Diode Laser Kinetic Studies of Radical Reactions. 1. Reaction of CF₃ Radicals with NO₂

Ko-ichi Sugawara,* Taisuke Nakanaga, Harutoshi Takeo, and Chi Matsumura

National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japan (Received: April 18, 1988; In Final Form: August 1, 1988)

The reaction of CF₃ radicals with NO₂ has been studied over the pressure range 4-20 Torr at 300 K. CF₃ radicals were produced by infrared multiphoton dissociation of CF₃I. The subsequent decay of the radicals was monitored by using time-resolved diode laser spectroscopy. Analysis of the decay rates gave an absolute rate constant of $(2.5 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ $s^{-1}(3\sigma)$. Further, formation of FNO and CF₂O was observed concomitant with the decay of CF₃, indicating that the reaction of CF₃ with NO₂ produces FNO and CF₂O.

Introduction

Reactions of methyl and halomethyl radicals (CX_3) with NO₂ are important elementary steps in oxidation and nitration processes of methane and halomethanes.¹ These reactions have been considered to be bimolecular atom transfers forming CX₃O and NO even though no one has observed formation of CX₃O in these reactions.2-5

Glänzer and Troe recorded the time profile of the concentration of NO₂ produced by the decomposition of shock-heated CH_3NO_2/Ar mixtures.² From this profile, a rate constant for the reaction of CH₃ with NO₂ was determined to be 2.2×10^{-11} cm³ molecule⁻¹ s⁻¹, which was temperature independent over the range 1100-1400 K. Rossi et al. studied the reactions of CF₃ with Br₂, ClNO, O₃, and NO₂ in a "very low pressure photolysis $(VLP\Phi)$ " cell at room temperature, using infrared multiphoton dissociation (IRMPD) of CF₃I to produce CF₃ and mass spectrometry to detect reaction products.³ They derived an expression that related the rate constant for the reaction of CF₃ with NO₂ to the yield of a secondary reaction product, CF2O. Analysis based on this expression gave the rate constant of $(2.7 \pm 0.5) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K. Gutman and co-workers used the IRMPD of $C_6F_5OCH_3$ and CCl_2F_2 and photoionization mass spectrometry to study the reactions of CH₃ and CClF₂ with NO₂.^{4,5} They observed the decay of the radicals but detected no reaction products other than NO. The products searched for but not detected were CH₃O, CClF₂O, CH₃NO₂, CClF₂NO₂, etc. From these results, it was concluded that the reactions observed were not association reactions but O atom transfers:

$$CH_1 + NO_2 \rightarrow CH_2O + NO$$
 (1)

$$CClF_2 + NO_2 \rightarrow CClF_2O + NO$$
 (2)

The rate constants for reactions 1 and 2 were determined to be $(2.5 \pm 0.5) \times 10^{-11}$ and $(9.6 \pm 1.9) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 295 K, respectively.

The number of such studies is remarkably few. Accordingly, new methods are needed to confirm the rate constants and to establish the reaction mechanism. Recently high-resolution diode laser spectroscopy has advanced considerably, and a number of transient species have been observed.⁶ This spectroscopic tech-

- (5) Slagle, I. R.; Gutman, D. J. Am. Chem. Soc. 1982, 104, 4741.
 (6) Hirota, E.; Kawaguchi, K. Ann. Rev. Phys. Chem. 1985, 36, 53.

nique has been used by several groups to study the kinetics of transient species, in particular, recombination of CH3 and three-body reaction of CH_3 with O_2 ,⁷ vibrational excitation in CO_2 caused by collisions with hot H atoms,⁸ vibrational distribution of CO₂ produced by UV photolysis of CH₃COCOOH,⁹ association reaction of ClO with NO_2 ,¹⁰ association and recombination re-actions of HO₂ and C₂H₅O₂,¹¹ photochemical processes of SO₂,¹² CS_2 ,¹³ and C_2H_2 ¹⁴ induced by an excimer laser, and reactions of CF_2 with Br_2 and Cl_2 .¹⁵ Throughout these studies time-resolved diode laser spectroscopy has been a useful probe of the reaction kinetics.

The aim of the present work is to use this spectroscopic technique for the investigation of the reaction of CF₃ with NO₂ and to establish the reaction mechanism. It has been greatly assisted by the observation by Yamada and Hirota of the high-resolution infrared spectrum of CF3 and their determination of the precise molecular constants.¹⁶

In this paper, detailed results of our investigation are reported. CF₃ radicals were produced by the IRMPD of CF₃I. The diode laser was tuned to a rotation-vibration line of CF₃, and its absorbance was monitored as a function of time. The rate constant for the reaction of CF₃ with NO₂ was determined from the decay rate of CF₃ measured at various pressures of NO₂ and of a buffer gas, N₂ or Ar. Further, we searched reaction products and succeeded in observing the formation rates of FNO and CF₂O. The previously postulated product, NO, was not detected in the same time region, although a large amount of NO was observed in the final products by using an FTIR spectrometer. These experimental results suggest that the reaction of CF_3 with NO_2 produces FNO and CF₂O via a four-centered transition state. Such a transition state has been postulated for unimolecular decomposition of CH₃ONO¹⁷ and for rearrangements on CH₃NO₂ potential surfaces by MINDO/3¹⁸ and ab initio calculations.¹⁹

- (7) Laguna, G. A.; Baughcum, S. L. Chem. Phys. Lett. 1982, 88, 568.
 (8) Chu, J. O.; Wood, C. F.; Flynn, G. W. J. Chem. Phys. 1984, 81, 5533. (9) Wood, C. F.; O'Neill, J. A.; Flynn, G. W. Chem. Phys. Lett. 1984, 109,
- 317
- (10) Cox, R. A.; Burrows, J. P.; Coker, G. B. Int. J. Chem. Kinet. 1984, 16, 445
- (11) Cattell, C. F.; Cavanagh, J.; Cox, R. A.; Jenkin, M. E. J. Chem. Soc., Faraday Trans. 2 1986, 82, 1999
- (12) Kanamori, H.; Butler, J. E.; Kawaguchi, K.; Yamada, C.; Hirota, E.
- (12) Kanamori, 17, Botter, J. E., Kawageon, K., Yanada, C., Hubta, E. J. Mol. Spectrosc. 1985, 113, 262; J. Chem. Phys. 1985, 83, 611.
 (13) Kanamori, H.; Hirota, E. J. Chem. Phys. 1987, 86, 3901.
 (14) Kanamori, H.; Seki, K.; Hirota, E. J. Chem. Phys. 1987, 87, 73.
 (15) Sugawara, K.; Nakanaga, T.; Takeo, H.; Matsumura, C. Chem. Phys.
- Lett. 1987, 134, 347.
 - (16) Yamada, C.; Hirota, E. J. Chem. Phys. 1983, 78, 1703. (17) Batt, L.; Islam, T. S. A.; Scott, H. Int. J. Chem. Kinet. 1978, 10,
- 1195
- (18) Dewar, M. J. S.; Ritchie, J. P.; Alster, J. J. Org. Chem. 1985, 50, 1031
- (19) Mckee, M. L. J. Am. Chem. Soc. 1986, 108, 5784.

Batt, L. In The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives; Patai, S., Ed.; Wiley: New York, 1982; p 417. Batt, L.; Robinson, G. N. In The Chemistry of Amino, Nitroso and Nitro Com-pounds and Their Derivatives; Patai, S., Ed.; Wiley: New York, 1982; p 1035.
 Glänzer, K.; Troe, J. Helv. Chim. Acta 1972, 55, 298; Ber. Bunsen-Ges. Phys. Chem. 1974, 78, 182.
 Gesei, M. J., Deriver, J. D. Chill, D. Chill, Ch

⁽³⁾ Rossi, M. J.; Barker, J. R.; Golden, D. M. J. Chem. Phys. 1979, 71, 3722

⁽⁴⁾ Yamada, F.; Slagle, I. R.; Gutman, D. Chem. Phys. Lett. 1981, 83, 409.



Figure 1. Schematic diagram of the apparatus.

The NO is presumably produced by secondary reactions of FNO.

Experimental Section

The experimental apparatus, shown schematically in Figure 1, is similar to that described previously.^{15,20,21} Briefly, a selected molecule is decomposed in a cylindrical Pyrex cell by irradiation from a pulsed CO_2 laser (Lumonics TEA-820) to produce the desired transient species, and its time-resolved infrared spectrum is observed with a diode laser spectrometer (Spectra-Physics LS-3).

The operating wavenumber of the diode laser was tuned by varying its temperature. A Ge etalon and reference gases were used for the calibration of the operating wavenumber. The diode laser beam crossed the volume irradiated by the CO₂ laser. A monochromator (JASCO CT-25C) was placed in front of an HgCdTe detector to prevent emission, which was induced by the CO_2 laser irradiation, from entering the detector. The signal from the detector was amplified and fed into a transient memory/signal averager combination (Kawasaki Electronica TMR-10/TMC-700) which was triggered by the CO2 laser pulse. A microcomputer (Sord M223) was used for signal processing and scanning the wavenumber of the diode laser. The overall response time of this system was about 1 μ s.

In this investigation, the CF₃ radicals were produced by the IRMPD of CF₃I at the R(14) line of the 9.6- μ m band at repetition rates of 1-3 Hz. For uniform production of the radicals along the length of the cell, the laser beam was concentrated with a telescope consisting of two BaF₂ lenses (+30 and -10 cm focal lengths). Three diode lasers (Spectra-Physics, Fujitsu), which emitted in the ranges 1250-1390, 1630-1870, and 680-840 cm⁻¹, were mounted in the spectrometer to detect CF₃, NO, CF₂O, and FNO.

Mixtures containing CF₃I (PCR, >97%), NO₂ (Takachiho, >99.5%), and a buffer gas, Ar (Hitachi Sanso, >99.9995%) or N₂ (Nihon Sanso, 99.9995%), were flowed through the cell (50-cm length, 5-cm diameter, BaF₂ windows) at partial pressures of 0.006-0.3, 0.03-4, and 4-20 Torr, respectively. The pressure of the gas mixture was monitored with a capacitance manometer (MKS), and the flow rate was regulated with a mass flow controller (STEC).

Product analysis was carried out in a second cross-shaped Pyrex cell (15- and 12-cm lengths, 3-cm diameter, two BaF2 and two KBr windows). The sample, containing CF₃I, NO₂, and N₂, was irradiated with up to 100 CO_2 laser pulses, and products were searched with both an FTIR spectrometer (Nicolet 7199, 0.06 cm⁻¹ resolution) and the diode laser spectrometer.

Results

IRMPD of CF_3I and Detection of CF_3 . It has been well established by several workers²²⁻²⁶ that the IRMPD of CF₃I with



Figure 2. Time-resolved signal of CF3 obtained with following CO2 laser irradiation of a mixture containing CF₃I (0.01 Torr), NO₂ (0.054 Torr), and Ar (5 Torr) at 300 K. The diode laser was tuned to the $R_{21}(22)$ line of the ν_3 band of CF₃.



Figure 3. First-order plots (logarithm of absorbance, A, versus time) for the decay of CF_3 in the presence of increasing pressures of NO_2 : O, O; ●, 0.012; △, 0.024; ▲, 0.054; □, 0.12 Torr.

an unfocused TEA CO₂ laser produces only CF₃ radicals and I atoms, that is

$$CF_3I + nh\nu \rightarrow CF_3 + I$$
 (3)

so that CF₃I is an excellent source of CF₃ for kinetic studies.

When 0.1 Torr of CF₃I diluted with 20 Torr of Ar was irradiated with the CO_2 laser at a fluence of 1 J cm⁻², this mixture absorbed only 3% of the laser energy and subsequently 10% of CF₃I was decomposed. These results suggested the uniform production of the radicals along the length of the cell. The initial concentration of the radicals was estimated from the dissociation yield of CF₃I. Typical pressures of CF₃I used for the measurement of rate constants were 0.01 Torr; this corresponds to initial CF₃ concentrations of 3×10^{13} molecules cm⁻³. A buffer gas (Ar or N_2) was used both to deactivate the vibrationally excited states of CF₃ and to investigate its effect on the reaction rate.

We observed more than 30 transient absorption lines in the range 1262.79-1263.40 cm⁻¹, which were assigned to the transitions of ν_3 band of CF₃.¹⁶ No lines due to vibrationally excited states were observed. For the sensitive detection of CF₃, the diode laser was tuned to a relatively strong transition, that is, ${}^{r}R_{21}(22)$ of the ν_3 band at 1263.060 cm⁻¹.

⁽²⁰⁾ Nakanaga, T. Takeo, H.; Kondo, S.; Matsumura, C. Chem. Phys. Lett. 1985, 114, 88.

⁽²¹⁾ Sugawara, K.; Nakanaga, T.; Takeo, H.; Matsumura, C. Chem. Phys. Lett. 1986, 130, 560.

⁽²²⁾ Bittenson, S.; Houston, P. L. J. Chem. Phys. 1977, 67, 4819.

 ⁽²³⁾ Kynazev, I. N.; Kudriavtzev, Yu. A.; Kuzmina, N. P.; Letokhov, V.
 S.; Sarkisian, A. A. Appl. Phys. 1978, 17, 429.

⁽²⁴⁾ Bagratashvili, V. N.; Doljikov, V. S.; Letokhov, V. S.; Ryabov, E. A. In Laser-Induced Processes in Molecules; Kompa, K. L., Smith, S. D., Eds.; Springer-Verlag: Berlin, 1979; p 179. (25) Drouin, M.; Gauthier, M.; Piolin, R.; Hackett, P. A.; Willis, C. Chem.

Phys. Lett. 1978, 60, 16.

⁽²⁶⁾ Rossi, M.; Barker, J. R.; Golden, D. M. Chem. Phys. Lett. 1979, 65, 523





Figure 4. Plot of the first-order decay rate constant of CF_3 against the pressure of NO₂. The decay rate was measured in the presence of varying pressures of Ar: O, 20; \triangle , 10; \square , 5 Torr.

Rate Constant for the Reaction of CF_3 with NO_2 . In the presence of excess reactant, $[CF_3]_0 \ll [NO_2]_0$, pseudo-first-order kinetics are observed, and the bimolecular rate constant is obtained by using the expression

n ([CF₃]₀/[CF₃]_t) = ln (
$$A_0/A_t$$
) = $k't = k[NO_2]t$ (4)

Here subscripts 0 and t are used for values at times 0 and t, respectively, A is CF₃ line absorbance, k' is the decay rate, and k is the rate constant for the reaction of CF₃ with NO₂.

1

Figure 2 shows a typical time-resolved signal obtained following the CO_2 laser irradiation of a mixture containing CF_3I (0.01 Torr), NO₂ (0.054 Torr), and Ar (5 Torr) at 300 K. The initial spike is due to electric noise induced by the CO_2 laser. The decay curve is easily fit to a single exponential over at least 3 lifetimes, as seen in Figure 3 (solid triangles). This figure shows representative first-order decay plots in the presence of varying pressures of NO₂. In the absence of NO_2 , slight increase is observed in the time region 10-100 μ s, and it depends on Ar pressure. The slopes of the straight lines in Figure 3 decrease with increasing NO_2 pressure. In Figure 4, the decay rate constant, which is equal to the slope in magnitude though opposite in sign, is plotted against the pressure of NO₂. This figure consists of the data obtained in the presence of varying pressures of Ar. The fact that all of the data fit on a single line means that the rate constant is independent of the buffer pressure in the range 5-20 Torr. The biomolecular rate constant was then determined to be

$$k = (2.5 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (3 σ)

from averaging the values for all data plotted in Figure 4. The value of this rate constant implies that CF_3 reacts with NO_2 at near gas kinetic collision frequencies.

The slight increase of the CF_3 signal observed in the absence of NO_2 may be due to vibrational relaxation. But, as can be seen from the intercept of the line in Figure 4, its influence on the rate determination is negligibly small.

Detection of Reaction Products. As described in the Introduction, NO was thought to be the most probable product of the reaction of CX₃ with NO₂. Since it was of interest to measure the kinetic behavior of NO, we tuned the operating wavenumber of the diode laser to several rotation-vibration lines of the fundamental band of NO (J = 5.5, 9.5, 10.5, and 11.5). A signal was searched for in the time region 0-10 ms in mixtures containing CF₃I (0.01-0.3 Torr), NO₂ (0.1-4 Torr), and N₂ (10 Torr). Figure 5 shows typical time-resolved spectra in the range 1857.01–1857.40 cm⁻¹ obtained with the mixture containing CF_3I (0.1 Torr), NO₂ (2.3 Torr), and N₂ (10 Torr). The line positions of ${}^{2}\Pi_{1/2}P(5.5)$ transitions of ${}^{14}N^{16}O$ at 1857.268 and 1857.280 cm⁻¹ are indicated by arrows. As can be seen from this figure, there is not clear doublet of NO, but a weak line at the position of the NO transition. We could detect no signals due to the transitions of NO in other ranges 1873.50-1874.13 cm⁻¹ even though the signal was followed for 10 ms after the laser pulse. All attempts to observe the kinetic behavior of NO have failed. The upper limit of the NO concentration was then estimated to be 2×10^{13} molecules cm⁻³ from the absorbance of the weak line.



Figure 5. Typical time-resolved spectrum in the range 5-100 μ s obtained with a mixture containing CF₃I (0.1 Torr), NO₂ (2.3 Torr), and N₂ (10 Torr). The line positions of ²Π_{1/2}P(5.5) lines of ¹⁴N¹⁶O are indicated by arrows. The doublet lines of NO are not clearly seen. The absorption lines can be assigned to the transitions of the ν_1 band of FNO.



Figure 6. Time evolution of FNO obtained in the presence of (a) 10 Torr of N₂ and varying pressures of NO₂: O, 0.40; \triangle , 0.17; \square , 0.09 Torr; (b) 0.4 Torr of NO₂ and varying pressure of N₂: O, 20; \triangle , 10; \square , 4 Torr. The diode laser was tuned to the ${}^{0}R_{5}(17)$ line of the ν_{1} band of FNO. The absorbance, A, is normalized with that obtained at the completion of the reaction of CF₃ with NO₂, A_{∞} .

Since $[CF_3]_0$ is 3×10^{14} molecules cm⁻³ under this experimental condition, the yield of NO is less than 0.07, which suggests that formation of CF₃O and NO is not a major path of the reaction of CF₃ and NO₂ under the present conditions.

Figure 5 also shows several absorption lines due to other reaction products. The positions of these lines were close to those for the transitions of the ν_1 band of nitrosyl fluoride, FNO. In addition, several lines assignable to the transitions of the ν_2 band of FNO were observed in the ranges 780.33–780.71 and 788.33–788.64 cm⁻¹. Assignment of the line positions was carried out by comparison with those calculated by using the molecular constants of the ν_1 and ν_2 bands of FNO which were reported by Allegrini et al.²⁷ and Foster et al.,²⁸ respectively.

⁽²⁷⁾ Allegrini, M.; Johns, J. W. C.; McKellar, A. R. W. J. Mol. Spectrosc. 1978, 73, 168.

TABLE I: Comparison of the Absolute Rate Constants $(10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ for the Reactions of CH₃, CClF₂, and CF₃ with NO₂

reaction	method ^a	temp, K	rate const	ref
$CH_3 + NO_2$	ST/A	1100-1400	2.2	2
	IRMPD/MS	295	2.5 ± 0.5	4
$CCIF_7 + NO_7$	IRMPD/MS	295	0.96 ± 0.19	4
$CF_3 + NO_2$	IRMPD/MS	298	0.27 ± 0.05	3
	IRMPD'/DL	300	2.5 ± 0.3	this worl

^aST, shock tube; *A*, absorption of NO₂; IRMPD, infrared multiphoton dissociation; MS, mass spectrometry; DL, diode laser spectroscopy.

The appearance of FNO in the vibrational ground state was observed at various pressure of CF₃I (0.01-0.21 Torr), NO₂ (0.06-1.02 Torr), and N₂ (4-20 Torr). The diode laser was set to the ${}^{q}R_{5}(17)$ line of the ν_{1} band of FNO at 1857.324 cm⁻¹. Figure 6 shows the typical result, that the formation of FNO becomes faster with increasing the pressures of both NO₂ and N₂. In this figure, each time-dependent absorbance, A, is normalized with the absorbance attained at completion of the reaction, A_{∞} , to facilitate comparison of the rise times. Solid lines indicate the results calculated by using a kinetic model given in the Discussion. Besides FNO, several absorption lines of ν_4 band of CF₂O were observed in the same wavenumber range as that used for the detection of CF₃. Kinetic behavior of CF₂O was close to that of FNO, and the formation was the mirror image of the decay of CF₃ at high pressure with N₂.

When mixtures containing CF_3I , NO_2 , and N_2 were irradiated with several CO_2 laser pulses in the cross-shaped static cell, the gaseous products observed with the FTIR and the diode laser spectrometers were mostly CF_2O , NO, and FNO, accompanied by traces of C_2F_6 , CF_3NO_2 , and CF_4 . The yields of CF_2O and NO were 1.0 ± 0.1 . The signal due to FNO slowly decayed with a lifetime of several minutes. In the absence of NO_2 , only C_2F_6 was observed as the reaction product.

Discussion

Influence of Secondary Reaction on the Determination of k. The IRMPD of CF₃I produces I atoms, which may complicate the kinetic system and influence the measurement of k. The initial concentration of I atoms, [I]₀, is the same as $[CF_3]_0$ (~3 × 10¹³ molecules cm⁻³ at 0.01 Torr of CF₃I), and the concentrations of any reaction products do not exceed [CF₃]₀. Accordingly, the decay rate of CF₃ due to the secondary reaction can be estimated to be 3×10^3 s⁻¹ by assuming the biomolecular rate constant of the secondary reaction to be 1×10^{-10} cm³ molecule⁻¹ s⁻¹, which was close to the upper limit for the reaction of neutral species. The decay rate of 3×10^3 s⁻¹ is much less than those shown in Figure 4 by a factor of 10-110, indicating that the influence of I atoms and secondary reactions must be negligibly small. This is also supported by the experimental result that the rate constant obtained for the data in Figure 4 is independent of the initial stoichiometry, $[NO_2]_0/[CF_3]_0$, in the range 10-400.

Comparison with a Literature Value for k. All the results of determination of the absolute rate constants for the reactions of CH₃, CClF₂, and CF₃ with NO₂ are summarized in Table I. The only other measurement of k for CF₃ and NO₂ is the value of $(2.7 \pm 0.5) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ due to Rossi et al.,³ which is less than that obtained here by a factor of about 9. Their experiments involved flowing CF₃I and NO₂ through a Teflon-coated VLP Φ cell and measuring steady-state mass spectrometric signals of CF₃I, NO₂, and CF₂O with the CO₂ laser on/off. For interpretation of their data, a reaction mechanism including complicated wall reactions was presented:

$$CF_3I + nh\nu \rightarrow CF_3 + I$$
 (3)

$$CF_3 + NO_2 \rightarrow CF_3O + NO$$
 (5)

$$CF_3O \rightarrow CF_2O + F$$
 (6)

$$F + CF_3 I \to CF_3 + FI \tag{7}$$

$$CF_3 \rightarrow CF_2O$$
 (wall reaction) (8)

$$CF_3 \rightarrow \text{products other than } CF_2O \text{ (wall reaction)}$$
 (9)

$$F \rightarrow \text{products (wall reaction)}$$
 (10)

The value of k was then determined following some assumptions: (a) reaction 6 was very fast and the escape of CF₃O was neglected, (b) a chain reaction involving F atoms did not influence the yield of CF₂O, (c) CF₂O was also produced via the wall reaction of CF₃ with NO₂ that was dissolved in the Teflon coating (reaction 8), and (d) the rate of wall reaction of CF₃ not yielding CF₂O was equal to that obtained in other experiments for reactions of CF₃ with Br₂ and ClNO. Further, it is difficult to accurately measure the NO₂ concentration because of the known tendency of NO₂ to dissolve in Teflon, suggesting less reliability in the determination of k. In our experiments it is not necessary to take into account such wall reactions and fewer assumptions were required. Therefore the value determined here seems to be more accurate and reliable.

Mechanism for the Reaction of CF_3 with NO_2 . We tried to explain the fast formation of FNO and CF_2O by the following stepwise mechanism:

$$CF_3 + NO_2 \rightarrow CF_3O + NO$$
 (5)

$$CF_3O + NO \rightarrow CF_2O + FNO$$
 (11)

$$CF_3O \rightarrow CF_2O + F$$
 (6)

$$F + NO + N_2 \rightarrow FNO + N_2 \tag{12}$$

The rate equation for the system of reactions 5 and 11 was numerically solved by using Runge-Kutta-Gill method. In the calculation the rate constant of reaction 5 was fixed to be 2.5×10^{-11} cm³ molecule⁻¹ s⁻¹ and that of reaction 11 was adjusted to reproduce the time evolution of FNO. The best fit to the fastest formation in Figure 6b was obtained at the value of $(4 \pm 2) \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹, which cannot be accepted as the rate constant for the reaction of neutral species. Moreover, the above stepwise mechanism does not account for the experimental result that the formation rate constant of the products is independent of [CF₃]₀. The result can be interpreted if the reaction of CF₃ with NO₂ directly produces FNO and CF₂O under the pseudo-first-order condition [CF₃]₀ << [NO₂]₀. Accordingly, it is considered that the direct mechanism is preferable to the stepwise mechanism.

For the explanation of the experimental results that the formation rate of FNO and CF_2O in their vibrational ground states increased with increasing the pressures of NO_2 and N_2 , the following mechanism was considered:

$$CF_3 + NO_2 - F_2 C + O - FNO^* \bullet CF_2 O^*$$
(13)

$$FNO^* + N_2 \rightarrow FNO + N_2 \tag{14}$$

$$CF_2O^* + N_2 \rightarrow CF_2O + N_2 \tag{15}$$

Here an asterisk indicates excited molecules. The reaction of CF_3 with NO_2 produces FNO* and CF_2O^* via the four-centered transition state. Vibrational relaxation was caused by collision with the buffer N_2 . The rate equation for this reaction system has a solution of the form

$$A/A_{\infty} = \{k_1[NO_2]\{1 - \exp(-k_{II}[N_2]t)\} - k_{II}[N_2] \times \{1 - \exp(-k_1[NO_2]t)\}\}/\{k_1[NO_2] - k_{II}[N_2]\}$$
(16)

where A is the time-dependent absorbance of the line of FNO or CF₂O, $k_{\rm I}$ is the rate constant for reaction 13, and $k_{\rm II}$ is the rate constant for relaxation 14 or 15. The value of $k_{\rm II}$ was determined to be 4×10^{-13} and 1.2×10^{-13} cm³ molecule⁻¹ s⁻¹ for relaxations 14 and 15, respectively, by fitting nine experiments to eq 16 for each product. Here $k_{\rm I}$ was fixed to the value of 2.5 × 10⁻¹¹ cm³

molecule⁻¹ s⁻¹ determined as k in this study. Typical fitting curves drawn in Figure 6 indicate excellent agreement, supporting this reaction mechanism quantitatively.

The formation of the final products, NO (major), C_2F_6 , CF_3NO_2 , and CF_4 (traces), and the slow decay of FNO can be explained by the following reaction:

$$CF_3 + CF_3 \rightarrow C_2F_6 \tag{17}$$

$$CF_3 + NO_2 + N_2 \rightarrow CF_3NO_2 + N_2$$
(18)

$$CF_3 + FNO \rightarrow CF_4 + NO$$
 (19)

$$FNO \rightarrow NO \text{ (wall reaction)}$$
 (20)

The very low yield of CF₃NO₂ is consistent with the failure to observe the dependence of the decay of CF_3 on buffer gas pressure.

The pressure of FNO in the static cell increases with the laser irradiation, and therefore CF_4 may be produced by reaction 19. Most of FNO is presumably converted into NO via wall reactions.

Conclusion

In this paper, we have presented kinetics and mechanism for the reaction of CF_3 with NO_2 . The time-resolved spectrum of CF₃ was observed by the diode laser spectroscopy. From the NO₂ pressure dependence of the decay rate of CF₃, the room temperature rate constant was determined to be $(2.5 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (3σ). Time-resolved spectra of FNO and CF₂O, appearing as the CF₃ decayed, were observed and interpreted in terms of the reaction path involving a four-centered transition state.

Registry No. CF₃, 2264-21-3; NO₂, 10102-44-0; CF₃I, 2314-97-8; FNO, 7789-25-5; CF₂O, 353-50-4; NO, 10102-43-9.

Second-Order Combination Reactions of Phenoxyl Radicals¹

Mingyu Ye and Robert H. Schuler*

Department of Chemistry and Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556 (Received: April 18, 1988; In Final Form: August 4, 1988)

Phenoxyl radicals, when produced pulse radiolytically at concentrations > 10^{-4} M, combine in second-order processes to give 2,2'-, 2,4'-, and 4,4'-dihydroxybiphenyl as the predominant products. The ratios of these products observed under a variety of conditions, 0.73:1.73:1.00, indicate that radical combination at the ortho and para positions of the ring occurs statistically with, however, reaction at the para site favored by a factor of 2.4 over that at the ortho site. This ratio is considerably greater than the ratio of 1.55 of the unpaired spin populations at the two sites as indicated by ESR data. There is essentially no reaction at the meta position where the unpaired spin population is negative. Approximately 10% of the radicals couple at oxygen to yield 2- and 4-phenoxyphenol. The yields of these two products are, however, considerably lower than might be expected from the unpaired spin population of 0.2 on the oxygen atom of phenoxyl. It is clear that factors in addition to the unpaired spin population are important in controlling the combination processes. Under optimum conditions these five products account for \sim 90% of the phenoxyl radicals initially produced so that electronic disproportionation or coupling to form diphenyl peroxide is relatively unimportant. Multiple-pulse experiments show that after products build up to concentrations comparable to that of the phenoxyl radical, secondary electron-transfer reactions lead to more complex products. In studies with γ -rays at low-dose rates phenoxyl radicals predominantly react with the products so that the yields of simple combination products are very low.

Introduction

 $\ensuremath{\mathsf{ESR}}$ studies^{2,3} show that the unpaired spin population in phenoxyl radical is highly delocalized with an appreciable fraction present on the 2- and 4-positions of the aromatic ring. It is of considerable interest to see how this delocalization is reflected in the reactions of these radicals. The qualitative observation that chemical oxidation of phenol leads to biphenyl hydroxylated at the 2- and 4-positions has been taken to indicate the involvement of a radical mechanism.⁴ Time-resolved optical,⁵ ESR,² and resonance Raman spectroscopic⁶ studies show that phenoxyl radicals can be generated quantitatively under well-controlled conditions by radiation chemical methods. The Raman experiments⁶ show that in basic solutions at phenoxyl concentrations of $\sim 10^{-4}$ M the radicals predominantly decay in second-order processes having a rate constant (2k) of $2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1.6}$ A similar value $(2.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$ has been determined pulse radiolytically in acidic solutions by absorption methods at radical concentrations more than 1 order of magnitude lower.⁷ In the present study we take advantage of pulse radiolytic approaches to explore quantitatively the effects of unpaired spin delocalization by examining the products of the second-order combination reactions of phenoxyl radicals produced at relatively high concentrations. Because these radicals can be generated under wellcontrolled conditions in pulse radiolytic experiments, one can, to a large extent, avoid secondary processes that otherwise complicate interpretation of the observed product distribution in terms of site reactivity.

Experimental Section

Pulse irradiations were carried out with \sim 30-ns pulses of 2-MeV electrons from a Febetron 705 accelerator. Irradiations were 10-50 cm from the accelerator window at doses of $(2-10) \times 10^{18}$ eV/g per pulse. The Super-Fricke dosimeter (O₂-saturated 10 mM ferrous sulfate) was used for dosimetry. Irradiations were in a 2-cm-diameter flat cell 0.2-0.4 cm thick so that dose deposition was reasonably uniform within the cell volume. At the doses used, initial radical concentrations were 0.2-1 mM. A ⁶⁰Co γ -source, having a dose rate of 2.8 \times 10¹⁶ eV g⁻¹ s⁻¹, was used for continuous irradiations. Solutions of 10^{-3} – 10^{-2} M phenol at pH \sim 11 were purged of oxygen and saturated with N₂O to

⁽¹⁾ The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-3081 from the Notre Dame Radiation Laboratory.

 ⁽²⁾ Stone, T. J.; Waters, W. A. J. Chem. Soc. 1964, 213, 4302.
 (3) Neta, P.; Fessenden, R. W. J. Phys. Chem. 1974, 78, 523.

⁽⁴⁾ Joschek, H.-I.; Miller, S. I. J. Am. Chem. Soc. 1966, 88, 3273. Nonhebell, D. C.; Walton, J. C. Free-Radical Chemistry; Cambridge Univ-

ersity Press: Cambridge, 1974; p 327. (5) Ye, M.; Madden, K. P.; Fessenden, R. W.; Schuler, R. H. J. Phys. Chem. 1986, 90, 5397.

⁽⁶⁾ Tripathi, G. N. R.; Schuler, R. H. J. Chem. Phys. 1984, 81, 113.

⁽⁷⁾ Tripathi, G. N. R.; Schuler, R. H. Chem. Phys. Lett. 1982, 88, 253.