Flash Photolysis Studies of Free-Radical Reactions: $C_3H_5 + C_3H_5$ (293–691 K) and $C_3H_5 + NO$ (295–400 K)

James M. Tulloch, Martyn T. Macpherson,[†] Carol A. Morgan, and Michael J. Pilling*

Physical Chemistry Laboratory, Oxford University, Oxford OX1 3QZ, England (Received: February 22, 1982; In Final Form: May 24, 1982)

A laser flash photolysis system, capable of producing kinetic data of high precision, is described and detailed consideration is given to the methods of data analysis. Measurements of the allyl radical recombination reaction at the high-pressure limit show that the rate constant decreases slightly with temperature and may be described by the Arrhenius parameters $A = (1.69 \pm 0.03) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and $E_a = -(1.1 \pm 0.1)$ kJ mol⁻¹, over the temperature range 293–571 K, if van den Bergh and Callear's absorption cross section is employed and assumed independent of temperature. The errors quoted refer to one standard deviation and do not include the error in the absorption cross section. The reaction between C₃H₅ and NO is also studied, over the temperature range 295–400 K, and is found to be pressure dependent. The limiting high-pressure rate constant decreases with temperature, with a negative activation energy of $-(3.4 \pm 0.1)$ kJ mol⁻¹.

Introduction

A knowledge of the kinetics of free radicals is of primary importance in the modeling of pyrolysis² and combustion³ reactions. It also provides data necessary for the establishment of thermodynamic parameters for free radicals⁴ and for the development and testing of models of chemical reactions.⁵ All these applications demand accurate kinetic data over a wide range of temperatures. Kinetic studies of free radical + molecule reactions at temperatures of interest in pyrolysis and combustion rely primarily on indirect methods, which suffer either from the necessity of proposing a mechanism or from reliance on assumed rate constants or both. Flash photolysis coupled with timeresolved monitoring of radical concentration suffers from neither of these problems provided a clean radical source is used. In addition, recent advances in digital methods of signal recording and analysis have significantly increased the precision with which flash photolysis decay measurements can be made.

This paper describes a flash photolysis/exciplex laser flash photolysis system which, at present, covers the temperature range 300-700 K. Because of the high degree of precision which is, in principle, available by use of this system, great care must be exercised in devising methods of analyzing the data and the techniques employed are described at some length.

The paper also describes the application of the technique to the determination of the rate constant for recombination of allyl radicals. Allara and Edelson² showed that, because of the comparative thermodynamic stability of the allyl radical and its consequently slow rate of H abstraction, it dominates the recombination reactions in the pyrolysis of C_n ($n \ge 3$) alkanes. Thus the rate constants for allyl + allyl and allyl + other radical recombination reactions are of utmost importance in modeling such systems.

The measurement of rate constants for reactions of radicals with molecules by flash photolysis presents some problems. The high radical concentrations needed for accurate monitoring mean that the pseudo-first-order radical + molecule reaction competes with the secondorder radical recombination reaction. One way of overcoming this problem is to use a long path length cell, with multipass optics, to obtain a good signal-to-noise ratio with

[†]SERC Research Fellow.

low radical concentrations.⁶ The short wavelengths and high temperatures required make this technique difficult in the present application. An alternative solution is to use signal averaging to improve signals at low radical concentrations, but the competition between first- and second-order reactions remains a problem, especially at short times, if high-precision rate constants are required. The use of the present system in the analysis of mixed first- and second-order kinetics is illustrated by measurements of the rate constant for C_3H_5 + NO over the temperature range 295-400 K.

Experimental Section

A schematic diagram of the laser flash photolysis system is shown in Figure 1. The photolysis pulse was provided by an exciplex laser (Oxford Lasers KX2) operating at 193 nm on the ArF transition. The laser produced 12-ns, 50mJ pulses at a maximum repetition rate of 2 Hz. The beam (rectangular cross section, $3 \text{ cm} \times 1 \text{ cm}$) was defocussed by a Spectrosil lens so that the central homogenous section just overfilled a 9.34 cm long, 2 cm diameter Spectrosil cell, mounted about 1 m from the laser, with its axis perpendicular to the laser axis. The primary advantages of the laser are that the reaction cell can be more easily heated to high temperatures than is the case if flash lamps are used and that the single photolysis wavelength permits a more accurate determination of the effective absorption cross section of the photolyte than is the case with white light. The optical depth can thus be more accurately determined and kept sufficiently small for homogeneous generation of radicals. A further advantage, particularly if the decays are to be monitored at short times, stems from the short photolysis pulse length and the low levels of scattered light which otherwise may lead to photomultiplier saturation. The reaction vessel was

⁽¹⁾ H. E. van den Bergh and A. B. Callear, *Trans. Faraday Soc.*, **66**, 2681 (1970).

⁽²⁾ D. L. Allara and D. Edelson, Int. J. Chem. Kinet. 7, 479 (1975).
(3) W. C. Gardiner and D. B. Olson, Annu. Rev. Phys. Chem., 31, 377 (1980).

⁽⁴⁾ G. M. Atri, R. R. Baldwin, G. A. Evans, and R. W. Walker, J. Chem. Soc., Faraday Trans. 1, 74, 366 (1978).

⁽⁵⁾ K. Glänzer, M. Quack, and J. Troe, Symp. (Int.) Combust. [Proc.], 16th, 959 (1977).

⁽⁶⁾ S. P. Sander and R. T. Watson, J. Phys. Chem., 84, 1664 (1980).



Figure 1. Schematic diagram of the laser flash photolysis apparatus.

contained in a heated stainless steel block, with Spectrosil end and side windows.

Some single-shot experiments were also conducted with flash lamps. An aluminum housing contained an 18 cm \times 2.5 cm diameter Spectrosil cell mounted between two Spectrosil flash lamps. A split ±10 kV supply was used with a total capacitance of 4 μ F, giving a total energy per pulse of 200 J. The flash lamp system was used over the temperature range 300–550 K.

A high-pressure xenon lamp (Wotan XBO 450W/1) was used as the monitoring source; it was powered by a Farnell 60/50 low ripple (<0.05%) dc supply. The light was dispersed, after passing through the cell, by a Czerny-Turner monochromator (Hilger-Engis, Monospek 1000), with a 1200 lines/mm grating, blazed at 300 nm (reciprocal dispersion, 0.84 nm/mm). Typically 0.73-mm entrance and exit slits were used, giving a bandpass (fwhm) of 0.6 nm. The monochromator was calibrated against the Zn line at 213.861 nm, to an accuracy of ± 0.003 nm. The light was detected by an EMI 9781B photomultiplier, using a modified form of the dynode circuit described by Fenster et al.⁷ The signal was passed to a low-noise amplifier, with a gain of 100 and a time constant which could be switched between 0.1 and 100 μ s. The signal was then digitised with a Datalab 920 recorder (2K, 8-bit store) and averaged with a Datalab 4000 system (4 K, 20-bit store). The data were analyzed on a Research Machines 380Z microcomputer, interfaced to the averager, and stored on floppy disks. The laser experiments were performed either single shot or with averaging, typically over 16 to 128 shots. All the flash lamp experiments were single shot.

End product analysis was performed by expanding the photolysis products into the gas-sampling valve of a Perkin-Elmer F11 chromatograph. Flame ionization detection was employed, after separation on a 2-m column of n-octane/Porasil C.

Gases were handled on a conventional, grease-free vacuum system, and pressures measured with a MKS Baratron type 221A gauge. In the experiments with signal averaging, the gases were flowed so that the cell contents were changed between flashes. A MKS Baratron type 254

(7) A. Fenster, J. C. Leblanc, W. B. Taylor, and H. E. Johns, *Rev. Sci. Instrum.*, 44, 689 (1973).

flow ratio controller was used, linked to three MKS FM360 mass flow meters and Brooks Instruments 5835 solenoid valves.

Hexa-1,5-diene (Koch-Light) was subjected to repeated freeze-pump-thaw cycles to remove dissolved oxygen, and nitric oxide (B.D.H. Ltd.) was purified by trap-to-trap distillation. Argon (B.O.C. Ltd., research grade) was used without further purification.

Data Analysis

Several distinct analytic time dependences of the net absorbance have been encountered in flash photolysis experiments and these are listed in Table I. The main kinetic rate laws are for first-order, second-order, mixed first- and second-order, and reversible first-order reactions. The analysis of these decays is more complex, however, if one of the products absorbs at the analysis wavelength; absorption time dependences for some of these cases are also given in Table I. For combinations of reactions which cannot be intergrated analytically numerical methods of integration must be used, e.g., a second-order reaction in competition with a reversible first-order reaction, which applies to the decay of allyl radicals in the presence of oxygen when there is significant reverse decomposition of the allylperoxy radical.²⁰

For the analytic integrated equations, either linear or nonlinear least-squares methods of analysis may be employed and their relative merits are discussed as follows.

Linear Least-Squares Method.⁸ The linear leastsquares method of analysis can be applied to any function y(t) which may be expressed in the form

$$y(t) = a_0 + \sum_j a_j X_j(t) \tag{I}$$

where the coefficients a_j (j = 1-n) are the parameters to be determined. The best fit is found by minimizing χ^2 , where

$$\chi^{2} = \sum_{i} [w_{i}(y_{i} - y(t_{i}))^{2}]$$
(II)

 y_i is the observed value, $y(t_i)$ is the fitted value at time t_i ,

⁽⁸⁾ P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York, 1969.

FABLE I :	Common Kin	netic Decay Laws and Their Corn	responding Absorption Time Dependenc	tes ^a		
	initial	G	quations			
reactions	concn	differential	integral	0.a	$q^0 I / I \nabla$	
$A \xrightarrow{k_1} B$	$\begin{bmatrix} A \end{bmatrix} = \begin{bmatrix} A \end{bmatrix}_{0}$ $\begin{bmatrix} B \end{bmatrix} = 0$	$d[A]/dt = -k_1[A]$ $d[B]/dt = k_1[A]$	$\begin{bmatrix} \mathbf{A} \end{bmatrix} = \begin{bmatrix} \mathbf{A} \end{bmatrix}_{0} \exp(-k_1 t)$ $\begin{bmatrix} \mathbf{B} \end{bmatrix} = \begin{bmatrix} \mathbf{A} \end{bmatrix}_{0} - \begin{bmatrix} \mathbf{A} \end{bmatrix}$	$ \begin{array}{l} \sigma_{\mathbf{A}} \neq 0; \sigma_{\mathbf{B}} = 0 \\ \sigma_{\mathbf{A}} \neq 0; \sigma_{\mathbf{B}} \neq 0 \end{array} $	$\frac{1 - \exp{\{a_1 \exp(-a_2 t)\}}}{1 - \exp{[a_1 \{\exp(-a_2 t)(1 - a_3) + a_3\}}]}$	(1a) (1b)
$A \xrightarrow{k_1 \atop k_{-1}} B$	[A] = [A] ₀	$d[A]/dt = k_{-1}[B] - k_{1}[A]$	$\begin{bmatrix} A \\ 1 \end{bmatrix} = \begin{bmatrix} A \\ 1 \end{bmatrix}_{0} \begin{bmatrix} K \exp\{-k_{1} + k_{-1}\}\} +$	$\sigma_{\mathbf{A}} \neq 0; \sigma_{\mathbf{B}} = 0$	$1 - \exp[a_1 \{a_4 \exp(a_5 t) + 1\}/(a_4 + 1)]$	(2a)
	[B] = 0	d[B]/dt = k_1 [A] - k_{-1} [B]	$ \begin{bmatrix} \mathbf{I} \\ \mathbf{I} \end{bmatrix} = \begin{bmatrix} \mathbf{A} \\ \mathbf{A} \end{bmatrix}_{0} - \begin{bmatrix} \mathbf{A} \end{bmatrix} $ $ K = k_{1}/k_{-1}$	$\sigma_{\mathbf{A}} \neq 0; \sigma_{\mathbf{B}} \neq 0$	$1 - \exp[a_1\{(1-a_3)(a_4\exp(a_5t) + 1)/(a_4 + 1) + a_3\}]$	(2b)
$2A \xrightarrow{k_2} C$	$\begin{bmatrix} A \end{bmatrix} = \begin{bmatrix} A \end{bmatrix}_0$ $\begin{bmatrix} C \end{bmatrix} = 0$	$d[A]/dt = -2k_2[A]^2$ $d[C]/dt = k_2[A]^2$	$\begin{bmatrix} \mathbf{A} \end{bmatrix} = (1/[\mathbf{A}]_0 + 2k_2 t)^{-1}$ $\begin{bmatrix} \mathbf{C} \end{bmatrix} = (\begin{bmatrix} \mathbf{A} \end{bmatrix}_0 - \begin{bmatrix} \mathbf{A} \end{bmatrix})/2$	$ \begin{array}{l} \sigma_{A} \neq \ 0; \ \sigma_{C} = 0 \\ \sigma_{A} \neq \ 0; \ \sigma_{C} \neq 0 \end{array} $	$\frac{1 - \exp\left\{(1/a_1 + a_6 t)^{-1}\right\}}{1 - \exp\left\{(1 - a_7)/(1/a_1 + a_6 t) + a_1 a_7\right\}}$	(3a) (3b)
$A \xrightarrow{k_1} B$	[A] = [A] ₀	$d[A]/dt = -k_1[A] - 2k_2[A]^2$	$\begin{bmatrix} \mathbf{A} \end{bmatrix} = \{ (1/[\mathbf{A}]_0 + 2k_2/k_1) \exp(k_1 t) - \frac{2k_2}{k_1} \}$	$\sigma_{\mathbf{A}} \neq 0; \sigma_{\mathbf{B}} = 0; \\ \sigma_{\mathbf{C}} = 0$	$1 - \exp\left[\left\{(1/a_1 + a_6/a_2)\exp(a_2t) - a_6/a_2\right\}^{-1} ight]$	(4a)
$2A \xrightarrow{k_2} C$	$[\mathbf{B}] = 0$ $[\mathbf{C}] = 0$	$d[B]/dt = k_1[A]$ $d[C]/dt = k_2[A]^2$	$[\mathbf{B}] = (k_1/2k_2) \{ \ln ([\mathbf{A}]_0/[\mathbf{A}]) - k_1 t \}$	$\sigma_{\mathbf{C}} = 0; \sigma_{\mathbf{B}} \neq 0; \\ \sigma_{\mathbf{C}} = 0$	$\frac{1 - \exp[\left\{\left[\left(1/a_1 + a_6/a_2\right) \exp(a_2 t) - a_6/a_2\right]^{-1} + (a_3a_2/a_6)\left\{\ln\left(\left(1 + a_1a_6/a_2\right) \exp\left(a_2 t\right) - a_1a_6/a_2\right) - a_2 t\right\}\right]}{a_3a_2/a_6}$	(4b)
^a Absorf	tion cross sect	tions (base e). $b a_1 = -\sigma_A [A]_0 l$	$a_2 = k_1, a_3 = \sigma_{\mathbf{B}}/\sigma_{\mathbf{A}}, a_4 = k_1/k_{-1}, a_1$	$s = -(k_1 + k_{-1})$, a_6	$= -2k_2/\sigma_A l, a_\gamma = \sigma_C/2\sigma_A.$	

Integrated rate equations are reduced to straight line form by appropriate transformations, and the weighting factors must also be transformed.⁹ The use of unweighted fits can lead to significant errors, especially for secondorder fits, where the transformed y axis is the reciprocal concentration. Thus the magnitude of the errors in yincreases as the signal decreases and an unweighted fit is unduly influenced by those points which have the largest error. Several methods of estimating the weighting factors were employed; the most satisfactory was to fit a quadratic through the transformed data by linear least-squares and then to fit a second quadratic through the modulus of the residuals from the first fit. The coefficients of this fit were used to calculate the standard deviations, σ_i , for each y_i and hence w_i (= σ_i^{-2}). The validity of this method was tested numerically with simulated data, conforming strictly to a second-order decay, but with normally distributed noise superimposed. The weighted fits gave a mean rate constant significantly closer to the rate constant used to generate the simulated data than did the unweighted fits: in addition, the scatter of the rate constants for the weighted fits was significantly smaller than for the unweighted fits.

Watkins¹⁰ discussed methods for reducing a mixed firstand second-order decay to a straight line, which involve integrating small sections of the concentration vs. time plots and then plotting a function of these vs. a function of time. Although linear least-squares methods may be employed, it is difficult to derive a correct statistical treatment. Uncertainties are also introduced into the xcoordinates and so a regression analysis is required for treating errors in both variables; the problem of calculating the weighting factors is, in consequence, exacerbated.

The final factor which militates against the use of the linear least-squares method for allyl radical absorption signals is the baseline shift which arises because of the formation of a primary stable molecular photoproduct absorbing at the analysis wavelength (vide infra). Thus the pretrigger light level cannot be used to estimate the baseline and the second-order nature of the decay obviates the use of the end of the trace signal, since the allyl radical has not completely reacted. Linear least-squares methods thus require estimates to be made of the final level and iterative calculations.

Nonlinear Least Squares Method.⁸ For mixed-order fits, for second-order fits with a baseline shift, or for decays in general which cannot be expressed in a linear form, the techniques described in the last section cannot be applied directly and nonlinear least-squares methods are more satisfactory. The fitting can be performed directly on the absorption decay curve so no transformation of the data is required and calculation of weighting factors is simplified. χ^2 is minimized with respect to each parameter, a_i , by searching the multidimensional χ^2 hypersurface. This is achieved most efficiently by using the linearization of function method¹¹ coupled with a Marquardt gradient expansion algorithm.¹² The method requires derivatives

(11) Reference 8, pp 232-42.

⁽⁹⁾ R. J. Cvetanovic, D. L. Singleton, and G. Paraskevopolous, J. Phys. Chem., 83, 50 (1979). (10) A. R. Watkins, Mol. Photochem., 7, 171 (1976).

of y with respect to each parameter for each value of t and this can be achieved numerically, using difference formulae:

$$\frac{\partial y_{o}(t)}{\partial a_{j}} = \frac{y_{o}(a_{j} + \Delta a_{j,t}) - y_{o}(a_{j} - \Delta a_{j,t})}{2\Delta a_{j}}$$

Alternatively, if the fitting functions are not too complex, analytic expressions for the derivatives may be used. Table I gives examples of the most common forms of the change in absorbance with time which we have found experimentally. Weighting factors are, once again, included in the expression for χ^2 but vary little with time since the untransformed data are employed and a single value may be used which is estimated from the variance of the pretrigger information. The noise level is primarily determined by shot noise and so is dependent on the total light level which, since the absorption signals are quite small, varies little during the decay trace.

The analysis programs were checked with simulated data for first-, second-, and mixed-order decays. In the first two cases, the precision and accuracy were comparable with those for weighted linear least-squares fitting, but the particular advantage of the nonlinear method is its ability to treat the case of a baseline shift.

Signal Averaging

It is possible to signal average any noisy decay trace, without introducing errors, provided the signals are reproducible from shot to shot. Only in the special case of single exponential decays can this requirement of reproducibility be relaxed. None of the decays studied with the present system are exponentials (first-order decays are not exponential since the fractional absorption does not vary linearly with the concentration). The laser pulse energy is not fully reproducible from shot to shot, thus it is necessary to examine, for each type of kinetic decay studied, the error introduced into the analysis by signal averaging with fluctuating initial concentrations.

The shot-to-shot reproducibility of the laser was determined by measuring pulse energies with a Gentec joulemeter, linked to the transient digitizer. From 50 sampled pulse energies taken from several hundred shots, the standard deviation of the pulse energy was found to be 4%.

The method of error assessment may be illustrated by reference to a mixed-order decay with a first-order buildup of an absorbing product, such as was used in the analysis of the C_3H_5 + NO reaction. Initial radical concentrations were selected from a normal distribution about a specified mean, with a standard deviation of 5%. Decay profiles were calculated for each initial concentration according to the analytic decay function (eq 4b in Table I). Specified numbers, n, of these decay curves were then added and the resultant summed decays analyzed by the method of nonlinear least squares to extract the first-order rate constant; the value of the second-order rate constant was held fixed. The error introduced by signal averaging was taken as the difference between the rate constant obtained by analysis of the simulated decay curve and that specified in the analytic decay function. Figure 2 shows the percentage error introduced in the first-order decay constant, $k_{\rm f}$, for two different $k_{\rm f}$ values, as a function of n. The error is greater for the small rate constant, where the first-order reaction makes a smaller contribution to the overall decay, but, in both cases, the error is always less than 1% provided more than eight summations are made.



Figure 2. Results of signal-averaging simulations; percentage error vs. number of summations: (a) error in first-order rate constant, k_t , determined by nonlinear least squares from an averaged mixed firstand second-order decay with first-order buildup of an absorbing product. A 5% standard deviation of initial radical concentration was used in generating the decays: -, true $k_t = 2.7 \times 10^3 \text{ s}^{-1}$; ---, $k_t = 1.1 \times 10^4 \text{ s}^{-1}$; (b) error in measured first-order rate constant, in a pure first-order decay; (c) error in measured second-order rate constant in pure second-order decay. The different lines in (b) and (c) correspond to different sets of random initial concentrations with a 25% standard deviation.

Simulations were also performed on pure first- and second-order decays under the more extreme conditions of a 25% standard deviation in the laser pulse energy. The errors introduced are also shown in Figure 2 and, once again, they are small, even under these exacting conditions, provided sufficient summations (>8) are performed.

These calculations were designed to test the conditions under which our own experiments were conducted. It is difficult to produce generalized results which are applicable over a wide range of conditions because of the large num-

TABLE II: Primary Photolysis Products of Hexa-1,5-diene



Figure 3. Percentage absorption vs. time for the decay of allyl radicals. Hexadiene pressure = 182 mtorr, argon pressure = 53 torr, T = 295 K, number of summations = 32. Also shown are the residuals obtained from a nonlinear least-squates fit to a second-order decay.

ber of variable parameters, but the simulation method we have described is easily implemented.

Results

End Product Analysis. The stable products resulting from the flash photolysis of hexa-1,5-diene were examined by gas chromatography as a function of nitric oxide concentration, which was used to differentiate between molecules formed as primary products and those with radical precursors. The products observed were allene, propene, ethylene, buta-1,3-diene, but-1-ene, and hexa-1,5-diene but the only products affected by NO were hexa-1,5-diene and but-1-ene. The latter was formed in a very low yield, which was reduced to zero as NO was added. On the basis of these results, the primary processes listed in Table II may be deduced. The radical products were C_3H_5 and CH_3 and because of the much higher yield of allyl, the methyl radicals were completely converted into 1-C₄H₈. The radical C5H7 was also presumably produced and combined with allyl to form C_8H_{12} , which was not detected under the analysis conditions employed. At the temperatures employed in the kinetic spectroscopy experiments, allyl would not react with any of the molecular products or with hexa-1,5-diene. Because of the low yields of CH_3 and C_5H_7 , the error introduced into the recombination measurements by cross combination is small (<5%).

Kinetic Spectroscopy. Allyl Recombination.

$$C_3H_5 + C_3H_5 \rightarrow C_6H_{10}$$

Figure 3 shows a typical trace of the time dependence of the allyl absorption, monitored at 223 nm. Experiments were performed with 200–1000 mtorr of hexa-1,5-diene in the single-shot experiments and 40–1000 mtorr in the signal-averaged experiments. Argon (0–250 torr) was used as a buffer gas. When both flash lamp and laser photolysis were used, a stable, reproducible, residual absorption was found, corresponding to 1–2% of the zero-time allyl absorbance. Traces recorded at 208 and 238 nm, where the allyl absorption is very small (<5% of the maximum at 223 nm) showed that the baseline shift occurred immediately



Figure 4. Arrhenius plot for k_1/σ . The points represent averages obtained from between 2 and 12 experiments and the error bars are one standard deviation.

after the photoflash, i.e., it can be ascribed to a primary molecular photoproduct. Allene and buta-1,3-diene do not fully account for the absorption and presumably a higher molecular weight compound, not detected in the end product analysis, must be formed. The decay curves were analyzed for second-order kinetics on the basis of an immediate shift in baseline, using the nonlinear least-squares method described above. Figure 3 includes the residuals vs. time from a second-order fit to the data.

The absorption technique directly determines k_1/σ where σ is the absorption cross section (base e) of the allyl radical at 223 nm. Using both single shot and signal averaging, we determined k_1/σ over a wide range of initial radical absorbances (0.002-0.25) and found no systematic variation, showing that the absorbance is linear in concentration, i.e., that the Beer-Lambert law is obeyed. Experiments over a range of pressures (1-250 torr) at 295 and 550 K showed that k_1/σ is independent of pressure and that the recombination reaction is at its high-pressure limit. No significant differences were found between single-shot and signal-averaged results or between those from flash lamp and laser experiments. The mean value of k_1/σ obtained from 120 separate determinations at 295 ± 2 K is $(4.60 \pm 0.35) \times 10^5$ cm s⁻¹, where the error limits refer to a single standard deviation. The percentage internal standard deviation for each determination was typically 1-2%, but the reproducibility was significantly worse than this, indicating that the error in k_1/σ is not noise limited. It was probably produced primarily from monitoring lamp intensity fluctuations in the single-shot experiments and drifts in lamp intensity, flow rates, and laser power in the averaging experiments.

The recombination reaction was examined over the temperature range 295–700 K and Figure 4 shows an Arrhenius plot for k_1/σ , using the data obtained from single-shot flash lamp and laser experiments. There is a distinct negative temperature dependence, over the temperature range 293–571 K, corresponding to a negative activation energy of 1.1 ± 0.1 kJ mol⁻¹. At higher temperatures, the measured rate constant begins to increase slightly with temperature and the straight line Arrhenius fit has been restricted to $T \leq 571$ K.

Allyl + NO. C_3H_5 reacts with NO to form C_3H_5NO

$$C_3H_5 + NO \rightarrow C_3H_5NO$$

which has a weak absorption at 223 nm. The residual absorption did not decay with time, showing that the adduct is stable on the experimental time scale. Signal-averaging experiments were conducted with an argon diluent



Figure 5. Percentage absorption vs. time for the decay of allyl radicals in the presence of 36 mtorr of NO; hexadiene pressure = 174 mtorr, argon pressure = 100 torr, T = 403 K, 64 summations. Also shown are the residuals obtained from a nonlinear least-squares fit to a mixed first- and second-order decay with first-order buildup of an absorbing product.

over the temperature range 295–400 K, at total pressures in the range 50-500 torr and at NO pressures of 20-100 mtorr. The hexadiene/argon ratio was kept below ~ 0.003 . The reaction competed with recombination under the experimental conditions and the data were analyzed with the nonlinear least-squares method for mixed-order kinetics with the buildup of an absorbing product (eq 4b, Table I). Allowance was also made for the baseline shift arising from the primary molecular photoproduct, although this correction had little effect on the results. The k_1/σ values obtained from the second-order analysis of the allyl decay in hexa-1,5-diene/argon mixtures were employed and the three unknown parameters used in the program were $k_2[NO]$, the pseudo-first-order rate constant for reaction 2, the initial absorbance, and R, the ratio of the absorption cross sections for C_3H_5NO and C_3H_5 at 223 nm. The accuracy of the results is not affected by the value of σ since the fitting function contains the ratio k_1/σ which is accurately and directly determined over the temperature range of interest. Figure 5 shows a typical decay plot and fit, together with the residuals. The even scatter of the residuals demonstrates the goodness of fit of the mixedorder kinetic model; slight deviations from this type of behavior can be readily observed.²⁰ Also, k_2 was found to be independent of nitric oxide concentration. Figure 6 and Table III show the pressure dependence of k_2 at the three temperatures studied.

Discussion

Van den Bergh and Callear¹ determined the absorption cross section for the allyl radical, following flash photolysis of hexa-1,5-diene, and obtained a value of 5.7×10^{-17} cm³ molecule⁻¹ cm⁻¹ at 223 nm. They also obtained a value for k_1/σ of $(2.5 \pm 0.9) \times 10^5$ cm s⁻¹, which is significantly lower than that reported here; the origin of this discrepancy is not clear. Using the van den Bergh and Callear absorption cross section and the mean k_1/σ value at 295 K reported in the previous section gives $k_1(295 \text{ K}) = (2.65 \pm 0.20) \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹. The error limits represent one standard deviation in k_1/σ and no uncertainty in σ has been included. The error in van den Bergh and Callear's value could be substantial and so a direct determination of σ is in progress.

Provided the absorption cross section can be assumed to be independent of temperature, then we can convert the values of k_1/σ into rate constants over the whole temperature range. Furthermore, although the temperature



Figure 6. Pressure and temperature dependence of k_2 , the rate constant for reaction between C_3H_5 and NO: O, 295 K; \oplus , 350 K; \oplus , 400 K. The points present averages obtained from between 6 and 30 determinations and the error bars one standard deviation. The curves are the best fits obtained from the reduced falloff methods described by Troe.¹⁹ The diluent gas is argon, with the hexadiene to argon ratio kept below ~0.003 and NO concentrations in the range 8×10^{-7} to 4×10^{-6} mol dm⁻³.

TABLE III: Rate Constants for Allyl and NO as a Function of Temperature and Pressure

T/K	press./ torr	no. of determi- nations	$10^{12}k_2/(\text{cm}^3)$ molecule ⁻¹ s ⁻¹) ^a
296	51 64 103 149 201 500	30 12 18 16 14 16	$7.40 \pm 0.58 \\ 8.50 \pm 0.91 \\ 9.31 \pm 0.55 \\ 9.66 \pm 0.78 \\ 10.74 \pm 0.70 \\ 11.19 \pm 0.60$
350	51 102 151 202 500	10 7 6 6 6	$\begin{array}{c} 4.83 \pm 0.23 \\ 6.59 \pm 0.07 \\ 7.21 \pm 0.20 \\ 7.72 \pm 0.12 \\ 9.03 \pm 0.35 \end{array}$
404	50 102 152 202 501	6 6 6 6	$\begin{array}{r} 3.25 \pm 0.15 \\ 4.53 \pm 0.08 \\ 5.10 \pm 0.07 \\ 5.55 \pm 0.05 \\ 6.86 \pm 0.07 \end{array}$

 a Quoted errors represent \pm one standard deviation of the data.

dependence is weak and the uncertainty in the absorption cross section is high, provided this assumption can be made, then the effective negative activation energy shown by (k_1/σ) can be translated to k_1 with no loss of precision.

Glänzer et al.¹³ calculated the expected temperature dependence of the peak absorption cross section for the methyl radical for a range of bandwidths. The spectrum shows rotational fine structure for CD₃, but this is lost for CH₃ because of faster predissociation. As the temperature increases, the radicals are distributed over a wider range of rotational levels and the population of excited vibrational levels also increases. The calculations show that the peak cross section for methyl decreases by a factor of ~2 over the temperature range 300–700 K for a bandwidth of 0.6 nm. These effects are likely to be much reduced for a large radical such as C₃H₅ since the spectrum is very broad and is probably little affected by changes in temperature; however, the net result will be to decrease σ at

⁽¹³⁾ K. Glänzer, M. Quack, and J. Troe, Symp. (Int.) Combust. [Proc.], 16th, 949 (1977).



Figure 7. Arrhenius plot for k_1 , the rate constant for recombination of allyl radicals: ●, this work; O, van den Bergh and Callear;¹ ♦, Throssel;¹⁴ □, Rossi et al.;¹⁵ ■, King.¹⁶

the higher temperatures and thus will lead to an even larger decrease in k_1 with temperature. High-precision measurements of σ over the experimental temperature range are clearly required if the precision in the present kinetic measurements is to be reflected fully in k_1 and its temperature dependence.

Figure 7 shows an Arrhenius plot for k_1 , assuming σ is independent of T, and compares the present values with those obtained in previous determinations. Throssel¹⁴ obtained a value of 1.15×10^{-11} cm³ molecule⁻¹ s⁻¹ over the temperature range 850-950 K, from measurements of the rate of pyrolysis of hexa-1,5-diene and 4-phenylbut-1-ene in a toluene carrier after assuming a cross combination ratio of 4 for methyl and allyl. This value of k_1 may, however, be below the high-pressure limit. The data of Rossi et al.¹⁵ at 625 K ((1.1 ± 0.2) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹) and 900 K ((3.2 ± 0.1) × 10^{-12} cm³ molecule⁻¹ s⁻¹). obtained from very low-pressure pyrolysis (VLPP), are certainly in the falloff region. The degree of falloff was evaluated with RRKM calculations giving values for $k_{1,\infty}$ at 625 and 900 K of 2.9×10^{-11} and 7.0×10^{-11} cm³ molecule⁻¹ s⁻¹, respectively. These values differ significantly from those reported in the present work, both quantitatively and in their qualitative temperature dependence; the RRKM extrapolation is likely to be a major source of error, particularly at the higher temperature. King¹⁶ reported a value of 4.8×10^{-11} cm³ molecule⁻¹ s⁻¹ between 915 and 1153 K. He also used VLPP and relied on thermochemical data for n-propyl, allyl, hex-1-ene, and propene and the geometric mean value rule for n-propyl + allyl.

James and Kambanis¹⁷ measured the disproportionation/combination ratio for allyl + allyl and obtained a value of 0.008 ± 0.001 over the temperature range 403-460 K. Thus, within the present experimental accuracy, measurements refer exclusively to recombination.

The negative temperature dependence of the recombination rate constant is qualitatively similar to that found for CH_3 , *i*- C_3H_7 , and *t*- C_4H_9 recombination. The slight increase in the apparent rate constant for recombination at temperatures greater than \sim 570 K is quite reproducible and may be associated with a real increase in k_1 . An alternative explanation is that an additional reaction is occurring such as H abstraction from hexadiene. A rate constant of $\sim 5 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ would be re-

TABLE IV: Limiting High-Pressure and Low-Pressure Rate Constants (k_{∞} and k_0 , respectively)^a for the Reaction $C_3H_5 + NO \rightarrow C_3H_6NO$ at 295, 350, and 404 K

T/K	$10^{11}k_{\infty}$	$10^{29}k_0$
295 350 404	$\begin{array}{c} 1.35 \pm 0.03 \\ 1.12 \pm 0.04 \\ 0.93 \pm 0.03 \end{array}$	4.0 ± 1.7 2.5 ± 1.0 1.6 ± 0.6

^{*a*} k_{∞} is in units of cm³ molecule⁻¹ s⁻¹ and k_0 in units of cm⁶ molecule⁻² s⁻¹.

quired at 700 K for the reaction to show the required perturbation of the overall kinetics and this seems at least two orders of magnitude larger than would be expected. Further experiments over a wider temperature range are needed before the reasons for the increase in rate constant can be elucidated.

The allyl + NO data show quite clearly that high-precision data can be obtained for radical + molecule reactions, despite the complications introduced by the mixed-order fit and the production of an absorbing product. The variation in the rate constant is quite small, yet the data are sufficiently precise to define the falloff curves quite clearly. The temperature dependence is of particular interest for this association reaction and the data show that the effective activation energy decreases with increasing pressure. The negative temperature dependence becomes greater as the pressure is reduced, because the reaction falls further into the falloff region at the high temperatures. Negative temperature dependences have been found experimentally for several systems,¹⁸ and in some cases these dependences have been remarkably strong. Because of the contribution of falloff to the apparent activation energy, however, it is important that the rate constants are realistically extrapolated to infinite pressure if the limiting temperature dependence is to be determined. Linear Lindemann plots are notoriously inadequate in the highpressure regime and more detailed models must be employed. The most readily applied analytic model is that developed by Troe¹⁹ and based on doubly reduced Kassel falloff curves. The C₃H₅NO vibrational frequencies (given in the Appendix) were determined by comparison with CH₃NO and CH₂CHCH₂Cl. The CNO bending and CN and NO stretching frequencies were equated to those in nitrosomethane, while those involving the carbon and hydrogen atoms were found from 3-chloropropene. A free internal rotation was assumed about the C-N-O bond. A bond dissociation energy of 100 kJ mol⁻¹ was assumed by comparison with CH₃NO (168 kJ mol⁻¹), CH₃O₂ (127 kJ mol⁻¹), and $C_3H_5O_2$ (76 kJ mol⁻¹).²⁰ Since the extrapolation is over a comparatively small range in k_2 , the final result is insensitive to the values of the parameters employed.

The pressure dependence was calculated by the technique outlined by Troe¹⁹ and the best fit to the experimental data obtained with k_{∞} , the high-pressure limiting rate constant, and k_0 , the low-pressure limiting third-order rate constant, as adjustable parameters. Table IV shows the values obtained; since the data were obtained close to the high-pressure limit, k_{∞} is quite well defined, but the error in k_0 is quite substantial. Variation of several of the

 ⁽¹⁴⁾ J. J. Throssel, Int. J. Chem. Kinet., 4, 273 (1972).
 (15) M. Rossi, K. D. King, and D. M. Golden, J. Am. Chem. Soc., 101, 1223 (1979).

⁽¹⁶⁾ K. D. King, Int. J. Chem. Kinet., 11, 1071 (1979).

⁽¹⁷⁾ D. G. L. James and S. M. Kambanis, Trans. Faraday. Soc., 65, 1350 (1969).

⁽¹⁸⁾ R. A. Cox and J. P. Burrows, J. Phys. Chem., 83, 2560 (1979). D.
D. Davis, R. E. Huie, and J. T. Herron, J. Chem. Phys., 59, 628 (1973).
D. L. Singleton and R. J. Cvetanovic, J. Am. Chem. Soc., 98, 6812 (1976).
R-R. Lii, R. A. Gorse, M. C. Sauer, and S. Gordon, J. Phys. Chem., 83, 1803 (1979).
I. W. M. Smith and R. Zellner J. Chem. Soc., Faraday Trans. 2, 69, 1617 (1973).

 ⁽¹⁹⁾ J. Troe, J. Phys. Chem., 83, 114 (1979).
 (20) C. A. Morgan, M. J. Pilling, J. M. Tulloch, R. P. Ruiz, and K. D. Bayes, submitted to J. Chem. Soc., Faraday Trans. 2.

3819

parameters involved in the fit, including the dissociation energy (±10%), the Whitten-Rabinovich factor (±25%), and the effective number of oscillators (±1), had very little effect (<±3%) on k_{∞} . A linear least-squares fit to $\ln k_{2_{\infty}}$ vs. 1/T gives the rate parameters $A = (3.5 \pm 0.6) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and $E_a = -(3.35 \pm 0.10)$ kJ mol⁻¹. Thus even in the high-pressure limit, the negative temperature dependence remains quite strong. Expressing the rate constant in the form $k_{2_{\infty}} = AT^n$ gives $n = -1.15 \pm 0.02$. Acknowledgment. We thank the Science and Engineering Research Council for financial support.

Appendix

Vibrational frequencies and degeneracies of C_3H_5NO used in fit to pressure dependence of k_2 were as follows: 3010 (2), 3000 (1), 2915 (2), 1802 (1), 1600 (1), 1430 (2), 1400 (2), 1297 (1), 1130 (2), 1080 (2), 995 (1), 940 (1), 800 (1), 628 (1), 400 (1), 150 (1), 80 (1).

Kinetics of the Reaction of Hydroxyl Radicals with Nitric Acid

James J. Margitan* and Robert T. Watson

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109 (Received: April 12, 1982; In Final Form: June 8, 1982)

The gas-phase reaction of hydroxyl radicals with nitric acid was studied in a flash photolysis system utilizing UV resonance fluorescence detection of the OH radicals formed by 266-nm laser photolysis of HNO₃ over the temperature range 225-415 K and pressures from 20 to 300 torr. The data were found to exhibit a slight pressure dependence, which increased in importance at lower temperatures. Room-temperature rate constants increased from 1.1×10^{-13} cm³ s⁻¹ at 20 torr to 1.22×10^{-13} cm³ s⁻¹ at 100 torr and 1.3×10^{-13} cm³ s⁻¹ at 300 torr. At 238 K, however, the observed rate constants increased from 2.05×10^{-13} cm³ s⁻¹ at 20 torr to 2.8×10^{-13} cm³ s⁻¹ at 100 torr. An Arrhenius plot over the entire 225-415 K temperature range is curved, with a negative T dependence below room temperature characterized by E/R = -800 K at 40 torr and E/R = -700 K for the purely bimolecular reaction component (extrapolated to zero pressure). At temperatures above 298 K, the T dependence is significantly weaker. These results are in excellent agreement with two recent flash photolysis studies but differ from a recent flow study and two older investigations. The negative T dependence and the pressure dependence are consistent with a reaction that proceeds through an intermediate complex. Additionally, the quantum yields for the production of O and H atoms from 266-nm HNO₃ photolysis were determined by direct observation as $\Phi(O) = 3 \times 10^{-2}$ and $\Phi(H) < 2 \times 10^{-3}$.

Introduction

The reaction of hydroxyl radicals with nitric acid

 $OH + HNO_3 \xrightarrow{k_1} products$

has recently become a topic of major concern in atmospheric chemistry due to the discrepancy between a recent flash photolysis-resonance fluorescence (FP-RF) study (Wine et al., $k_1(298) = 1.3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}, E/R = -650 \text{ K}$) and two earlier investigations by discharge flow-resonance fluorescence (DF-RF) (Margitan et al.²) and flash photolysis-resonance absorption (FP-RA) (Smith and Zellner³), both of which had obtained $k_1 = 0.9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ independent of temperature. Since all three groups were using well-established techniques in proven OH kinetics systems, the divergence of results was particularly troubling, especially since the new faster rate constant made reaction 1 the dominant HO_x loss process in the lower stratosphere.¹ In an attempt to resolve the controversy, we have performed an extensive study of the reaction in a laser photolysis-resonance fluorescence system. Several other groups have undertaken concurrent investigations of the reaction by a variety of techniques.⁴⁻⁶

While the new results consistently obtain a significant negative temperature dependence (reported E/R's from -430 to -750 K) below room temperature with a definite leveling off above 298 K, the spread in actual rate constants is surprisingly wide. Furthermore, we have observed a definite pressure dependence over the 20-100-torr range, which increases in importance at lower temperatures. This behavior was not found in the other studies but is consistent with the mechanism of the overall reaction (proceeding through an intermediate adduct), inferred from the T dependence.

Experimental Section

We have studied the OH + HNO₃ reaction by flash photolysis-resonance fluorescence wherein a frequency quadrupoled Nd:YAG laser (Quanta Ray DCR-1) was used to photolyze HNO₃ at 266 nm. The photolytically generated OH was followed by resonance fluorescence at 309 nm, excited by using a microwave discharge of a He-H₂O flowing mixture at 1 torr and detected by a wide band interference filter (Corion SB1 200-350 nm) and a photomultiplier (EMI 9859Q). Photon pulses were accumulated on an ND 100 MCA (typically 512 channels at 100 μ s/channel) and summed for generally ~600 laser flashes (60 s at 10 pulses s⁻¹). The total signal counts/channel

⁽¹⁾ P. H. Wine, A. R. Ravishankara, N. M. Kreutter, R. C. Shah, J. M. Nicovich, R. L. Thompson, and D. J. Wuebbles, *J. Geophys. Res.*, 86, 1105–12 (1981).

<sup>(105-12 (1981).
(2)</sup> J. J. Margitan, F. Kaufman, and J. G. Anderson, Int. J. Chem. Kinet. Symp. 1, 281-7 (1975).
(3) I. W. M. Smith and R. Zellner, Int. J. Chem. Kinet. Symp. 1,

⁽³⁾ I. W. M. Smith and R. Zellner, Int. J. Chem. Kinet. Symp. 1, 341-51 (1975); R. Zellner and I. W. M. Smith, Chem. Phys. Lett., 26, 72-4 (1974).

⁽⁴⁾ H. H. Nelson, W. J. Marinelli, and H. S. Johnston, Chem. Phys. Lett., 78, 495-9 (1981).

⁽⁵⁾ M. J. Kurylo, K. Cornett, and J. Murphy, J. Geophys. Res., 87, 3081-5 (1982).

⁽⁶⁾ P. Connell and C. J. Howard, to be submitted for publication.