therefore, we propose for that whole region $k_2(T) = 1.4 \times 10^{-12} \exp(-4250 \text{ K}/T) + 3.6 \times 10^{-10} \exp(-7980 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The recommended $k_1(T)$ and $k_2(T)$ and their ratio, which gives the kinetic isotope effect, compare well with calculations we have made based on recent ab initio methods (ICVT/LAG and CEQB), also discussed in our forthcoming manuscript on the $\text{O} + \text{H}_2$ and D_2 reactions. This comparison suggests that the first terms of our $k_1(T)$ and $k_2(T)$ expressions represent quantum-mechanical tunneling contributions.

III. PLANS FOR THE REMAINDER OF THE PRESENT GRANT YEAR

The $\text{O} + 1,3$ butadiene reaction has previously been studied by Nip et al,¹³ who worked at 299 and 448 K, with $[\text{M}] \approx 8 \times 10^{17} \text{ cm}^{-3}$ and by Atkinson and Pitts¹⁴ who worked from 297 to 439 K at $[\text{M}] \approx 5 \times 10^{17} \text{ cm}^{-3}$. They found a rate coefficient of $\approx 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, essentially independent of temperature. Our initial measurements are in good agreement with theirs for the same pressure and temperature range. However, we find that in the 600-800 K range the k -values are about 1.5 to 2 times larger than near room temperature.

*It can be shown that secondary reactions can not be neglected in the observations of Refs. 10 and 11, due to the high O-atom concentrations used (on the order of 10^{14} cm^{-3}).

We have further noticed that in the 360 to 400 K range plots of the pseudo first-order rate coefficients versus butadiene concentrations show upward curvature with increasing butadiene concentrations for $[M] \approx 1.3 \times 10^{19} \text{ cm}^{-3}$, whereas such plots are linear for lower $[M]$. At higher temperatures, or when CO_2 is used as photolyte instead of O_2 , the non-linearity starts at lower $[M]$. These third-body effects suggest a change in mechanism. A more complete investigation, including work at higher temperatures, is in progress.

Upon completion of the investigation of the butadiene reaction, we plan to start the study of

Cohen's reevaluation of the published experimental data for this reaction from 250 to 400 K suggests that the rate coefficients are overestimated by factors of two to three due to impurities in the reactants and to secondary reactions, which have not adequately been taken into account.¹⁵ There is also substantial disagreement between the two sets of discharge flow-reactor measurements in the 500-1000 K range.^{16,17} There are apparently no experimental data at higher temperatures. The lack of reliable data on reaction (3) impedes satisfactory comparisons to theoretical treatments of this reaction.^{18,19} A reliable experimental data set would facilitate semi-empirical modeling of other $\text{O} + \text{alkane}$ reactions. We plan to study reaction (3) from room temperature upward using adequately purified gases. With the low $[\text{O}]$ of our work ($\leq 10^{11} \text{ cm}^{-3}$) secondary reactions will not play a role.

IV. REFERENCES

1. A. Fontijn and R. Zellner, in Reactions of Small Transient Species. Kinetics and Energetics, A. Fontijn and M.A.A. Clyne, Eds. (Academic Press, London, 1983), Chap. 1.
2. K. Mahmud, P. Marshall and A. Fontijn, J. Phys. Chem., in press; see also Appendix A.
3. P. Marshall and A. Fontijn, J. Chem. Phys. 85, 2637 (1986).
4. P. Marshall. Computers and Chemistry, in press; see also Appendix C.
5. N. Presser and R.J. Gordon, J. Chem. Phys. 82, 1291 (1985).
6. R.N. Dubinsky and D.J. McKenney, Can. J. Chem. 53, 3531 (1975).
7. J.W. Sutherland, J.V. Michael, A.N. Pirraglia, F.L. Nesbitt and R.B. Klemm, in 21st Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, 1986), in press.
8. N. Cohen and K.R. Westberg, J. Phys. Chem. Ref. Data 12, 531 (1983).
9. J. Warnatz, in Combustion Chemistry, W.C. Gardiner, Jr., Ed. (Springer-Verlag, New York, 1984), Chap. 5.
10. A.A. Westenberg and N. deHaas, J. Chem. Phys. 47, 4241 (1967).
11. M.A.A. Clyne and B.A. Thrush, Proc. Roy. Soc. A275, 544 (1963).
12. K.M. Pamidimukkala and G.B. Skinner, J. Chem. Phys. 76, 311 (1982).
13. W.S. Nip, D.L. Singleton and R.J. Cvetanovic, Can. J. Chem. 57, 949 (1979).
14. R. Atkinson and J.N. Pitts, Jr., J. Chem. Phys., 67, 2492 (1977).
15. N. Cohen, Int. J. Chem. Kinet. 18, 59 (1986).
16. T. Tanzawa and R.B. Klemm, 179th ACS National Meeting, Houston, 1980, Abstract Phys. 48.
17. J.M. Caymax and J. Peeters, in 19th Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, 1982), p. 51.
18. N. Cohen and K.R. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).
19. J.V. Michael, D.G. Keil and R.B. Klemm, Int. J. Chem. Kin. 15, 705 (1983).

APPENDIX A

An HTP Kinetics Study of the Reaction of $O(^3P)$ Atoms With Ethylene From 290 to 1510 K

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The $O + C_2H_4$ reaction has been investigated in a high-temperature photochemistry (HTP) reactor at temperatures from 290 to 1510 K and pressures from 60 to 500 torr. Ground-state O atoms were generated by flash photolysis of CO_2 and monitored by time-resolved atomic resonance fluorescence with pulse counting. Measurements were made under pseudo-first order conditions $[O] \ll [C_2H_4]$. Rate coefficients from 290 to 850 K are in good agreement with the numerous earlier measurements in that range. Above those temperatures a sharp rise in $k(T)$ with increasing T is evident. Based on the present and other measurements by isolated elementary reaction techniques we recommend

$$k(T) = 1.3 \times 10^{-11} \exp(-830 \text{ K}/T) + 1.9 \times 10^{-9} \exp(-6940 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

as a fit expression for the 290-1510 K range. Confidence limits are discussed in the text. It is shown that the accepted transition state treatment for channels significant at $T < 850$ K cannot account for the sharp upward curvature. Other channels will have to be considered at higher temperatures.

1. Introduction

Kinetic data on isolated elementary reactions covering wide temperature ranges and obtained in one apparatus are rare. Yet, such data are much desired to help arrive at a reliable experimental data base needed to improve our understanding of the influence of temperature on reactions. We have developed one such technique suitable for reactions involving species unstable with respect to collisions with high temperature walls, the HTP (high-temperature photochemistry) technique.^{1,2} Here we report HTP measurements on the reaction

over the 290 to 1510 K range. The oxidation reactions of ethylene are a common subset in the combustion of higher molecular weight hydrocarbons and the subsequent formation of acetylenic compounds is significant to soot formation.^{3,4} In recent years there have been several studies of reaction (1) to determine the temperature dependence of the rate coefficient in the 200-850 K range⁵⁻⁷ and to elucidate the reaction mechanism in that temperature regime.⁵⁻¹³ The observations there can be attributed to intermediate formation of an O-atom adduct to the double bond

Among the product channels resulting from the addition reaction, $\text{H} + \text{CH}_2\text{CHO}$ and $\text{CH}_3 + \text{HCO}$ are the most significant at lower temperatures.¹⁴ However, at higher temperatures the only experimental information available on reaction (1) is derived from flame and shock tube studies, which require extensive modelling and hence are subject to considerable uncertainty. The aim of the

present study has been to obtain direct measurements on the rate coefficients of the title reaction at higher temperatures under conditions $[O] \ll [C_2H_4]$ where secondary reactions can be excluded. We have concentrated on the 850-1510 K regime, but have also included some measurements from 290-850 K to check for agreement with earlier work. Simultaneously with this study, Klemm *et al.*¹⁵ have made similar measurements covering the 240-1050 K regime.

2. Technique

2.1 Experimental

A schematic of the apparatus is shown in Fig. 1. The HTP technique follows the same basic principles as the lower temperature flash-photolysis resonance-fluorescence (FP-RF) technique, but ceramic and metal reactor construction parts are used to allow operation at temperatures as high as about 1800 K. A significant difference with FP-RF apparatus is the use of a movable cooled inlet system, which can reduce the residence time for thermally unstable species upstream of the reaction zone to periods on the order of 10^{-3} s and which creates an essentially wall-less reaction zone. The temperature inside the cooled inlet system can be maintained at 500 K at the highest reaction zone temperatures. A mixture of photolyte and reactant-in-excess (in this case, CO_2 and C_2H_4 , respectively) flow through the cooled inlet to mix with the heated bath gas Ar, upstream of the reaction zone. Photolysis pulses from the flashlamp generate O atoms. The cw resonance flow lamp is used to generate the fluorescence by which the decrease in $[O]$ is followed under pseudo-first order conditions at a given pressure $P = [Ar]$, temperature T and $[C_2H_4]$.

The reactor comprises an alumina tube, 5 cm diam. and 91 cm long, situated in a steel vacuum chamber. It is heated over a 40 cm distance using

silicon carbide spiral heating elements. Reaction zone temperature measurements are made using a retractable Pt/Rh thermocouple, doubly shielded to minimize radiation effects.¹⁶ Four perpendicular 2.4 cm diam. ports are aligned with 2.5 cm diam. windows on the vacuum chamber. The resonance flow lamp is powered by a 100 W cw microwave source and is equipped with a 2.5 cm diam. 15 cm focal length CaF_2 plano-convex lens to focus the exciting radiation and filter out the Lyman- α line. Further collimation is provided by 1 cm i.d. alumina rings in the flow lamp and PMT side arms.

The high intensity capacitive discharge flash lamp, consists of a 10 cm o.d. plexiglass body, two 1 cm radius elkonite electrodes separated by a 4 cm gap and a 2.5 cm diam. MgF_2 window. The lamp operates on 100 to 500 torr N_2 at about 1 Hz. A 0.5 μF 25 kV capacitor delivers between 10 and 70 J per flash. A 555 timer chip controls the repetition rate of the flash. 5 V square pulses are fed into an EG&G TM11-A trigger module, which initiates the flash on the rising edge of the square pulses. A photodiode on the flashlamp triggers the Nicolet 12/70 multi-channel scaler on the falling edge of the flash to initiate data acquisition. The fluorescence is detected through a MgF_2 window by an EMI G-26E314LF photomultiplier tube. This PMT has a 1.6 cm diam. CsI photocathode and a MgF_2 window and is operated at 2600 V with a gain of 5×10^6 . The PMT signal is fed through an EG&G PAR 1121-A amplifier-discriminator to the multi-channel scaler, the fluorescence decay information from which is transferred to an IBM personal computer for data handling.

CO_2 is photolysed by the 120 to 167 nm portion of the flash continuum to yield predominantly $\text{O}(^1\text{D})$,^{17,18} which is rapidly quenched to $\text{O}(^3\text{P})$. The resonance lamp operates on He (99.999% U.H.P.), which, due to trace impurities, yields the O atom 130.2 to 130.6 nm resonance triplet. The reactor gases

(Linde) used are 99.998% Ar from liquid Ar, 1% and 0.1% C₂H₄ (99.5% c.p.) in Ar (99.998%, prepurified) and CO₂ (99.99% precision aquarator). In a few experiments O₂ (99.99% hydrocarbon-free U.H.P.) was used as photolyte instead of CO₂. Flow and pressure measurements are made using Teledyne-Hastings digital flowmeters and an MKS baratron respectively.

The average gas velocity and flash repetition rate are such as to allow essentially complete replenishment of the gas mixture in the reaction zone between flashes. Reaction zone residence times, however, are large compared to reaction times so that the reaction system may be assumed to be pseudo-static. Signals from between 100 and 1000 flashes are averaged to construct temporal profiles of the O-atom fluorescence intensity, such as Fig. 2, at a given T, P and [C₂H₄].

2.2 Data Handling

The measured O-atom fluorescence intensity decay plots, Fig. 2, yield pseudo-first order rate coefficients k_{ps1} based on the relation:

$$-d \ln [O]_{rel} / dt = k_{ps1} = k [C_2H_4] + k_D \quad (2)$$

where $[O]_{rel}$ is the $[O]$ relative to the concentration of O at the end of the photolysis pulse, k_D represents essentially diffusional O-atom loss and k is the rate coefficient of reaction (1) at the given T and P. In the calculation of k_{ps1} and associated standard deviations, errors in time are assumed to be negligible and each value of y_i (number of counts in any one channel) is assigned a variance equal to y_i following Poisson statistics. The points are assigned statistical weights ω_i , proportional to the inverse of their respective variances, and initial estimates of the slope k_{ps1} and intercept I_0 then made. An iteration procedure is then used which employs ω_i , k_{ps1} and

I_0 values obtained from the previous iteration to estimate new values of ω_j , k_{ps1} and I_0 .¹⁹ The iteration continues until the difference between two consecutive estimates of k_{ps1} is negligible. A goodness of fit test²⁰ is then used to determine whether the count data is of the form $I_0 \exp(-k_{ps1}t)$.

Plots of k_{ps1} against $[C_2H_4]$, such as Fig. 3, are then used to determine $k \pm \sigma_k$ values, Table I. Each line in that Table thus corresponds to several k_{ps1} measurements, typically five to ten. Determination of σ_k requires an estimate of the uncertainty in $[C_2H_4]$ values. To obtain these, statistical uncertainties in the flowmeter readings are estimated at 1.5% of full scale. An added 1.5% error in calibration is allowed for. In view of these uncertainties, random and systematic errors¹⁶ in the pressure and temperature are found to have a negligible influence. By treating these uncertainties as standard deviations, concentration values and their variances are determined by a propagation of errors treatment. An iterative procedure is then used again to determine $k \pm \sigma_k$.^{2,21} Statistical weights ω_j proportional to $(\sigma_{k_{ps1},j}^2 + m^2 \sigma_{c,j}^2)^{-1}$, where $\sigma_{k_{ps1},j}^2$, m and $\sigma_{c,j}^2$ denote variance in k_{ps1} , estimate of slope and variance in $[C_2H_4]$ respectively, are assigned to each point. The iteration continues until satisfactory convergence is obtained. Errors in both k_{ps1} and $[C_2H_4]$ measurements are thus taken into account in determining a value for k and its variance.

To derive $k(T)$ expressions from the individual k values a weighted non-linear least squares fitting routine^{20,22} is used. σ_T is taken into account along with σ_k in the Newton-Raphson iterative procedure.²³

3. Results

Forty measurements of k were made from 290 to 1510 K. These are summarized in Table I. As shown there, experiments were performed over a wide range of $[M]$, $(0.76 \text{ to } 8.5) \times 10^{18} \text{ cm}^{-3}$. The data reveal no consistent

variation in results with $[M]$, showing the k values to be independent of pressure. The average gas velocity $\bar{v}$ was varied from 5 to 83 cm s⁻¹, the distance from the cooled reactant inlet tip to the center of the observed reaction zone z from 2.5 to 13 cm and the flash lamp input energy F from 12 to 70 J, to ascertain the absence of influence of these implicit experimental parameters on the obtained k values. The independence of the results of $\bar{v}$ and z , i.e. of residence time, indicates that thermal equilibrium between the bath gas Ar and the CO₂ and C₂H₄ flows had been achieved and that no significant pyrolysis of the C₂H₄ had occurred. However, at $T \geq 1300$ K we noticed that k values measured at residence times in excess of about 0.1 s were significantly smaller than those at shorter times. This may be attributed to heterogeneous decomposition of the ethylene. These measurements are therefore not included in Table I.

A number of fit expressions to the data of Table I have been attempted. The double exponential equation

$$k(T) = (8.3 \pm 1.0) \times 10^{-12} \exp(-660 \pm 50 \text{ K/T}) \\ + (2.8 \pm 1.6) \times 10^{-9} \exp(-7210 \pm 740 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (3)$$

gives a good fit²³ to the data set. In this expression the error limits in the parameter values are one standard deviation.

In Fig. 4 the present k measurements are compared to other measurements by isolated elementary reaction techniques^{5-7,15} covering the lower part of the present temperature range. The agreement between these data is very satisfactory. The sharp increase in k with T , which has its onset at about 800 K, is also evident in the measurements by Klemm et al.¹⁵ Using all of these measurements we can now derive a new fit expression. Rather than eva-

luate the accuracy of the individual measurements of k we calculate a best unweighted fit:

$$k(T) = (1.3 \pm 0.1) \times 10^{-11} \exp(-830 \pm 30 \text{ K}/T) + (1.9 \pm 1.2) \times 10^{-9} \exp(-6940 \pm 830 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (4)$$

The error limits represent one standard deviation in each parameter. These limits can be combined with the covariances, using the method described by Wentworth,²⁴ to yield confidence limits for $k(T)$ at the 95% level of about $\pm 7\%$ for $T < 850$ K. The confidence limits rise to $\pm 18\%$ at 1510 K. Because the fit for $T > 850$ K is dominated by our data, we allow for possible systematic errors of 25% by increasing the confidence limits there to $\pm 30\%$. We favor this empirical double exponential expression since it reproduces the strong upward curvature better than other standard expressions, such as $AT^n \exp(-B/T)$. The first term alone fits the low temperature data very well and is close to that derived by Klemm *et al.*¹⁵

Equation (4) is the fit shown in Fig. 4. Also given in that figure are shock tube²⁵ and flame²⁶ results. While these are in broad agreement with our measurements they suggest different temperature dependences. Such discrepancies, especially with flame studies, are not uncommon in view of the necessary assumptions regarding the other reactions occurring in those experiments.

4. Discussion

In order to evaluate the physical significance of the sharp rise in k above 800 K we use a transition state theory (TST) treatment. For the regime $T < 850$ K, dominated by reactions (1a), k has been interpreted by a number of authors^{5,11,12,27} in terms of the expression

$$k_{1a} = (k_B T/h) [Q(\text{CH}_2\text{CH}_2\text{O}^\ddagger)/\{Q(\text{O}) \cdot Q(\text{C}_2\text{H}_4)\}] \exp(-B/T) \quad (5)$$

This expression is commonly simplified by making two assumptions. These are that the temperature variation of the partition function for O atoms, $Q(\text{O})$, is

accounted for largely by the translational contribution $T^{3/2}$ and that the temperature dependences of $Q(\text{CH}_2\text{CH}_2\text{O}^\ddagger)$ and $Q(\text{C}_2\text{H}_4)$ cancel except for the three new modes in the activated complex introduced by the addition of the O atom. One mode is factored out as the reaction co-ordinate and the other two correspond to degenerate $\text{O}\bullet\text{C}=\text{C}$ bending with frequency ω (the single dot refers to a one-electron bond). This yields^{5,11}

$$k_{1a} = \alpha (T/K)^{-0.5} \{ (1 - \exp(-hc\omega/k_B T)) \}^{-2} \exp(-\beta/T) \quad (6)$$

Explicit effects arising from the electronic partition function of $\text{O}(^3\text{P})$, as discussed by Cohen and Westberg,²⁸ have been left out; the small contribution to the temperature dependence of $Q(\text{O})$, an increase by a factor of 1.25 from 290 to 1510 K, is absorbed into the β term.

As Browarzik and Stuhl have noted,¹¹ for the case of O-atom addition to propene, satisfactory fits may be obtained with a wide range of ω values, 100-300 cm^{-1} in their case, while Perry⁵ gives 100-600 cm^{-1} . We select $\omega = 270 \text{ cm}^{-1}$ based on Benson's data for bending vibrations.^{29a} By requiring the calculated k_{1a} to agree with the average of the data in Fig. 4 at 300 K and 500 K, 7.8×10^{-13} and $2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively, we obtain $\alpha = 4.72 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $\beta = 567 \text{ K}$. Equation (6) is solved at several temperatures and the resulting values are fitted to the form $AT^n \exp(-\beta/T)$, giving

$$k_{1a} = 5.30 \times 10^{-16} (T/K)^{1.435} \exp(-267 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (7)$$

which is shown on Fig. 5. Clearly agreement with Eq. (4) for $T < 850 \text{ K}$ is excellent and slight non-Arrhenius behavior is evident in the addition channels. However, if an attempt is made to improve agreement at higher temperatures by fitting k_{1a} at 290 K and 1510 K instead, then the resulting curve

(Fig. 5) is in poor agreement with the experimental data over much of the 290-1510 K range. This suggests that another channel becomes significant above 850 K. The rate coefficient k_8 for this postulated channel must have both a larger activation energy and a larger pre-exponential factor than k_{1a} . Melius has made ab initio thermochemical calculations using the BAC-MP4 method on the $O + C_2H_4$ system,³⁰ results of which are shown in Fig. 6. From this figure, the abstraction reaction

would be a logical candidate, based on the high activation energy. To test this hypothesis TST calculations have been carried out employing the principles outlined by Benson^{29b} to estimate properties of the $CH_2CH(OH)^\ddagger$ transition state, TS. Tables II and III summarize the results.

CH_2CHF was selected as a model compound for the TS. $C_{p,1500}^0 K$ was approximated by fitting a quadratic function of T to available data^{29a} and extrapolating. The contribution of spin to $\Delta S_{300}^{0\ddagger} K$ was taken to be similar to that for Benson's example for $O + C_2H_6 \rightarrow OH + C_2H_5$.^{29c} Following this example two different TS's were investigated, the linear case and one where the C-H-O angle was 150° . To estimate changes in moments of inertia the bond lengths and angles for ethylene³¹ were combined with bond lengths for C-F^{29a} and C-H-O²⁸ in the TS. Contributions to $\Delta S_{300}^{0\ddagger} K$ from the internal rotor in the non-linear TS were assumed to be equal to those for $O + C_2H_6$ ^{29c} and $O + CH_4$.³² The kinetic parameters A and E_a , defined by $E_a = -d \ln k_8 / d(1/T)$ and $k_8 = A \exp(-E_a/RT)$, were obtained from $\Delta S^{0\ddagger}$ and $\Delta H^{0\ddagger}$ using³³

$$A = 2.098 \times 10^{-11} (T/K)^2 \exp(\Delta S^{0\ddagger}/R) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (9)$$

$$E_a = \Delta H^{0\ddagger} + 2 RT \quad (10)$$

$\Delta S^{0\ddagger}$ was calculated for 300 to 1500 K and $\Delta H_{1500 K}^{0\ddagger}$ adjusted so that k_8 equalled the observed difference between k_{1a} and k at 1500 K. $\Delta H^{0\ddagger}$ and hence k_8 were then extrapolated to lower temperatures. The non-linear model gives

$$k_{8N} = 1.18 \times 10^{-15} (T/K)^{1.55} \exp(-3770 K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (11)$$

while the linear model gives

$$k_{8L} = 2.50 \times 10^{-17} (T/K)^{1.91} \exp(-1880 K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (12)$$

where these parameterized expressions lie within 2% of the calculated points (Table III). The sums $k_{1a} + k_{8N}$ and $k_{1a} + k_{8L}$ are plotted on Fig. 5. There is somewhat better agreement between experiment and TST for the non-linear model, although both curves lie above the observed data at $T \approx 1000$ K.

It is therefore plausible that another channel, not apparent from the current BAC-MP4 calculations,³⁰ may contribute to O-atom removal, together with or instead of H-atom abstraction. A more detailed theoretical treatment including not only the triplet surface described there,³⁰ but also a singlet surface, would be desirable.

Acknowledgements

This work was supported by the Department of Energy, Office of Basic Energy Sciences, Dr. A.H. Laufer, Technical Monitor, under Grant DE-FG02-84ER13224. We thank W.F. Flaherty for his dedicated help with the experiments and D.F. Rogowski, G.C. Billiard and R.C. Hahn for technical assistance. The advice and interest of Drs. R.B. Klemm and J.V. Michael is gratefully acknowledged. We thank Drs. C.F. Melius et al. and R.B. Klemm et al. for communicating their data before publication.

References

1. Felder, W., Fontijn, A., Volltrauer, H.N., Voorhees, D.R., Rev. Sci. Instrum. 1980, 51, 195.
2. Marshall, P., Fontijn, A., J. Chem. Phys. 1986, 85, 2637.
3. Warnatz, J. "18th Symposium (International) on Combustion", The Combustion Institute, Pittsburgh, 1981, p. 369.
4. Westbrook, C.K., Dryer, F.L., Schug, K.P., "19th Symposium (International) on Combustion", The Combustion Institute, Pittsburgh, 1982, p. 153.
5. Perry, R.A., J. Chem. Phys. 1984, 80, 153.
6. Westenberg, A.A., deHaas, N., "12th Symposium (International) on Combustion", The Combustion Institute, Pittsburgh, 1969, p. 289.
7. Nicovich, J.M., Ravishankara, A.R., "19th Symposium (International) on Combustion", The Combustion Institute, Pittsburgh, 1982, p. 23.
8. Hunziker, H.E., Knepe, H., Wendt, H.R., J. Photochem. 1981, 17, 377.
9. Sridharan, W.C., Kaufman, F., Chem. Phys. Lett. 1983, 102, 45.
10. Fonderie, V., Maes, D., Peeters, J., Bull. Soc. Chim. Belg. 1983, 92, 614.
11. Browarzik, R., Stuhl, F., J. Phys. Chem. 1984, 88, 6004.
12. Singleton, D.L., Cvetanovic, R.J., J. Am. Chem. Soc. 1976, 98, 22.
13. DuPuis, M., Wendoloski, J.J., Takada, T., Lester, W.A., J. Chem. Phys. 1982, 76, 481.
14. Smalley, J.F., Nesbitt, F.L., Klemm, R.B., J. Phys. Chem. 1986, 90, 491.
15. Klemm, R.B., Smalley, J.F., Lee, J.H., Skolnik, E.G., Nesbitt, F.L., adjoining paper.
16. Fontijn, A., Felder, W., "Reactive Intermediates in the Gas Phase. Generation and Monitoring", Setser, D.W., Ed., Academic Press, New York, 1979, Chap. 2.
17. Okabe, H., "Photochemistry of Small Molecules", Wiley, New York, 1978, p. 212.
18. The production of $O(^1S)$ is energetically possible below 120 nm. Above 167.2 nm the only energetically possible primary process is production of $O(^3P)$, but the absorption coefficients are very small at those wavelengths.
19. Cvetanovic, R.J., Singleton, D.L., Paraskevopoulos, G.J., J. Phys. Chem. 1979, 83, 50.

20. Bevington, P.R., "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York, 1969.
21. Irvin, J.A., Quickenden, T.I., J. Chem. Educ. 1983, 60, 711.
22. Rogowski, D.F., Fontijn, A., "21st Symposium (International) on Combustion", The Combustion Institute, Pittsburgh, in press.
23. Optimal values of the parameters were determined by minimizing χ^2 defined by

$$\chi^2 = \sum_{m=1}^{40} [\ln k_m - \ln\{A \exp(-B/T_m) + C \exp(-D/T_m)\}]^2 \omega_m$$

where,

$$\omega_m = [(\sigma_{k,m}/k)^2 + (d \ln k/dT)_{T=T_m}^2 \sigma_T^2]$$

Here σ_T is estimated to be 10 K.

24. Wentworth, W.E., J. Chem. Educ. 1965, 42, 96.
25. Frank, P., Just, Th., "Shock Tubes and Waves", R.D. Archer and B.E. Milton, Eds., New South Wales University Press, Sidney, 1983, p. 705.
26. Peeters, J., Mahnen, G., "Combustion Institute European Symposium 1973, F.J. Weinberg, Ed., Academic, London, 1973, p. 53.
27. Cvetanovic, R.J., Singleton, D.L., Rev. Chem. Intermed. 1984, 5, 183.
28. Cohen, N., Westberg, K.R., Int. J. Chem. Kinet. 1986, 18, 99.
29. Benson, S.W., "Thermochemical Kinetics"; 2nd Edition; Wiley, New York, 1976.
(a) Tables A.8. through A.18; (b) Chapters 2 and 4; (c) p. 155.
30. Melius, C.F., Binkley, J.S., Koszykowski, M.L., Private communications, May 1984 and March 1986.
31. "JANAF Tables", Dow Chemical Co., frequently updated.
32. Golden, D.M., J. Phys. Chem. 1979, 83, 108.
33. Golden, D.M., J. Chem. Educ. 1971, 48, 235.

TABLE I

Summary of Rate Coefficient Measurements on $O + C_2H_4$

T, K	P, torr ^a	[M], 10 ¹⁸ cm ⁻³	[C ₂ H ₄], 10 ¹³ cm ⁻³	[CO ₂], 10 ¹⁵ cm ⁻³	$\bar{v}$, cm s ⁻¹	ℓ , cm	F, J	$k \pm \sigma_k$, ^e 10 ⁻¹³ cm ³ molecule ⁻¹ s ⁻¹
293	112	3.69	(1.6-10) ^b	20	13	14.2	61	9.40 ± 0.44
295	259	8.48	(4.1-40) ^b	17 ^d	6	14.2	12	9.07 0.15
296	115	3.75	(2.1-11) ^b	21	13	8.8	48	8.35 0.14
328	101	2.97	(1.2-15) ^b	72	15	14.2	20	10.5 0.5
332	101	2.94	(0.9-15) ^b	10 ^d	15	14.2	12	9.80 0.45
392	60	1.48	(1.1-15) ^b	15	20	8.8	30	14.7 0.7
405	102	2.43	(1.1-8.7) ^b	34	23	6.3	48	18.5 0.5
413	203	4.81	(1.4-16) ^b	73	12	6.3	48	13.6 0.9
465	110	2.29	(1.1-30) ^b	26	21	14.2	48	18.2 1.1
548	250	4.41	(0.1-9.1) ^{b,c}	9	15	8.8	61	28.4 1.0
554	202	3.61	(1.6-10) ^b	55	16	6.3	37	25.9 1.0
613	500	7.88	(0.1-8) ^{b,c}	115	5	14.2	37	29.3 1.4
702	318	2.38	(1.6-15) ^b	62	13	6.3	37	34.3 2.0
707	177	2.42	(1.4-9.6) ^b	27	24	6.3	37	34.9 2.2
844	405	4.63	(0.4-2.3) ^c	105	12	6.3	61	46.5 1.1
848	314	3.58	(0.7-7.0) ^b	80	16	6.3	61	39.5 0.9
861	240	2.69	(0.3-4.6) ^b	8	36	8.8	37	56.6 5.6
904	500	5.34	(0.5-2.4) ^b	178	11	5.0	61	46.9 1.6
912	306	3.24	(0.3-1.5) ^c	110	19	5.0	61	62.1 5.1
953	103	1.04	(0.2-2.1) ^b	4.6	53	5.0	37	53.0 2.8
967	400	3.99	(1.2-7.6) ^c	82	15	6.2	37	54.0 1.4
1019	503	4.77	(0.4-2.2) ^c	75	12	5.0	48	54.0 2.6

1028	320	3.01	(0.2-1.3) ^c	47	20	5.0	48	83.7	4.9
1029	384	3.61	(0.6-1.8) ^c	77	15	5.0	37	60.7	3.1
1036	382	3.56	(0.3-1.6) ^c	77	15	6.2	37	62.4	5.2
1077	305	2.74	(0.2-1.3) ^c	93	21	6.2	37	79.5	2.8
1083	305	2.71	(1.2-8.2) ^b	97	21	6.2	48	65.8	3.9
1090	159	1.30	(0.4-3.7) ^b	83	42	6.2	48	68.2	7.6
1125	169	1.45	(0.9-6.5) ^b	25	41	6.2	37	109	9
1140	308	2.59	(0.2-1.2) ^c	40	23	3.7	37	100	4
1150	308	2.59	(0.2-1.2) ^b	40	23	5.0	37	115	3
1212	180	1.43	(0.6-5.3) ^b	33	40	6.2	37	160	14
1258	501	3.85	(0.3-1.8) ^c	63	15	3.7	61	150	10
1264	297	2.27	(0.1-1.0) ^c	36	26	3.7	37	140	8
1330	430	3.12	(0.1-1.4) ^c	59	19	3.7	37	170	11
1331	430	3.12	(0.5-3.5) ^b	55	37	3.7	61	229	12
1397	114	0.76	(0.2-2.5) ^b	27	83	6.3	37	206	8
1465	500	3.21	(0.3-4.3) ^b	63	27	3.7	58	208	10
1490	364	2.69	(0.2-2.6) ^{b,c}	47	25	3.7	48	239	19
1509	426	2.35	(0.07-0.9) ^c	42	33	3.7	70	245	19

-
- (a) 1 torr = 133.3 Pa
 (b) 1% ethylene in Argon
 (c) 0.1% ethylene in Argon
 (d) O₂ used as photolyte instead of CO₂
 (e) σ_k is based on random and systematic errors

TABLE II

 $\Delta S^{0\ddagger}$ and $\Delta C_p^{0\ddagger}$ for the Reaction $O + C_2H_4 \rightarrow OH + C_2H_3$. (a)

	$\Delta S_{300\text{ K}}^{0\ddagger}$	$\Delta C_{p,400\text{ K}}^{0\ddagger}$	$\Delta C_{p,800\text{ K}}^{0\ddagger}$	$\Delta C_{p,1250\text{ K}}^{0\ddagger}$
Model molecule CH ₂ CHF	-30.5	-3.3	-3.1	-4.75
Spin (triplet TS)	2.2			
Translation	-0.13			
External rotation, linear TS	2.19			
non-linear TS	1.92			
1100 cm ⁻¹ C-F stretch + reaction co-ordinate	-0.05	-0.63	-1.45	-1.72
New O-H stretch, 2100 cm ⁻¹	0	0.07	0.68	1.14
2 O●H●C bends, 600 cm ⁻¹ , linear TS	1.0	2.74	3.60	3.80
1 O●H●C bend and 1 internal rotor, non-linear TS	0.5 +3.6	1.37 +1.0	1.80 +1.0	1.90 +1.0
FCH bend, 1200 cm ⁻¹ + (O●H)●C bond, 700 cm ⁻¹	0.3	0.70	0.37	0.20
F-C=C bend, 410 cm ⁻¹ + (O●H)●C=C bond, 270 cm ⁻¹	0.6	0.17	0.05	0.03
Total, Linear TS	-24.39	-0.25	0.15	-1.30
Total, Non-Linear TS	-21.56	-0.62	-0.65	-2.20

(a) All quantities in cal mol⁻¹ K⁻¹.

TABLE III

Arrhenius Parameters for $O + C_2H_4 \rightarrow OH + C_2H_3$ derived from Transition State Theory.

	T, K			
	300	500	1000	1500
LINEAR TS				
$\Delta S^{0\ddagger}$, cal mol ⁻¹ K ⁻¹	-24.39	-24.52	-24.42	-24.95
A, cm ³ molecule ⁻¹ s ⁻¹	8.81×10^{-12}	2.29×10^{-11}	9.65×10^{-11}	1.66×10^{-10}
$\Delta H^{0\ddagger}$, cal mol ⁻¹	3670	3620	3690	3040
E_a , cal mol ⁻¹	4860	5600	7660	9000
k_{8L} , cm ³ molecule ⁻¹ s ⁻¹	2.6×10^{-15}	8.2×10^{-14}	2.0×10^{-12}	8.1×10^{-12}
NON-LINEAR TS				
$\Delta S^{0\ddagger}$, cal mol ⁻¹ K ⁻¹	-21.56	-21.88	-22.33	-23.22
A, cm ³ molecule ⁻¹ s ⁻¹	3.66×10^{-11}	8.66×10^{-11}	2.76×10^{-10}	3.97×10^{-10}
$\Delta H^{0\ddagger}$, cal mol ⁻¹	7190	7060	6740	5640
E_a , cal mol ⁻¹	8380	9050	10710	11600
k_{8N} , cm ³ molecule ⁻¹ s ⁻¹	2.9×10^{-17}	9.6×10^{-15}	1.3×10^{-12}	8.1×10^{-12}

Figure Captions

Fig. 1 Schematic diagram of the HTP reactor.

Fig. 2 Pseudo-first order decay of O-atom fluorescence signal with background subtracted. Data at $T = 1393$ K, $[C_2H_4] = 2.74 \times 10^{12} \text{ cm}^{-3}$ and $P = 114$ torr.

Fig. 3 Plot of pseudo-first order rate coefficient, k_{psl} vs $[C_2H_4]$ yielding $k(1397 \text{ K})$. Uncertainties shown are one standard deviation.

Fig. 4 Comparison of present k values to other major measurements on the temperature dependence of the $O + C_2H_4$ rate coefficient above 290 K.

(o) Present study, 290-1510 K.

(Δ) Perry,⁵ FP-RF, 260-860 K.

(x) Nicovich and Ravishankara,⁷ FP-RF, 300-810 K.

(□) Klemm et al.,¹⁵ FP-RF and discharge-flow reactor, 240-1050 K.

(●) Westenberg and deHaas,⁶ discharge-flow reactor with ESR, 195-715 K.

(—) Best fit.

(-----) Frank and Just,²⁵ shock tube, 1600-2300 K.

(+ + + +) Peeters and Mahnen,²⁶ flame, 1200-1700 K.

Fig. 5 Comparison of transition state calculations to best fit of experimental data.

Fig. 6 Calculated reaction pathways for the $O + C_2H_4$ reaction based on BAC-MP4 heats of formation for stable and transition state structure species. Figure from Melius et al.,³⁰ by permission.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

REACTION OF $C_2H_4 + O$

Fig. 6

APPENDIX B

An HTP Kinetics Study of the Reaction of $O(^3P)$ Atoms with Acetylene From 290 to 1510 K

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Overall rate coefficients for the $O + C_2H_2$ reaction have been measured in a high-temperature photochemistry (HTP) reactor at temperatures from 290 to 1510 K and pressures from 120 to 630 torr. Ground-state O atoms were generated from flash photolysis of O_2 or CO_2 and monitored by time-resolved atomic resonance fluorescence with pulse counting. Measurements were made under pseudo-first order conditions $[O] \ll [C_2H_2]$. Rate coefficients from 290 to 1300 K are in good agreement with flow reactor measurements in that range. The strongly curved Arrhenius-type plot obtained is contiguous with that found in recent shock tube work from 1500 to 2600 K. A weighted fit to our measurements leads to the expression

$$k(T) = 1.1 \times 10^{-19} T^{2.6} \exp(-330 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Combining the present data set with other experimentally determined k values yields, for the 290 to 2600 K temperature range,

$$k(T) = 3.6 \times 10^{-20} T^{2.8} \exp(-250 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1};$$

the accuracy is assessed as 35% at the 1σ confidence level.

1. Introduction

Acetylene reactions play an important role in the oxidation of many hydrocarbons, for example as intermediates in soot formation in flames.¹ The reaction with O atoms

is the most important fuel-consuming process in acetylene flames from lean to slightly rich conditions.² The O/C₂H₂ reaction system is also of interest because of the associated chemiluminescence and chemi-ionization phenomena.³⁻⁵ There have been a number of measurements in fast-flow reactors of the temperature dependence of the overall rate coefficient k_1 at temperatures up to about 700 K.⁶⁻⁹ In one instance such a study was extended to 1300 K.¹⁰ There is reasonably good agreement between these measurements. At higher temperatures agreement is less satisfactory. Two recent shock tube studies yielded very similar results for k_1 in the 1500 to 2600 K range;^{11,12} such determinations depend on careful accounting of secondary reactions. Ab initio calculations¹³ suggested lower values. The difference between these¹¹⁻¹³ respective $k_1(T)$ expressions increases with temperature and is about a factor of 3 at 2500 K. Kinetic information deduced from flame profiles^{14,15} differs from that of other studies.

The present study was undertaken to provide an overlap between the k_1 measurements obtained by the lower and higher temperature techniques and to help decide between the shock tube measurements and the theoretical work. The high-temperature photochemistry (HTP) adaptation of the flash photolysis-resonance fluorescence (FP-RF) technique is used. This isolated elementary

reaction technique has already been applied to kinetic measurements on a number of reactions over wide temperature ranges, for example $O + C_2H_4$,¹⁶ $O + CH_4$,¹⁷ $H + NH_3$ ¹⁸ and $H + N_2O$ ¹⁹. Since the present work also represents the first FP-RF type study of reaction (1) over an extended temperature range, it is also of interest for comparison to measurements obtained using flow reactors.

2. Technique

2.1 Experimental

The basic principles and details of construction of the HTP reactor used have been described in detail previously.^{16,18} A brief outline follows. The HTP technique is a pseudo-static real time method. Important features which distinguish it from lower temperature apparatus include a reaction tube constructed from alumina, so as to be able to withstand high temperatures, the SiC heating elements, and a movable cooled reactant inlet that allows for short residence times for thermally unstable gases and minimizes heterogeneous decomposition. Variation of the inlet to reaction zone distance and of the (slow) flow velocities allow for checking of adequate mixing, thermal accommodation and lack of decomposition of reactants.

A mixture, of photolyte (O_2 or CO_2) and reactant-in-excess (C_2H_2), flows through the cooled inlet and mixes with the heated bath gas Ar, upstream of the reaction zone. $O(^3P)$ atoms are generated by photolysis pulses from a high intensity capacitive discharge flash lamp operated at approximately 1 Hz. A MgF_2 window separates the reactor from the flash lamp. The $O(^3P)$ formation is essentially summarized by:

While the use of O_2 leads to higher $[\text{O}]$ and hence stronger fluorescence signals, at elevated temperatures it results in secondary O-atom production through the strongly temperature-dependent H/O_2 reaction.²⁰ Therefore, CO_2 was the preferred photolyte for the higher temperature measurements.

As reaction (1) proceeds, the decrease in $[\text{O}]$ is measured from the decrease in fluorescence intensity generated by a cw resonance lamp. A 15 cm focal length CaF_2 plano-convex lens is attached to the resonance lamp to focus the exciting radiation and filter out the Lyman- α line. The fluorescence is detected through a MgF_2 window by an EMI G-26E314LF photomultiplier tube (PMT). The PMT signals are fed into a Nicolet 12/70 multichannel scaler via an EG&G PAR 1121-A amplifier discriminator. The fluorescence decay information is subsequently transferred to an IBM PC for analysis.

Reaction zone temperature measurements are made using a retractable Pt/Rh thermocouple, doubly shielded to minimize radiation effects.²¹ Flow and pressure measurements are made using Teledyne-Hastings digital flow meters and an MKS baratron respectively. The resonance lamp operates on He (99.999% U.H.P.) supplied by Linde. The reactor gases used are Ar from the liquid (99.998%), CO_2 (99.99%, precision aquarator) and O_2 (99.6%, zero grade), all from Linde. Acetylene, 0.101% and 0.937% (99.6%, purified) in Argon (99.998%, prepurified), was obtained from Matheson.

2.2 Data Handling

The O-atom fluorescence intensity decrease information is used to determine the pseudo-first order rate coefficient k_{ps1} , based on the relation

$$\frac{-d[O]}{dt} = \{ k[C_2H_2] + k_D \} [O] = k_{ps1} [O] \quad (2)$$

Here k_D accounts for O-atom loss essentially by diffusion. As

$$[O] \propto I_t$$

where I_t is the fluorescence intensity at time t in relative units, we can write

$$I_t = I_{t=0} \exp(-k_{ps1}t) + B \quad (3)$$

Here, B represents a background level mostly accounted for by scattered light from the resonance lamp.

Plots of k_{ps1} against $[C_2H_2]$ are used to determine $k \pm \sigma_k$ values, Table I. Each such plot and each line in Table I thus correspond to several k_{ps1} values, typically five to nine, obtained under the same general (P,T, etc.) reaction conditions. $k \pm \sigma_k$ reflects both systematic and random errors. A weighted non-linear least squares fitting routine is subsequently used to determine the parameters and the associated uncertainties for various $k(T)$ expressions; σ_T is taken into account along with σ_k in the calculations. These data reduction and error analysis procedures have been described in detail previously.^{16,18}

3. Results and Discussion

Measurements of k_1 were made from 290 to 1510 K. 45 measurements were taken, which are summarized in Table I. Here, $[M]$ denotes total concentration, F represents energy dissipated in the flash lamp, $\bar{v}$ the average gas velocity and z the distance between the tip of the cooled inlet and the center of the

observed reaction zone.

It may be seen that the experiments were performed over a wide range of $[M]$ (1.3 to 16.6) $\times 10^{18}$ cm^{-3} , $\bar{v}$ (4 to 49) cm s^{-1} and three values of z . The data reveals no consistent variation of k with $[M]$ showing these to be independent of pressure. The results are also independent of $z\bar{v}^{-1}$, the mean residence time, indicating that there has been no significant pyrolysis of C_2H_2 and that thermal equilibrium between the bath gas and reactants has been achieved. F has been varied from 7 to 37 J per flash and Table I again indicates that the k_1 values are independent of F . O_2 has been used as photolyte from 293 to 762 K and CO_2 as photolyte from 738 to 1510 K. No significant differences in k_1 values with photolyte are evident in the overlap region. The results are also independent of the C_2H_2 in Ar stock mixture used.

The present data set is plotted in Fig. 1. It can be fitted by a three-parameter $AT^n \exp(-E/T)$ expression

$$k(T) = 1.13 \times 10^{-19} T^{2.6} \exp(-330 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (4)$$

with variances and covariances

$$\begin{aligned} \sigma_A^2 &= 7.64 \text{ A}^2 & \sigma_{An} &= -9.96 \times 10^{-1} \text{ A} \\ \sigma_n^2 &= 1.3 \times 10^{-1} & \sigma_{nE} &= -9.14 \times 10^1 \\ \sigma_E^2 &= 6.81 \times 10^4 & \sigma_{AE} &= 7.05 \times 10^2 \text{ A} \end{aligned}$$

Other fit expressions, such as a four-parameter double exponential expression,¹⁶ were also attempted but did not lead to improved fits.

In Fig. 2 the present data set, as represented by Eq. (4), is compared to

those from earlier studies.⁶⁻¹⁵ It may be seen that the present set agrees very well with the fast-flow reactor studies of James and Glass,⁶ Aleksandrov et al⁸, Hoyermann et al⁹, and Homann and Wellmann.¹⁰ Though agreement with the measurements of Westenberg and deHaas⁷ is also reasonable, their data indicate a stronger non-Arrhenius behavior at lower temperatures than is evident in the present and other studies. Deviations between that pioneering work and other studies has also been noted for several reactions and has been attributed to inadequate stoichiometry corrections.²² The agreement between the calculations of Harding and Wagner¹³ and the various experimental results below about 1100 K is excellent; at higher temperatures their results begin to deviate strongly from the present work and the two shock tube studies.^{11,12} It therefore appears that a further refinement of the theoretical work for the higher temperatures would, when possible, be desirable. Eq. (4) yields at 1500 K a k value 16% lower than that derived by Frank et al.¹² This agreement is about as good as can be expected from any comparison of experimental results. An extrapolation of Eq. (4) to 2500 K leads to a k value 13% lower than theirs. While the flame modelling studies^{14,15} are in broad agreement with the present study in the region of overlapping temperatures, they suggest different temperature dependences. This is not surprising in view of the many assumptions on the other reactions occurring in the flames that are required in such work.

In view of the good agreement it appears useful to combine all experimentally determined k values, excluding those from the flame studies^{14,15} and from Westenberg and deHaas,⁷ to derive a $k(T)$ expression valid from 290 to 2600 K. The other authors do not give individual values of k . Therefore we

have constructed the combined data set as follows. The various suggested $k(T)$ expressions are used to generate k values at 50 K intervals in their respective temperature ranges.²³ Since insufficient information is available to estimate the uncertainty of these k values we use an unweighted fit to obtain, again in an $AT^n \exp(-E/T)$ format,

$$k(T) = 3.55 \times 10^{-20} T^{2.8} \exp(-250 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (5)$$

with variances and covariances

$$\begin{aligned} \sigma_A^2 &= 3.5 \times 10^{-1} \text{ A}^2 & \sigma_{An} &= -4.47 \times 10^{-2} \text{ A} \\ \sigma_n^2 &= 5.7 \times 10^{-3} & \sigma_{nE} &= -4.3 \\ \sigma_E^2 &= 3.45 \times 10^3 & \sigma_{AE} &= 3.4 \times 10^1 \text{ A} \end{aligned}$$

In arriving at confidence intervals for this $k(T)$ expression we need to take into account both the variances associated with each parameter and the covariances associated with the different pairs of parameters, since the parameters are dependent.²⁴ The resulting 1σ confidence levels are about 34% below 700 K, 23% between 700 and 1500 K and 18% above 1500 K. These statistical limits are lower at higher temperatures as fewer data sets are available. Thus scatter arising from unrecognized systematic errors is not revealed. The $k(T)$ fit between 730 and 1500 K is based on one data set only (i.e. that from the present work) and the fit above 1500 K reflects only the two shock tube studies. We thus allow for possible systematic errors of 25% in these temperature ranges. This leads to a recommended 1σ confidence level of about 35% for Eq. (5) over the 290 to 2600 K temperature range.

The exothermic reactions (1a) and (1b) are the commonly considered major

channels, e.g. Refs. 8, 11, 12, 25. The potential H-atom abstraction channel is not considered a likely candidate in the temperature range for which experimental data are available, as it is about 31 kcal mol^{-1} endothermic.²⁶ The present O-atom disappearance studies do not allow one to distinguish between k_{1a} and k_{1b} and possible minor²⁷ channels. Channels (1a) and (1b) are thought to proceed through a common adduct (lifetime $\approx 10^{-9} \text{ s}$ for $P = 2 \text{ Torr}$ and room temperature).^{28,29} Recent work suggests that the branching ratio ($k_{1a}/k_1 = \alpha$) is essentially temperature independent. The significance of channel (1b) near room temperature has been a subject of controversy.^{25,30} The recent on-line mass spectrometer studies of Vinckier, Peeters et al^{30,31} has shown that both CH_2 and C_2HO are important primary products in the 300 to 600 K range and that α is nearly temperature independent. The shock tube work by Frank et al¹² yielded a value of approximately 0.65 for α and suggested α to be essentially independent of temperature. These results are in qualitative agreement with that of Harding and Wagner,¹³ who concluded that α is greater than 0.25 and most probably higher than 0.5 with a weak temperature and no pressure dependence. The conclusion from the present work that the reaction can be fitted over the 290-2600 K range with a single equation is in accord with these findings and is consistent with formation of the initial common adduct being the rate controlling process.

Except for a room temperature (297 K) study by Westenberg and deHaas,³² there are apparently no other reported measurements of reaction (1) using the FP-RF technique. In that work complications due to background chemiluminescence in the vacuum ultraviolet were encountered and measurements had to be made with the resonance lamp alternately on and off. It is not obvious why this complication was not encountered in our work. The vacuum ultraviolet chemiluminescence of the Fourth Positive band system of CO ($A^1\Pi \rightarrow$

χ^1_Σ) is known to accompany reaction (1). Maximum intensities require O and C_2H_2 concentrations of equal magnitude.⁵ While absolute [O] was not measured in either study and both were carried out under conditions such that [O] $\ll$ [C_2H_2], as witnessed by the pseudo-first order [O] decays observed, it is possible that [O] in the present work was lower than in the earlier work. We note that our k values at 293 K, 1.18×10^{-13} and 1.25×10^{-13} compare favorably with theirs of $1.20 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Acknowledgements

This work was supported by the Department of Energy, Office of Basic Energy Sciences, Dr. A.H. Laufer, Technical Monitor, under Grant DOE-FG02-84ER1324. We wish to thank W.F. Flaherty, for invaluable technical assistance throughout the course of the experiments, and Dr. P. Marshall and D.F. Rogowski for helpful discussions and assistance with the data analysis. Also, we thank Drs. Th. Just and A.F. Wagner and their coworkers for preprints of their papers and useful discussions.

References

1. Bittner, J.D. and Howard, J.B., Prog. in Astronaut. and Aeronaut., 1978, 62, 335.
2. Miller, J.A., Mitchell, R.E., Smooke, M.O., "19th Symposium (International) on Combustion", The Combustion Institute, Pittsburgh, 1982, p. 181.
3. Fontijn, A., Ed., "Gas Phase Chemiluminescence and Chemi-Ionization", North-Holland, Amsterdam, 1985, Chaps. 1 and 6.
4. Fontijn, A., Miller, W.J., Hogan, J.M., "10th Symposium (International) on Combustion", The Combustion Institute, Pittsburgh, 1965, p. 565.
5. Fontijn, A., Johnson, S.E., J. Chem. Phys. 1973, 59, 6193.
6. James, G.S., Glass, G.P., J. Chem. Phys. 1969, 50, 2268.
7. Westenberg, A.A., deHaas, N., J. Phys. Chem. 1969, 73, 1181.
8. Aleksandrov, E.N., Arutyunov, V.S., Kozlov, S.N., Kinet. Catal. 1981, 22, 391.
9. Hoyer mann, K., Wagner, H. Gg., Wolfrum, J., Z. Physik. Chem. Neue Folge 1969, 63, 193.
10. Homann, K.H., Wellmann, Ch., Ber. Bunsenges. Phys. Chem. 1983, 87, 527.
11. Lohr, R., Roth, P., Ber. Bunsenges. Phys. Chem., 1981, 85, 153.
12. Frank, P., Bhaskaran, K.A., Just, Th., "21st Symposium (International) on Combustion", in print.
13. Harding, L.B., Wagner, A.F., J. Phys. Chem., 1986, 90, 2974.
14. Vandooren, J., Van Tiggelen, P., "16th Symposium (International) on Combustion", The Combustion Institute, Pittsburgh, 1977, p. 1133.
15. Peeters, J., Mahnen, G., "Combustion Institute European Symposium 1973", Weinberg, F.J. Ed., Academic, London, 1973, p. 53.
16. Mahmud, K., Marshall, P., Fontijn, A., submitted to J. Phys. Chem.
17. Felder, W., Fontijn, A., Chem. Phys. Lett. 1979, 67, 53.
18. Marshall, P., Fontijn, A., J. Chem. Phys., 1986, 85, 2637.
19. Marshall, P., Fontijn, A., Melius, C.F., to be submitted to J. Chem. Phys.
20. Cohen, N., Westberg, K.R., J. Phys. Chem. Ref. Data 1983, 12, 531.

21. Fontijn, A., Felder, W., "Reactive Intermediates in the Gas Phase. Generation and Monitoring", Setser, D.W., Ed., Academic, New York, 1979, Chap. 2.
22. Nicovich, J.M., Ravishankara, A.R., "19th Symposium (International) on Combustion", The Combustion Institute, Pittsburgh, 1982, p.23.
23. Homann and Wellman,¹⁰ recommend their $k(T)$ expression only for $300\text{ K} < T < 500\text{ K}$, though their experiments covered the 300-1300 K temperature range. We therefore used their k values for $T < 500\text{ K}$ only.
24. Wentworth, W.E., J. Chem. Educ. 1965, 42, 96.
25. Huie, R.E., Herron, J.T., Progr. React. Kin. 1975, 8, 1.
26. Wodtcke, A.M., Lee, Y.T., J. Phys. Chem. 1985, 89, 4744.
27. Williamson, D.G., Bayes, K.D., J. Phys. Chem. 1969, 73, 1232.
28. Arrington, C.A., Brennen, W., Glass, G.P., Michael, J.V., Niki, H., J. Chem. Phys. 1965, 43, 525.
29. Mitchell, M.B., Nava, D.F., Stief, L.J., J. Chem. Phys., 1986, 85, 3300.
30. Vinckier, C., Schaekers, M., Peeters, J., J. Phys. Chem. 1985, 89, 508.
31. Peeters, J., Schaekers, M., Vinckier, C., J. Phys. Chem. 1986, 90, 6552.
32. Westenberg, A.A., deHaas, N., J. Chem. Phys. 1977, 66, 4900.

TABLE I

Summary of Rate Coefficient Measurements on $O + C_2H_2$

T, K	P, torr ^a	[M] 10^{18} cm^{-3}	$[C_2H_2]$, 10^{12} cm^{-3}	[photolyte], 10^{16} cm^{-3}	$\bar{\nu}$, cm^{-1}	λ , cm	F, J	$10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$k \pm \sigma k$,
293	206	6.79	(78.1-317) ^d	0.025 ^b	9	12.5	37	0.118 $\pm$ 0.004	
293	206	6.79	(686-2492) ^d	0.321 ^b	9	12.5	37	0.125 0.020	
333	300	8.70	(392-2018) ^d	1.31 ^b	8	12.5	37	0.216 0.004	
362	400	10.8	(179-1389) ^d	1.40 ^b	5	12.5	37	0.301 0.018	
367	632	16.6	(49-598) ^d	1.86 ^b	4	12.5	37	0.328 0.005	
384	205	5.16	(384-2205) ^d	0.922 ^b	12	12.5	37	0.335 0.007	
412	218	5.11	(110-1055) ^d	1.04 ^b	12	12.5	7	0.382 0.010	
424	457	10.41	(173-1104) ^d	1.50 ^b	6	12.5	7	0.559 0.030	
458	407	8.58	(52-268) ^d	1.09 ^b	7	12.5	12	0.508 0.014	
474	460	9.37	(20-376) ^d	1.30 ^b	7	12.5	37	0.774 0.047	
528	422	7.72	(42-322) ^d	1.22 ^b	8	12.5	12	0.976 0.024	
613	432	6.81	(3.15-214) ^d	1.10 ^b	9	12.5	37	1.51 0.07	
689	206	2.89	(10.1-119) ^d	0.460 ^b	22	12.5	37	2.14 0.05	
738	116	1.52	(10.6-65.9) ^d	3.12 ^c	41	14	19	2.34 0.09	
751	400	5.14	(51.2-209) ^d	0.750 ^b	13	12.5	37	2.45 0.09	
762	208	2.64	(11.5-107) ^d	0.414 ^b	25	12.5	37	2.38 0.06	
773	119	1.49	(7.05-52.3) ^{d,e}	3.04 ^c	41	14	37	2.27 0.12	
777	396	4.92	(2.59-97.6) ^{d,e}	12.1 ^c	13	12.5	27	3.69 0.48	
783	398	4.91	(12.6-74.0) ^{d,e}	10.7 ^c	13	12.5	27	4.30 0.43	
810	177	2.11	(3.56-43.3) ^{d,e}	3.51 ^c	16	12.5	27	4.51 0.09	
861	358	4.02	(2.02-18.0) ^e	7.47 ^c	16	14	19	3.97 0.12	

901	121	1.30	(7.38-30.9) ^e	2.41 ^c	49	14	37	5.19	0.40
913	487	5.15	(2.59-21.6) ^e	9.96 ^c	12	14	37	5.78	0.33
915	177	1.87	(13.4-55.5) ^e	4.4 ^c	34	14	37	5.84	0.26
973	356	3.53	(1.76-16.3) ^e	6.9 ^c	17	14	37	6.41	0.31
1019	440	4.17	(8.80-68.4) ^e	3.6 ^c	15	12.5	27	7.32	0.65
1033	485	4.53	(2.04-20.0) ^e	10 ^c	14	14	37	9.78	0.50
1088	600	5.33	(3.08-22.7) ^e	6.8 ^c	12	12.5	27	9.08	0.73
1090	175	1.55	(0.94-23.7) ^e	3.5 ^c	40	14	37	10.4	0.60
1119	469	4.05	(3.37-18.2) ^e	8.4 ^c	16	14	15	12.3	0.50
1122	468	4.03	(2.80-16.9) ^e	8.6 ^c	16	14	37	10.8	1.3
1125	471	4.04	(4.68-32.5) ^e	8.2 ^c	8	14	27	10.8	1.1
1138	246	2.09	(1.86-9.64) ^e	4.7 ^c	29	14	37	13.9	0.20
1246	404	3.13	(5.04-14.4) ^e	6.8 ^c	20	14	37	12.8	1.0
1250	246	1.90	(0.07-8.77) ^e	4.10 ^c	32	14	37	12.3	0.8
1299	405	3.01	(1.63-13.7) ^e	6.8 ^c	20	14	27	10.8	0.7
1303	264	1.96	(3.70-37.0) ^e	4.3 ^c	31	14	37	12.9	1.2
1345	484	3.48	(1.85-16.0) ^e	1.3 ^c	17	10	38	20.7	1.7
1354	218	1.56	(2.11-20.4) ^e	3.5 ^c	14	10	38	17.8	1.0
1399	417	2.88	(5.20-48.0) ^e	6.8 ^c	22	12.5	27	13.8	0.2
1424	503	3.41	(2.10-15.7) ^e	2.7 ^c	18	10	38	23.2	0.6
1440	487	3.27	(5.04-12.2) ^e	4.7 ^c	19	12.5	27	19.9	1.3
1469	487	3.20	(4.11-14.0) ^e	4.9 ^c	20	12.5	27	21.6	2.0
1503	537	3.45	(0.55-4.83) ^e	2.8 ^c	17	10	30	21.6	3.0
1510	408	2.61	(1.15-12.7) ^e	1.7 ^c	23	10	24	31.9	2.0

(a) 1 torr = 133.3 Pa

(b) O₂ used as photolyte

(c) CO₂ used as photolyte

(d) 0.937% C₂H₂ in Ar

(e) 0.101% C₂H₂ in Ar

Figure Captions

Fig. 1 Summary of HTP measurements of the $O + C_2H_2$ rate coefficient from 290 to 1510 K.

Fig. 2 Comparison of present k_1 values to some other major determinations of the temperature dependence of the $O + C_2H_2$ rate coefficient above 290 K. Literature curves are respectively from Westenberg and deHaas,⁷ Hoyer mann, Wagner and Wolfrum,⁹ James and Glass,⁶ Aleksandrov et al⁸, Homann and Wellmann,¹⁰ Vandooren and Van Tiggelen,¹⁴ Peeters and Mahnen,¹⁵ Lohr and Roth,¹¹ Frank, Bhaskaran and Just¹² and Harding and Wagner.¹³

Figure 1

Figure 2

A METHOD FOR ANALYZING EXPONENTIAL DECAYS

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Work supported by the US Department of Energy,
Office of Basic Energy Sciences, under grant DE-FG02-84ER13224

The non-linear least-squares routine KPS1 is presented for the analysis of data from counting experiments which follow single exponential decays. It gives appropriate weighting to individual points, is compact (52 statements) and converges more rapidly than the widely used CURFIT program of Bevington. The routine quantifies the goodness of fit and the uncertainty in the decay coefficient. KPS1 is particularly useful for microcomputer analysis when interfaced directly to laboratory equipment. A FORTRAN listing is included which may easily be adapted for BASIC.

1. Introduction

Many "real time" experiments rely on detection of signals which fall exponentially with time. Examples include kinetic studies in which resonance fluorescence, laser-induced fluorescence or chemiluminescence is used as the diagnostic of reactant concentration, measurements of excited-state lifetimes and studies involving radio-isotopes. If the signals are weak single pulse counting methods can be employed, with the counts accumulated in a multichannel scaler, often linked to a microcomputer for storage and display of the data. After capture the data may be transferred to a larger computer for analysis, but clearly it would be convenient to interpret decays in the course of the experiments. A short program KPS1, which uses little memory and therefore is particularly suited to small and inexpensive microcomputers, is described for the analysis of a signal y_t which decays as a function of time t . y_t is fitted to the form $f(t)$ where

$$f(t) = A \exp(-k t) + B \quad (1)$$

k is the pseudo first-order decay coefficient and A and B are constants.

A number of ways of extracting k , especially where the background B is zero, have been discussed elsewhere (Wentworth, 1965; Swain *et al.*, 1980; Demas, 1983; Hovanec & Ward, 1984). Here it is simply noted that subtracting a measurement made after a "long" time (y_∞) to eliminate the B term requires certainty that the first term has completely decayed, gives excessive weight to y_∞ and may introduce errors if there is a second slow process, on a much longer timescale than $1/k$, which affects y_t . Non-linear

least-squares programs have been published which fit data to the form of Eq. (1) such as LSG and LSKIN1 (DeTar, 1968) and CURFIT (Bevington, 1969), which are relatively lengthy and do not always converge for poor data (Swain et al., 1980). KORE (Swain et al., 1980) is conveniently short, yields the uncertainty in k and quantifies the goodness of fit. The routine KPS1 given here is a modification of KORE which takes proper weighting of multichannel scaler data into account and uses an alternative statistical analysis to derive the goodness of fit and the standard deviation of k , whilst retaining KORE's compactness. KPS1 is a subroutine able to be included in a data collection program interfaced to experimental apparatus.

2. Principles

The method of least-squares aims to minimize

$$\chi^2 = \sum_{t=1}^n [y_t - f(t)]^2 w_t \quad (2)$$

with respect to the parameters of $f(t)$, where w_t represents a statistical weighting factor equal to the reciprocal of the variance of y_t (Bevington, 1969). The importance of correct weighting, particularly for poor data, has been emphasized previously (Demas, 1983). For pulse counting experiments Poisson statistics apply so that $w_t = 1/y_t$. Minimizing Eq. (2) for A and B and solving the simultaneous equations in terms of k yields optimized values of A and B for any particular k :

$$A = \{\sum y_t^{-1} \sum e^{-kt} - n \sum e^{-kt} y_t^{-1}\} / \{\sum y_t^{-1} \sum e^{-2kt} y_t^{-1} - (\sum e^{-kt} y_t^{-1})^2 / n\} \quad (3)$$

$$B = (n - A \sum e^{-kt} y_t^{-1}) / \sum y_t^{-1} \quad (4)$$

where Σ means summation of the n data points over t . k is sought such that $g(k) = \partial \chi^2 / \partial k$ is zero. An iterative technique is applied so that

$$k_{i+1} = k_i - (1+F) g(k) [\partial g(k) / \partial k]^{-1} \quad (5)$$

gives an improved estimate k_{i+1} from an earlier estimate k_i . The condition $F=0$ corresponds to the traditional Newton-Raphson method but Swain et al. showed that provided F is adjusted suitably a dramatically faster convergence can be obtained using $F>0$, which forms their over-relaxation technique (Swain et al., 1980). Iteration is repeated with updated values of A and B until changes in k are sufficiently small.

Swain et al. used a correlation coefficient to quantify the goodness of fit, but a more convenient quantity which is widely tabulated is the reduced chi square χ^2_{ν} . The number of degrees of freedom ν is $n-4$ (Demas, 1983) and χ^2_{ν} is easily calculated via Eq. (2) since $\chi^2_{\nu} = \chi^2 / (n-4)$: it should be approximately unity if Eq. (1) is indeed a fair fit to the observed data. Distributions of χ^2_{ν} give bounds at various confidence levels and degrees of freedom. To obtain the uncertainty in k the error matrix $\underline{\epsilon}$ is employed (Bevington, 1969). With parameters α_1, α_2 and α_3 the elements α_{lm} of the curvature matrix $\underline{\alpha}$ are defined by $\alpha_{lm} = 0.5 \partial^2 \chi^2 / \partial \alpha_l \partial \alpha_m$. The error matrix is given by $\underline{\epsilon} = \underline{\alpha}^{-1}$. The variances of the parameters then lie on the leading diagonal of $\underline{\epsilon}$, thus $\sigma_{\alpha_1}^2 = \epsilon_{11}$.

3. Algorithm

Figure 1 is a listing of the KPS1 routine as used with a Digital

Research FORTRAN-77 compiler for an IBM PC. On entry the datapoints are in the array Y, NPTS being the number of points and TBASE the time per channel. K should contain an initial estimate of the decay coefficient (see later) and a rough value can be obtained from the expression

$$K = (3./NPTS)*LOG((Y(1)-Y(NPTS))/(Y(NPTS/3)-Y(NPTS))) \quad (6)$$

Operation is with single precision arithmetic and iteration stops when K changes by less than 1 part in 10^5 . This may be unnecessarily precise for most kinetic data but serves for demonstration. In the program the array of consecutive exponentials E is generated without repeated calls to the EXP function, which can save significant time for large numbers of points (Demas, 1983). The accumulated error after 256 points using this procedure is about 1 part in 10^5 (or less than 2 parts in 10^6 with IBM interpreted Advanced BASIC, BASICA). The variables S1 to S4 accumulate the summations of Eq. (3) and (4), F is the over-relaxation factor (Swain et al., 1980) and lines from 106 onwards evaluate the curvature matrix and calculate σ_K . Values returned are the decay coefficient K, its standard deviation SDK, the other fitted parameters A and B, and χ^2_ν as RCS. The array Y is unaltered.

The routine will fail if the initial value of K is so large that the Newton-Raphson correction overshoots and makes K negative. Like any comparable program KPS1 will also fail if any of the data are zero since no meaningful weight can be attached for a Poisson distribution.

4. Results

In Table 1 KPS1 is compared to CURFIT, one of the more commonly referenced general least-squares programs (Bevington, 1969), using synthetic input data where $A=50$, $B=20$ and $k=0.2$ for 16 points ($TBASE=1$, $t=1$ to 16). KPS1 has only 52 statements whereas CURFIT and its subroutines occupy 157. KPS1 needs only an initial estimate of k while CURFIT requires estimates of all three parameters: here A and B were set to their "true" values to begin with. Table 1 illustrates the results. Clearly CURFIT is much more sensitive than KPS1 to the starting value of k . The crude estimate Eq. (6) is therefore suitable for KPS1 which converges to the same answer irrespective of the starting value. Equation (6) could be added to the start of the subroutine.

Table 2 is a comparison of the two routines with a scattered dataset of 16 numbers. The first and last were used as initial estimates of $A+B$ and B (not required for KPS1). Although CURFIT executes faster (30 s versus 60 s for KPS1) several consecutive runs, using the previous output as initial estimates, are needed to ensure convergence. KPS1 converges in a single run and so has the shorter overall time.

The KPS1 program is easily translated into other popular microcomputer languages such as BASIC. In fact it executes some three times more rapidly under BASICA on an IBM PC and for large numbers of points (more typical of an experimental dataset) the execution time is less than 1 s per point, the exact time depending on their scatter. The algorithm presented here is therefore a useful addition to a computerized data acquisition system because

of its small size, few input parameters and rapid convergence.

Acknowledgement

Thanks are due to Dr Arthur Fontijn for pointing out the need for this work and for his encouragement and advice.

References

Bevington, P.R. (1969), "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York.

Demas, J.N. (1983), "Excited State Lifetime Measurements", chapter 5, Academic Press, New York.

DeTar, D.F. (1968), "Computer Programs for Chemistry", Vol. 1, W.A. Benjamin, New York.

Hovanec, J.W & Ward, J.R. (1985), Computers and Chemistry 9, 23.

Swain, C.G., Swain, M.S. & Berg, L.F. (1980), J. Chem. Inf. Comput. Sci. 20, 47.

Wentworth, W.E. (1965), J. Chem. Educ. 42, 96.

Table 1. Comparison of KPS1 and CURFIT with "perfect" data
(entries rounded to 4 decimal places)

Initial k	Final k, KPS1	Final k, CURFIT
0.02	0.2000	0.0644
0.15	0.2000	0.1954
0.21	0.2000	0.1999
0.25	0.2000	0.1951
0.30	0.2000	0.1772
0.40	0.2000	0.1796

Table 2. Comparison of KPS1 and CURFIT with scattered data^(a)
(entries rounded to 4 significant figures)

run	parameter values at beginning of run							
	KPS1				CURFIT			
	A	B	k	T ^(b)	A	B	k	T ^(b)
1	36.00	24.00	0.1100	60	36.00	24.00	0.1100	30
2	40.62	23.06	0.1340	10	40.24	23.02	0.1322	30
3	40.62	23.06	0.1340	10	40.63	23.03	0.1336	30
4	40.62	23.06	0.1340	10	40.62	23.05	0.1339	30
5	40.62	23.06	0.1340	10	40.62	23.06	0.1339	30

(a) 16 points: 60, 58, 42, 55, 44, 36, 44, 34, 32, 40, 30, 36, 38, 24, 33, 24

(b) Execution time in s

Figure Caption

Fig.1 FORTRAN-77 Listing of KPS1

```

SUBROUTINE KPS1(NPTS,K,A,B,Y,TBASE,SDK,RCS)
DIMENSION Y(256),E(0:256)
REAL K,M
DATA E(0),F,DELTA2,S2,RCS,A12,A13/1.,4.,0.,0.,0.,0.,0./
DO 102 I=1,NPTS
102 S2=S2+1./Y(I)
103 S1=0.
S3=0.
S4=0.
X=EXP(K)
DO 104 I=1,NPTS
E(I)=E(I-1)/X
S1=S1+E(I)/Y(I)
S3=S3+E(I)*E(I)/Y(I)
104 S4=S4+E(I)
A=(S4-S1*NPTS/S2)/(S3-S1*S1/S2)
B=(NPTS-A*S1)/S2
T1=0.
T2=0.
DO 105 I=1,NPTS
U=I*E(I)/Y(I)
T1=T1+(Y(I)-A*E(I)-B)*U
105 T2=T2+(2*A*E(I)-Y(I)+B)*I*U
IF (F.EQ.0) GOTO 106
DELTA=T1/T2
K=K-(1.+F)*DELTA
M=1.
T=DELTA2/DELTA
IF (T.LE.0.7) THEN
M=0.5
ELSE IF (T.LT.4) THEN
M=2.
END IF
IF (F*M.GT.0.5) THEN
F=F*M
ELSE
F=0.5
END IF
DELTA2=DELTA
IF (ABS(DELTA/K).LT.1E-5) F=0.
GOTO 103
106 DO 107 I=1,NPTS
T=Y(I)-A*E(I)-B
RCS=RCS+T*T/Y(I)
U=I*E(I)/Y(I)
A12=A12+(T-A*E(I))*U
107 A13=A13-A*U
RCS=RCS/(NPTS-4)
DET=A*T2*(S3*S2-S1*S1)-A12*(A12*S2-S1*A13)+A13*(A12*S1-
+ S1*A13)
SDK=SQRT((S3*S2-S1*S1)/DET)/TBASE
K=K/TBASE
END

```