

TABLE V: Summary of Kinetic and Thermodynamic Data for Reactions Involving Cl(²P) and O(³P) Atoms

reaction	k , cm ³ molecule ⁻¹ s ⁻¹	ΔH_{298} , kcal mol ⁻¹
Cl + Cl ₂ O → Cl ₂ + ClO	9.8×10^{-11} ^a	-23.72
Cl + OClO → 2ClO	5.9×10^{-11}	-4.55
Cl + O ₃ → ClO + O ₂	1.2×10^{-11}	-38.60
O + Cl ₂ O → 2ClO	4.1×10^{-12}	-29.81
O + OClO → O ₂ + ClO	5.0×10^{-13}	-59.60
O + O ₃ → 2O ₂	9.5×10^{-15} ²	-93.65

^a This study: average of the two values shown in the abstract.

of the error ranged from 10 to 50%. Consequently, this suggests that if Miziolek and Molina's value of k_{17} is correct then other factors were involved in causing the high result of Freeman and Phillips. Two such factors could be the following: (a) The presence of small concentrations of atomic hydrogen would have contributed to the removal of Cl₂O as the H + Cl₂O reaction is expected to be quite rapid,¹⁸ and (b) inhomogeneous mixing of Cl₂O within the short reaction times (0.5–3.0 ms) might have affected the kinetic analysis. To conclude it should be noted that the discrepancies that exist between the three determinations of k_{17} cannot be completely resolved, but the experimental observations of Basco and Dogra can be satisfactorily simulated by using our value for k_1 (Cl + Cl₂O) in conjunction with a value of $\sim 1 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ for k_{17} (O + Cl₂O).

It should be noted that the high value for k_1 (Cl + Cl₂O), and the relatively lower value for k_{17} (O + Cl₂O), are consistent with other rate constants for similar chlorine and oxygen atom reactions (see Table V). From Table V it can be noted that there is no correlation between the exothermicity and the rate constants for these reactions.

Acknowledgment. The research described in this paper was carried out at the Jet Propulsion Laboratory, Cali-

fornia Institute of Technology, under NASA Contract NAS7-100.

References and Notes

- (1) (a) National Academy of Sciences, "Halocarbons: Effects on Stratospheric Ozone", Washington, D.C., 1976; (b) R. D. Hudson, Ed., NASA Reference Publication 1010, 1977.
- (2) Baulch, D. L.; Cox, R. A.; Hampson, Jr., R. F.; Kerr, J. A.; Troe, J.; Watson, R. T. CODATA Bulletin No. 33, 1979. Also *J. Phys. Chem. Ref. Data* in press.
- (3) Bemand, P. B.; Clyne, M. A. A.; Watson, R. T. *J. Chem. Soc., Faraday Trans. 1*, **1973**, *69*, 1356.
- (4) (a) Clyne, M. A. A.; Watson, R. T. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 2250. (b) Zahniser, M. S.; Kaufman, F. *J. Chem. Phys.* **1977**, *66*, 3673. (c) Leu, M. T.; DeMore, W. B. *J. Phys. Chem.* **1978**, *82*, 2049.
- (5) Basco, N.; Dogra, S. K. *Proc. R. Soc. London, Ser. A* **1971**, *323*, 401.
- (6) Ray, G. W.; Watson, R. T., to be submitted for publication.
- (7) Michael, J. V.; Nava, D. F.; Payne, W. A.; Lee, J. H.; Stief, L. J. *J. Phys. Chem.* **1979**, *83*, 2818.
- (8) Martin, L. R.; Wren, A. G.; Wun, M. *Int. J. Chem. Kinet.* **1979**, *11*, 543.
- (9) Bemand, P. B.; Clyne, M. A. A. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 1132.
- (10) Keyser, L. F. *J. Chem. Phys.* **1978**, *69*, 214.
- (11) Watson, R. T. *J. Phys. Chem. Ref. Data*, **1977**, *6*, 871.
- (12) Lin, C. L. *J. Chem. Eng. Data* **1976**, *21*, 411.
- (13) Molina, L. T.; Molina, M. J. *J. Phys. Chem.* **1978**, *82*, 2410.
- (14) Knauth, H. D.; Alberti, H.; Clausen, H. *J. Phys. Chem.* **1979**, *83*, 1604.
- (15) Clyne, M. A. A.; Coxon, J. A. *Proc. R. Soc. London, Ser. A* **1968**, *303*, 207.
- (16) Schack, C. J.; Lindahl, C. B. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 387.
- (17) Marrero, T. R.; Mason, E. A.; *J. Phys. Chem. Ref. Data* **1972**, *1*, 3.
- (18) This value has been estimated.
- (19) Miziolek, A. W.; Molina, M. J.; *J. Phys. Chem.* **1978**, *82*, 1769.
- (20) Ravishankara, A. R.; Smith, G.; Davis, D. D., to be submitted for publication.
- (21) Kaufman, F. *Prog. React. Kinet.* **1961**, *1*, 1.
- (22) Perry, R. H. and Chilton, C. H., Eds. "Chemical and Engineering Handbook", 5th ed.; McGraw-Hill: New York, 1973; pp 3-320-4.
- (23) Edgecombe, F. H. C.; Norrish, R. G. W.; Thrush, B. A. *Proc. R. Soc. London, Ser. A*, **1957**, *243*, 24.
- (24) Basco, N.; Dogra, S. K. *Proc. R. Soc. London, Ser. A*, **1971**, *323*, 29.
- (25) Freeman, C. G.; Phillips, L. F. *J. Phys. Chem.* **1968**, *72*, 3025.

Shock-Wave Study of the High-Temperature UV Absorption and the Recombination of CF₃ Radicals

K. Glänzer, M. Maier, and J. Troe*

Institut für Physikalische Chemie der Universität, D-3400 Göttingen, West Germany (Received November 13, 1979)

The high-temperature UV absorption and the recombination of CF₃ radicals have been investigated in shock-wave experiments. CF₃ radicals were produced near 1300 K in the fast dissociation of (CF₃)₂N₂ and of CF₃NO. At pressures of the bath gas Ar between 0.3 and 25 atm, the recombination reaction was found to be in the unimolecular falloff range closer to the high than to the low pressure limit. Extrapolation to the high pressure limit gives $k_{\text{rec},\infty}(\text{CF}_3) = (1.9 \pm 0.9) \times 10^{13}$ cm³ mol⁻¹ s⁻¹ at $T = 1300$ K. Earlier low-temperature results are compared with the present data by using unimolecular rate theory.

Introduction

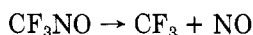
The formation and the fission of the C–C single bond in a chemical reaction has often been used as a model system in gas kinetics. A consistent set of experimental data on the recombination–dissociation rate constant of the reaction $2\text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_6$ over a large temperature range together with a detailed theoretical analysis is now available (see, e.g., ref 1 and 2). The situation is less clear for the analogous system $2\text{CF}_3 \rightleftharpoons \text{C}_2\text{F}_6$. Measurements of

the CF₃ recombination rate constant obtained at low temperatures by various techniques^{3–7} differ by about one order of magnitude between 3×10^{12} (ref 5) and 2.3×10^{13} cm³ mol⁻¹ s⁻¹ (ref 4). At high temperatures, the reverse dissociation of C₂F₆⁸ and the recombination of CF₃,⁹ the latter in the falloff regime, have been studied. In order to compare these results, the relatively uncertain thermochemistry of the C₂F₆ \rightleftharpoons 2CF₃ system¹⁰ has to be established and the falloff curve constructed. Because of the

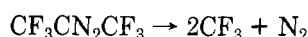
high degree of falloff, the data of ref 9 do not allow for a precise extrapolation toward the high-pressure recombination rate constant; extrapolated values may range between 5×10^{12} and $5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

In theoretical treatments of the CF_3 recombination reaction,^{3,9,11} values between 1.7×10^{13} (ref 3) and $3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (ref 11) have been derived for low temperatures. An almost temperature-independent value of $\sim 5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was proposed in ref 9.

In a recent study of CF_3NO decomposition¹² we observed that the UV absorption of the CF_3 radical at high temperatures extends up to about 230 nm. In the present work the CF_3 absorption in the range 200–230 nm is more closely investigated. We take advantage of this absorption to follow CF_3 concentration profiles directly and to study their recombination. The fast decomposition of CF_3NO ,¹²



or the similarly fast decomposition of hexafluoroazomethane,^{9,13}



at temperatures around 1300 K are used to produce CF_3 radicals. Since the analogous recombinations of CH_3 and CD_3 were found to be in the (pressure-dependent) falloff range under typical shock-wave conditions,¹ the falloff behavior of CF_3 recombination has been studied in particular in the present work. In addition to these experiments we also present calculations of the dissociation and recombination rate coefficients in the low and the high pressure limit. These calculations allow for a comparison of the reported rate data over a large temperature range.

Experimental Section

The details of the shock tube and the experimental technique have been described previously.¹⁴ Absorption signals of CF_3NO (around 690 nm), of $(\text{CF}_3)_2\text{N}_2$ (near 205 nm), and of CF_3 radicals (200–230 nm) were detected with an EMI 6256 A photomultiplier. The monitoring light from a Varian VIX-150 high-pressure Xe arc was analyzed by using a 0.5-m McPherson grating monochromator with a typical spectral bandwidth of $\Delta\lambda = 1.25 \text{ nm}$ (fwhm).

Measurements were made behind incident or reflected shock waves. The reaction mixtures of CF_3NO or $(\text{CF}_3)_2\text{N}_2$ and Ar (reactant mole fractions in the range 10^{-4} – 10^{-2}) were prepared in a 10-L stainless steel cylinder with high-purity argon ($\geq 99.997\%$) at pressures up to 40 atm. The $(\text{CF}_3)_2\text{N}_2$ or CF_3NO pressures were measured by using an absolute pressure gauge with an accuracy of ± 0.033 torr, and the argon was measured with a high-pressure gauge having an accuracy of ± 0.6 atm. This gave a maximum uncertainty of $\sim 3\%$ in the mole fractions of the reaction mixture. There was no significant wall adsorption in the time between the preparation and the use of the mixtures. The quality of the samples was confirmed each time by taking infrared spectra. Trifluoronitrosomethane (Fluorochem Ltd.) was dried over silica gel and degassed before use. Hexafluoroazomethane was synthesized according to the method described in ref 15: ClCN was first prepared in the standard way¹⁶ by passing chlorine gas through a solution of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and KCN and collecting the product in a liquid nitrogen cooled trap. The product, identified spectroscopically as ClCN , needed no further purification. $(\text{CF}_3)_2\text{N}_2$ was then prepared by passing ClCN , carried in a stream of nitrogen, over AgF_2 contained in a glass tube surrounded by a water jacket. The product, which was collected in a trap cooled with liquid air, was found to be well over 90% hexafluoroazomethane with some CF_3NO contamination. Separation was easily per-

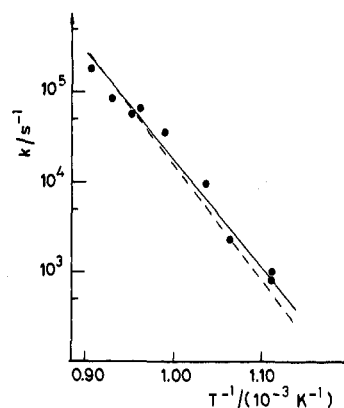


Figure 1. Arrhenius plot of the apparent first-order rate constants for the decomposition of hexafluoroazomethane; (---) extrapolated from low temperature results, ref 13.

formed by trap-to-trap distillation because of the significant difference in boiling points (CF_3NO , -81°C ; $(\text{CF}_3)_2\text{N}_2$, -31°C). The identification and purity of the sample were confirmed by NMR and infrared spectra. $(\text{CF}_3)_2\text{N}_2$ could be stored at dry-ice temperature without noticeable decomposition.

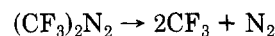
Results

(a) *Thermal Decomposition of $(\text{CF}_3)_2\text{N}_2$* . Whereas the thermal dissociation of CF_3NO has been studied under shock-wave conditions,¹² this appears not to be the case for $(\text{CF}_3)_2\text{N}_2$. In a first set of our experiments we have therefore investigated the thermal decomposition of $(\text{CF}_3)_2\text{N}_2$ in shock-wave experiments in the temperature range 900–1100 K. Total gas concentrations $[\text{Ar}]$ were in the range 5.0×10^{-5} – $7.5 \times 10^{-5} \text{ mol cm}^{-3}$; the mole fraction of the azo compound was 1×10^{-3} . The absorption, around 205 nm, results essentially from the parent compound alone²³ due to the much smaller effective extinction coefficient of the product CF_3 (see below). The decomposition followed a first-order time law

$$d \ln [(\text{CF}_3)_2\text{N}_2] / dt = -k$$

with the rate constants k shown in Figure 1. Our data (although not investigated further with respect to a possibility of falloff behavior, cf. ref 2a) agree very well with the high-pressure rate constant $k_\infty = 10^{16.2} \exp(-231.4 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$ ($T = 572$ – 634 K) of ref 13 extrapolated to our temperatures (Figure 1). An Arrhenius expression of this kind is also consistent with results obtained under low-pressure conditions in the falloff range and temperatures between 720 and 1050 K.⁹ There is sufficient amount of evidence^{9,13} that the decomposition of $(\text{CF}_3)_2\text{N}_2$ leads to the formation of two CF_3 radicals and N_2 . At the temperatures of our recombination experiments ($T \approx 1300 \text{ K}$, see below) this dissociation step can be expected to be so fast that any radical-parent molecule reactions are negligible. It should be noted that the decomposition of $(\text{CF}_3)_2\text{N}_2$ closely resembles in many aspects the decomposition of azomethane and perdeuterioazomethane¹ which have been studied earlier under similar conditions.

(b) *Absorption Spectrum of CF_3 Radicals in the Range 200–230 nm*. In this part of the experiments we investigated the absorption of the CF_3 radical between 200 and 230 nm around 1300 K by using the fast decomposition reaction



as a precursor for the radicals. The concentration of radicals, $[\text{CF}_3]_0$, directly behind the shock front (reaction

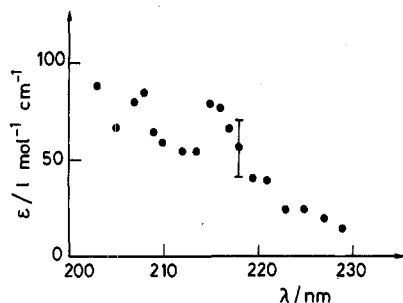


Figure 2. Absorption coefficients of CF₃ radicals ($T \approx 1300$ K); the bandwidth $\Delta\lambda$ is 1.25 nm (fwhm).

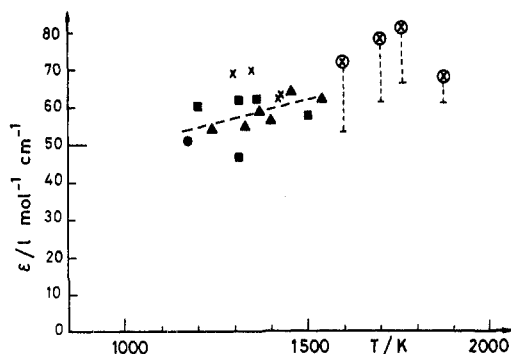


Figure 3. Temperature dependence of the CF₃ absorption coefficient ϵ_{CF_3} ($\lambda = 218$ nm, $\Delta\lambda(\text{fwhm}) = 1.25$ nm): (●) $[(CF_3)_2N_2]/[Ar] = 2.8 \times 10^{-3}$; (▲) $[(CF_3)_2N_2]/[Ar] = 3.1 \times 10^{-3}$; (×) $[CF_3NO]/[Ar] = 6.8 \times 10^{-3}$; (■) $[(CF_3)_2N_2]/[Ar] = 3.3 \times 10^{-3}$; (⊗) from observations of the equilibrium $2CF_3 \rightleftharpoons C_2F_6$ and the equilibrium constant of ref 10, see text.

time $t = 0$) is then given by two times the initial concentration of the parent compound. From the absorption signal directly behind the shock front, the extinction coefficients

$$\epsilon_{CF_3} = \log(I_0/I)_{t=0}/([CF_3]_0 l)$$

were determined, where I_0 is the light intensity with no absorption, I the light intensity with absorption, and l the optical path length. The recombination of CF₃ within the period of the schlieren signal (typically 1–2 μ s) was easily corrected for by use of the recombination constant determined later. In order to keep the corrections small, the measurements were made at relatively small reactant concentrations ($\leq 1.5 \times 10^{-8}$ mol cm⁻³) and total gas concentrations $[Ar] \approx 3 \times 10^{-6}$ mol cm⁻³. The wavelength dependence of ϵ_{CF_3} is shown in Figure 2. Although the uncertainty of a single point is relatively large (about 25% for the most accurate point at 218 nm, see below), there appears to be some structure (cf. also ref 5). It is not impossible that the observed absorption belongs to hot bands of CF₃. There are experiments underway in our laboratory to investigate further details of the CF₃ spectrum. From the results of Figure 2 it appears that the CF₃ spectrum resembles more the spectrum of, e.g., NH₃ at high temperatures than the spectra of the (planar) CH₃ or CD₃ radicals.¹⁷ Since we intended to use the absorption at $\lambda = 218$ nm for the kinetic measurements (see next section), we were interested in the temperature dependence of ϵ_{CF_3} at this wavelength. The results are shown in Figure 3; the data were obtained by using different reaction mixtures. A slight increase of ϵ_{CF_3} between 1200 and 1500 K seems to follow from these results. At $T = 1300$ K, the value of the effective extinction coefficient

$$\epsilon_{CF_3}(\lambda = 218 \text{ nm}, \Delta\lambda(\text{fwhm}) = 1.25 \text{ nm}) = (57 \pm 15) \text{ L mol}^{-1} \text{ cm}^{-1}$$

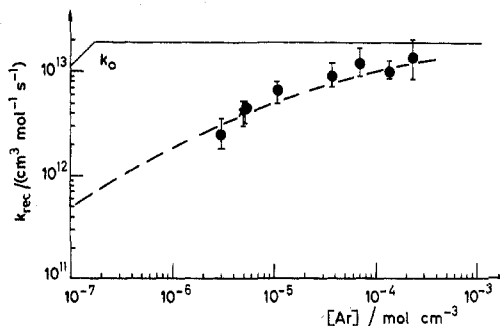


Figure 4. Experimental rate coefficients k_{rec} for CF₃ recombination at $T \approx 1300$ K as a function of total gas concentration $[Ar]$: (●) experiments using the dissociation of $(CF_3)_2N_2$ as precursor of CF₃ radicals; (×) experiments using the dissociation of CF₃NO as precursor of CF₃ radicals.

is obtained. The error limits correspond to one statistical standard deviation and an estimate of the systematic errors. As follows from the thermodynamic data,¹⁰ a substantial amount of free CF₃ radicals will exist in partial equilibrium with C₂F₆ at temperatures in the range 1600–1900 K and concentrations typical for our experiments. The establishment of this equilibrium could be observed in the present experiments. When high total gas concentrations ($[Ar] \approx 2 \times 10^{-4}$ mol cm⁻³) are used, the equilibrium is reached within about 10 μ s. The remaining absorption from CF₃, in equilibrium with C₂F₆, stays practically constant over more than 50 μ s. With a known initial concentration $[CF_3]_0$, the mass balance ($2CF_3 \rightleftharpoons C_2F_6$), and the equilibrium constant K_c of ref 10, one obtains via the relations

$$[CF_3]_{eq} = -\frac{K_c}{4} + \left[\left(\frac{K_c}{4} \right)^2 + \frac{K_c}{2}[CF_3]_0 \right]^{1/2}$$

$$\log(I_0/I)_{eq} = \epsilon_{CF_3}[CF_3]_{eq} l$$

an additional determination of the extinction coefficient at higher temperatures. The results thus obtained are included in Figure 3. If, in the calculation of K_c , the heat of the reaction $2CF_3 \rightleftharpoons C_2F_6$ ($\Delta H^\circ_0 = 401.7 \pm 12.6$ kJ mol⁻¹)¹⁰ were decreased by 12.6 kJ mol⁻¹, the lower bounds of ϵ_{CF_3} given in Figure 3 would be obtained (cf. also Discussion). Apparently, the magnitude of ϵ_{CF_3} is confirmed by these independent measurements.

(c) *Recombination of CF₃ Radicals.* The recombination of CF₃ radicals was measured behind the reflected shock waves. The reaction followed a second-order rate law

$$-d[CF_3]/dt = 2k_{rec}[CF_3]^2$$

The rate coefficient was independent of reactant concentration in the range investigated ($10^{-8} \leq [CF_3]_0 \leq 10^{-7}$ mol cm⁻³) and was the same as if the thermal dissociation of CF₃NO or $(CF_3)_2N_2$ were used to produce CF₃ radicals. However, a dependence on the total gas concentration $[Ar]$ ($3 \times 10^{-6} \leq [Ar] \leq 2.3 \times 10^{-4}$ mol cm⁻³) was observed, indicating that the recombination reaction is in its unimolecular falloff range.

The results on k_{rec} are shown in Figure 4. The data points are averages of 6–18 single experimental rate coefficients at a given total gas concentration. The vertical lines indicate one statistical standard deviation. No temperature dependence of k_{rec} could be observed for $1250 \leq T \leq 1400$ K; the small variation of the apparent extinction coefficient as suggested by the data of Figure 3 has been taken into account. The results in Figure 4 are for temperatures near 1300 K. Although closer to the pressure-

independent high-pressure range, the observed recombination rate constants correspond neither to the high pressure limit ($k_{\text{rec},\infty}$) at the highest nor to the low pressure limit ($k_{\text{rec},0}$) at the lowest Ar densities. In order to obtain these quantities from our data, we have used the extrapolation procedure described in ref 18. This procedure takes weak collision effects into account. The fit of the doubly reduced falloff curve (Figure 4) to our data yields the limiting high-pressure rate constant as $k_{\text{rec},\infty} = (1.9 \pm 0.9) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The error given includes the uncertainty of the experimental rate coefficients (mainly due to the error of ϵ_{CF_3} , see above) and an estimate of the error due to extrapolation. An extrapolation to the low pressure limit from our data is, however, much more uncertain. The falloff curve of Figure 4 corresponds to $k_{\text{rec},0}/[\text{Ar}] = 1.1 \times 10^{20} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

Discussion

(a) *Experimental Results on the Reaction $2\text{CF}_3 \rightleftharpoons \text{C}_2\text{F}_6$.* The present study indicates that the CF_3 radicals, which are formed in the very fast dissociation of $(\text{CF}_3)_2\text{N}_2$ or CF_3NO , recombine with a rate constant of 1.0×10^{13} – $1.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at $T \approx 1300 \text{ K}$ and Ar densities of $[\text{Ar}] = 1.3 \times 10^{-4}$ – $2.3 \times 10^{-4} \text{ mol cm}^{-3}$. At lower densities, the effective recombination rate decreases because of unimolecular falloff. The present data permit a reliable extrapolation to the high pressure limit which leads to $k_{\text{rec},\infty} = 1.9 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ($T = 1250$ – 1400 K). This value of the CF_3 recombination rate constant can be compared well with the analogous recombinations of CH_3 and CD_3 radicals,¹ which were found as $k_{\text{rec},\infty}(\text{CH}_3) = (1.8 \pm 0.9) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{\text{rec},\infty}(\text{CD}_3) = (1.9 \pm 1.0) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively.

At comparable temperatures (1300–1600 K), results on the reverse dissociation $\text{C}_2\text{F}_6 \rightarrow 2\text{CF}_3$ are available from a shock-wave study by Tschuikow-Roux.⁸ At total gas concentrations of $[\text{Ar}] = 3.5 \times 10^{-5}$ – $4.0 \times 10^{-5} \text{ mol cm}^{-3}$, the dissociation rate constants $k_{\text{diss}} = 4.3 \times 10^{17} \exp(-395.8 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$ are reported. As can be seen from Figure 4, at the total gas densities of these experiments the rate constants do not correspond to the high pressure limit. When the same extrapolation technique as described above is used, the data of ref 8 lead to $k_{\text{diss},\infty} \approx 1.6 \times 10^{12} \text{ s}^{-1}$ (1300 K) and $k_{\text{diss},\infty} \approx 2.1 \times 10^{14} \text{ s}^{-1}$ (1500 K). Together with the K_c from ref 10, $k_{\text{rec},\infty} \approx 3.4 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (1300 K) and $k_{\text{rec},\infty} \approx 4.2 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (1500 K) follow from these results. Apart from experimental uncertainties involved in the measurements of ref 8 (the evaluation of k_{diss} depends on assumptions about the reaction mechanism of the decomposition in the presence of H_2), the conversion of k_{diss} depends on the uncertainty of K_c which is about a factor of 3 at the temperatures of interest (see results). This would allow for values of $k_{\text{rec},\infty}$ of as low as $\approx 1.3 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. On the other hand, a decrease of the heat of reaction ΔH°_0 ($= 401.7 \text{ kJ mol}^{-1}$)¹⁰ by, e.g., 10 kJ mol^{-1} , would give a value of $k_{\text{rec},\infty}$ close to the present one. A decrease of ΔH°_0 by this magnitude would also lead to a better agreement of the ϵ_{CF_3} determined below 1400 K from the concentration of the shock-heated mixtures and the ϵ_{CF_3} obtained from the partial equilibria $2\text{CF}_3 \rightleftharpoons \text{C}_2\text{F}_6$ at $T = 1600$ – 1800 K (see results and Figure 3). The possibility of a smaller value for ΔH°_0 as compared to the one recommended in ref 10 needs, however, to be checked in more accurate experimental studies.

The recombination of CF_3 has also been measured directly under very low pressure conditions in the temperature range 930–1110 K.⁹ Apparent rate constants of $k_{\text{rec}} \approx 5 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ indicate considerable falloff at $T \approx 1000 \text{ K}$. When various model calculations are used

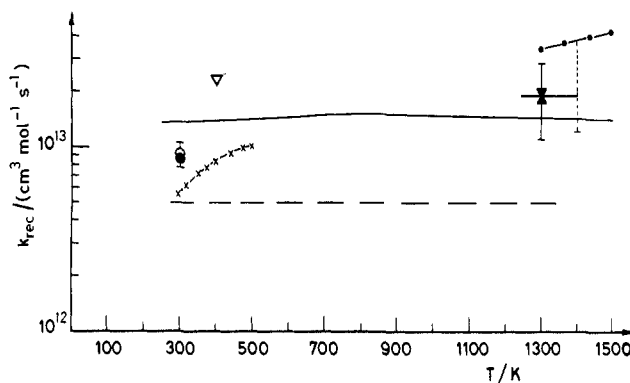


Figure 5. Rate constants $k_{\text{rec},\infty}$ for CF_3 recombination as a function of temperature. Experimental data: (∇) ref 3; (\circ) ref 4, $M = 400$ torr of N_2 ; (\bullet) ref 4, $M = 400$ torr of CO_2 ; ($x-x-x$) ref 7, pressure unknown; (∇) this work; (---) from C_2F_6 dissociation, ref 8, see text. Theoretical results: (---) ref 9; (—) this work.

(see ref 9), a high-pressure recombination rate constant $k_{\text{rec},\infty}$ in the range 5×10^{12} – $5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is shown to be consistent with the experimental data.⁹

At lower temperatures the following experimental results on CF_3 recombination have been obtained. Hiatt and Benson⁶ derived from measurements of the equilibrium $\text{CH}_3 + \text{CF}_3\text{I} \rightleftharpoons \text{CH}_3\text{I} + \text{CF}_3$ (equilibrium constant K) at $T = 419 \text{ K}$ an expression for $K[k_{\text{rec}}(\text{CF}_3)/k_{\text{rec}}(\text{CH}_3)]^{1/2}$. Although a reliable value of the reference rate constant $k_{\text{rec}}(\text{CH}_3)$ is now available,^{1,2a} their determination remains uncertain because of uncertainties of the thermochemical quantities entering K . Using the uncertainties of the heats of formation of CF_3 ($\pm 4.2 \text{ kJ mol}^{-1}$)¹⁰ and of CF_3I and CH_3I (uncertainties $\pm 4.2 \text{ kJ mol}^{-1}$ each),⁶ one easily obtains maximum uncertainties in K of more than one order of magnitude and hence of $k_{\text{rec}}(\text{CF}_3)$ of more than a factor of 100. "Best estimates" of K reported in ref 6 place the values of $k_{\text{rec}}(\text{CF}_3)$ into the range 1.8×10^{12} – $1.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

At $T = 400 \text{ K}$, Ayscough³ reports a value of $k_{\text{rec}} = 2.3 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ obtained from modulated photolysis of ca. 40 torr of CF_3COCF_3 in the presence of CH_4 . The evaluation of experimental results depends on the mechanism of the photochemically induced reactions. Probably not all possible reactions have been taken into account (cf. ref 4 and 19). The reliability of the result is quoted to be of the order of a factor of 2.

Using flash photolysis of CF_3I and direct measurements of CF_3 concentration–time profiles by rapid-scan IR absorption spectroscopy, Ogawa et al.⁴ determined a recombination rate constant of $(9.2 \pm 0.9) \times 10^{12}$ and $(8.8 \pm 0.9) \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at $T = 298 \text{ K}$ and a pressure of 400 torr of N_2 or CO_2 , respectively. When a pressure of 100 torr of Ar is used, a somewhat lower value ($5.9 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) is observed.⁴ A still smaller value of $\approx 3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ($T \approx 300 \text{ K}$, Ar pressure ≈ 100 torr) was obtained from flash photolysis experiments and direct measurements of CF_3 decay profiles by using the vacuum-UV absorption of the radical.⁵ Ogawa et al.⁴ quote a small increase in the rate coefficient with temperature in experiments with constant Ar pressure (100 torr); these data are almost identical with those of ref 7. The experimental results of ref 3, 4, 7, 8 and the present work are included in a plot of $k_{\text{rec},\infty}$ vs. temperature (Figure 5). The use of unimolecular rate theory appears to be helpful to compare the data at lower temperatures with our results. Such calculations are described in the following.

(b) *Calculations of the CF_3 Recombination Rate Constant in the High Pressure Limit.* The rate constant $k_{\text{rec},\infty}$ for the recombination of CF_3 radicals in the high pressure

limit has been calculated² according to eq 1. For the

$$k_{\text{rec},\infty} = K_c^{-1}(kT/h)[Q^*(T)/Q(T)] \exp(-\Delta H^0_0/RT) \quad (1)$$

evaluation of the partition function $Q^*(T)$ of the activated complex, the maximum free energy criterion²⁰ has been used. The thermochemical properties ($\Delta H^0_0 = 401.7$ kJ mol⁻¹ and the appropriate equilibrium constant K_c) as well as the thermodynamic functions (S^0 , $H^0_T - H^0_0$) of CF₃ and C₂F₆ entering the calculation (cf. ref 20) were used as in the JANAF evaluation.¹⁰ The force constant of the dissociating C-C bond, $F_{\text{C-C}} = 4.5 \times 10^5$ dyn cm⁻¹ as obtained from a force field analysis of the C₂F₆ infrared spectrum²¹ and a "looseness" parameter $\gamma = 0.75$ Å (cf. ref 20), were used in the evaluation of eq 1. The results thus obtained are as follows. The average positions of the "activated complexes" were found at C-C distances of 5.0 (300 K), 4.35 (700 K), 4.05 (1100 K), and 3.80 Å (1500 K). The recombination rate constants computed are practically temperature independent, with values of 1.36 (300 K), 1.51 (700 K), 1.46 (1100 K), and 1.40 (1500 K), respectively, all in units of 10¹³ cm³ mol⁻¹ s⁻¹. One should note that in contrast to the reverse dissociation rate constant, $k_{\text{diss},\infty}$, the calculations of $k_{\text{rec},\infty}$ are practically independent of the uncertainty in the heat of the reaction ΔH^0_0 (cf. ref 1 and 2a). Expressing the high pressure dissociation rate constants in Arrhenius form in the temperature range 1100–1500 K, $k_{\text{diss},\infty} = A_\infty \exp(-E_{A,\infty}/RT)$, one predicts according to eq 1 that $A_\infty = 2.1 \times 10^{17}$ s⁻¹ and $E_{A,\infty} = \Delta H^0_0 - 17.6$ kJ mol⁻¹. At lower temperatures, higher preexponential factors and activation energies closer to ΔH^0_0 are found.

In other calculations reported in the literature, the use of the Gorin model³ (i.e., the limiting case of a "completely loose" activated complex) led to a value of $k_{\text{rec},\infty} \approx 1.7 \times 10^{13}$ cm³ mol⁻¹ s⁻¹ ($T = 400$ K). The deficiencies of this model have been outlined earlier (see, e.g., the case of CH₃ recombination, ref 1 and 2a); the nevertheless good agreement with $k_{\text{rec},\infty}$ obtained from eq 1 is due to a very "loose" transition state of the CF₃ recombination at low temperatures as indicated by the positions of the activated complex at "large" C-C distances (cf. above); the strong increase of the rate coefficient with temperature predicted by the Gorin model is an artifact.^{2a} Benson¹¹ used thermochemical estimates of the properties of an activated complex in the 2CF₃ ⇌ C₂F₆ system and obtained $k_{\text{rec},\infty} \approx 3.2 \times 10^{12}$ cm³ mol⁻¹ s⁻¹ ($T = 300$ K). However, Benson used a frequency of the C-C stretch vibration ($\nu_3 \equiv$ reaction coordinate) of 1000 cm⁻¹ which does not correspond to ν_3 in perfluoroethane ($\nu_3 = 349$ cm⁻¹).²¹ More recently Rossi and Golden⁹ presented RRKM calculations with different transition-state models which they named "vibrational" or "rotational" models. The "vibrational model" led to an increase of $k_{\text{rec},\infty}$ with temperature from about 4×10^{12} cm³ mol⁻¹ s⁻¹ ($T = 300$ K) to $\geq 10^{14}$ cm³ mol⁻¹ s⁻¹ ($T \geq 1000$ K); the "rotational model" led to a practically temperature-independent value of $k_{\text{rec},\infty} \approx 5 \times 10^{12}$ cm³ mol⁻¹ s⁻¹. Rossi and Golden⁹ suggest the rotational model to be the better one. This result and the recombination rate constants predicted by eq 1 are also included in Figure 5.

The comparison of experimental and theoretical results (Figure 5) shows that $k_{\text{rec},\infty}$ of eq 1 agrees within a factor of 1.5 with the present high-temperature result at $T = 1250$ – 1400 K, the data of Ogawa et al.⁴ obtained at room temperature and the highest gas pressures ($P = 400$ torr of N₂ or CO₂), and the result of Ayscough³ near 400 K. There is less good agreement with the data obtained at lower pressures ($P = 100$ torr of Ar) and the results of ref 7 at the low-temperature end. The result of Rossi and

Golden⁹ fits the bulk of the room-temperature data within a factor of 2 (an exception is Ayscough's value³) and is nearly a factor of 4 below our high-temperature data and also the lower limit obtained from the C₂F₆ dissociation measurements⁸ (cf. above). Since only the direct measurements of Ogawa et al.⁴ and of the present study determine the CF₃ recombination rate constant near to the high pressure limit, an almost constant value of $k_{\text{rec},\infty} = (1.4 \pm 0.7) \times 10^{13}$ cm³ mol⁻¹ s⁻¹ (300–1500 K) appears to be most probable. This value agrees well with the theoretical prediction given above.

(c) *Rate Constants for CF₃ Recombination in the Low Pressure Limit.* The limiting low-pressure rate constants $k_{\text{rec},0}$ for CF₃ recombination were calculated by using eq 2.¹⁸ At $T = 1300$ K, the following quantities were evalu-

$$k_{\text{rec},0} \approx \frac{[\text{Ar}]}{K_c} \beta_c(\text{Ar}) Z_{\text{LJ}} \frac{\rho_{\text{vib,h}} k T F_{\text{anh}}}{Q_{\text{vib}} F_{\text{E}} F_{\text{rot}} F_{\text{rot int}} \exp(-E_0/kT)} \quad (2)$$

ated: the Lennard-Jones collision frequency $Z_{\text{LJ}} = 2.8 \times 10^{14}$ cm³ mol⁻¹ s⁻¹ (calculated with $\sigma_{\text{C}_2\text{F}_6} = 5.1$ Å, $\sigma_{\text{Ar}} = 3.54$ Å, $\epsilon_{\text{C}_2\text{F}_6}/k = 225$ K, and $\epsilon_{\text{Ar}}/k = 93.3$ K), the anharmonic vibrational state density at E_0 , $\rho_{\text{vib,h}}(E_0) \times F_{\text{anh}} = 7.0 \times 10^{12}/(\text{cm}^{-1})$ (the vibrational frequencies used for the calculation of ρ and of the vibrational partition function Q_{vib} were from ref 21); the factors $F_{\text{E}} = 1.54$, $F_{\text{rot int}} = 1.62$, and $F_{\text{rot}} = 2.02$ were determined as described in ref 18b. This leads to $k_{\text{rec},0}/[\text{Ar}] \approx 6.6 \times 10^{20} \times \beta_c(\text{Ar})$ cm⁶ mol⁻² s⁻¹ which has to be compared with our extrapolated value of $k_{\text{rec},0}/[\text{Ar}] \approx 1.1 \times 10^{20}$ cm⁶ mol⁻² s⁻¹ (see results). This suggests a value for the collision efficiency factor $\beta_c(\text{Ar})$ of ≈ 0.17 , which falls into the range observed in the recombinations of CH₃ or CD₃ radicals¹ and also of other systems at similarly high temperatures.²²

Acknowledgment. Helpful discussions with M. Quack are gratefully acknowledged. Valuable advice during the preparation of the (CF₃)₂N₂ was given by A. Waterfeld. We also thank the Deutsche Forschungsgemeinschaft for financial support of this work.

References and Notes

- (1) (a) K. Glänzer, M. Quack, and J. Troe, *Chem. Phys. Lett.*, **39**, 304 (1976); (b) *Symp. (Int.) Combust., [Proc.]*, **16**, 949 (1977).
- (2) (a) M. Quack and J. Troe, *Gas Kinet. Energy Transfer*, **2**, 175 (1977); (b) D. B. Olson, T. Tanzawa, and W. C. Gardiner, Jr., *Int. J. Chem. Kinet.*, **11**, 23 (1979); (c) H. E. Van Den Bergh, *Chem. Phys. Lett.*, **43**, 201 (1976).
- (3) P. B. Ayscough, *J. Chem. Phys.*, **24**, 944 (1956).
- (4) T. Ogawa, G. A. Carlson, and G. C. Pimentel, *J. Phys. Chem.*, **74**, 2090 (1970).
- (5) N. Basco and F. G. M. Hathorn, *Chem. Phys. Lett.*, **8**, 291 (1971).
- (6) R. Hlatt and S. W. Benson, *Int. J. Chem. Kinet.*, **4**, 479 (1972).
- (7) M. B. Fagarash, F. B. Moin, and U. V. Shevchuk, X. Ukrainskaya Konferentsiya po Fizicheskoi Khimii, Tezisy dokadov, Kiev, 1972. (Cited in "Third Supplementary Tables of Biomolecular Gas Reactions", J. A. Kerr and E. Ratajczak, Eds., Birmingham, 1977; unfortunately only few experimental details of the original work are mentioned in the data compilation.)
- (8) E. Tschulkow-Roux, *J. Chem. Phys.*, **43**, 2251 (1965); *J. Phys. Chem.*, **69**, 1075 (1965).
- (9) M. Rossi and D. M. Golden, *Int. J. Chem. Kinet.*, **11**, 775 (1979).
- (10) JANAF Thermochemical Tables, 2nd ed., *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 37 1972.
- (11) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976, p 164.
- (12) K. Glänzer, M. Maier, and J. Troe, *Chem. Phys. Lett.*, **61**, 175 (1979).
- (13) E. Leventhal, C. R. Simonds, and C. Steel, *Can. J. Chem.*, **40**, 930 (1962).
- (14) (a) K. Glänzer and J. Troe, *Helv. Chim. Acta*, **55**, 2884 (1972); (b) K. Glänzer, *Chem. Phys.*, **22**, 367 (1977).
- (15) O. Glemser, H. Schröder, and H. Haeseler, *Z. Anorg. Chem.*, **282**, 80 (1955).
- (16) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie", Ferdinand Enke Verlag, Stuttgart, 1978.
- (17) G. Herzberg, "Molecular Structure and Molecular Spectra III", Van Nostrand, Toronto, 1966.

- (18) (a) K. Luther and J. Troe, *Symp. (Int.) Combust., [Proc.]*, **17**, (1979);
 (b) J. Troe, *J. Phys. Chem.*, **83**, 114 (1979).
 (19) A. S. Gordon, *J. Chem. Phys.*, **36**, 1330 (1962).
 (20) M. Quack and J. Troe, *Ber. Bunsenges. Phys. Chem.*, **81**, 329 (1977).
 (21) R. A. Carney, E. A. Piotrowsky, A. G. Meister, J. H. Braun, and F. F. Cleveland, *J. Mol. Spectrosc.*, **7**, 209 (1961).
 (22) H. Endo, K. Glänzer, and J. Troe, *J. Phys. Chem.*, **83**, 2083 (1979).
 (23) J. R. Dacey and D. M. Young, *J. Chem. Phys.*, **23**, 1302 (1955).

Infrared Laser Single Photon Absorption Reaction Chemistry in the Solid State. Reactions of Nitrogen Oxides with Sulfur Hexafluoride

Edward Catalano*

Lawrence Livermore Laboratory, Livermore, California 94550

and Robert E. Barletta

Argonne National Laboratory, Argonne, Illinois 60439 (Received January 21, 1980)

Publication costs assisted by Lawrence Livermore Laboratory

The infrared laser induced reactions between SF₆ as a guest reactant matrix isolated within nitrogen oxides as host reactants at low temperatures are described. These reactions proceed via single-photon excitation of the ν_3 band of SF₆ from the $v = 0 \rightarrow 1$ vibrational states. They are further examples of a process known as single-photon absorption reaction chemistry in the solid state (SPARCSS). The spectral data show that SPARCSS reactions can be very rapid. In the NO(N₂O₃)-SF₆ system, the primary photoreaction was completed within 0.075 s at a photon flux density of 33 mW cm⁻². The activation energy for these SPARCSS reactions, which is \leq photon energy, is dramatically smaller than the gas-phase thermal reaction between NO and SF₆. The nitrogen oxides-SF₆ SPARCSS reactions provide further evidence of potential energy surfaces for reactions that are drastically different from those for gas-phase reactions because of configurational aspects of a general matrix phenomenon.

Introduction

Examples of chemical reactions photoinduced by direct, single-photon excitation of the $v = 0 \rightarrow v = 1$ vibrational transitions in a guest reactant matrix isolated within a host reactant at cryogenic temperatures have previously been briefly described,¹ and one has been described in detail.² These reactions were used as experimental examples of the bases for the process of single photon absorption reaction chemistry in the solid state (SPARCSS). The process is itself a manifestation of a more general phenomenon involving photochemistry in which the reactants are in fixed relative spatial configurations. In two cases that have been investigated in detail, SiH₄² and CH₄ were the hosts with the UF₆ and BCl₃ as their respective guests. The excitations were performed by using very small photon flux densities.

These reactant systems are illustrative of several aspects of the SPARCSS process. Experiments on both reactant systems showed that activation energy barriers for infrared laser SPARCSS (IRL-SPARCSS) can be considerably lower than gas-phase thermal activation energy barriers between the same reactant pairs. This is the result of a change in the potential energy surface for reaction which is caused by the host matrix interacting with the guest reactant. Such a change may result in reaction products which are the same as or different from those produced in gas-phase thermal reactions. The SiH₄-UF₆ IRL-SPARCSS reaction yields products that are ostensibly the same as those of the gas-phase reaction. The new pathways may yield products that are quite different from those for gas-phase thermal reaction. The CH₄-BCl₃ system appears to be one in which products are obtained that are different from those obtained in gas-phase thermal reaction. Furthermore, the example CH₄-BCl₃ system shows

that quite different photochemical responses to vibrational excitation under IRL-SPARCSS conditions are obtained which are most probably caused by site differences among the matrix isolated guest molecules. Also, the variation in photochemical response provides evidence for the inhomogeneities in the absorption band of the guest molecules.

In this report, IRL-SPARCSS experiments on nitrogen oxides-SF₆ systems are described. Attempts were made to produce chemical reaction by direct excitation of the $v = 0 \rightarrow v = 1$ transition of the ν_3 (asymmetric stretching) mode of the SF₆ guest with small photon flux densities. Four systems were chosen for study: (a) NO-SF₆; (b) N₂O-SF₆; (c) NO(N₂O₃)-SF₆; and (d) NO(N₂O)-SF₆. Systems c and d possess an additional nitrogen oxide as a guest molecule. Gas-phase thermal reactions between any of these reactant sets do not occur at temperatures below 1000 °C. The extent of IRL-SPARCSS reactions ranges from zero for a and b to a large percentage for c. In c and d, the ν_3 band of SF₆ appears to be homogeneously broadened.

The solid-state chemistry and structures of the oxides of nitrogen are very complex. Pure solid NO consists of a lattice of dimers, and solid deposits of mixtures of oxides of nitrogen are known to form many structural arrangements at cryogenic temperatures.³ Bandwidth studies of SF₆ isolated in N₂, Ar, Kr, Xe, CH₄, CO, N₂O, and NO matrices show that the bandwidth is anomalously large for NO and N₂O matrices.⁴

Mixtures of NO and SF₆ have been the subject of gas-phase, high-power, multiphoton laser chemistry experiments by Basov et al.⁵ In these experiments the excitation energy was rapidly thermalized. Sensible reactions occur only at temperatures in excess of ~ 1000 °C. The postu-