J. Phys. Chem. 1992, 96, 6115–6117

gineering, founding members E. I. du Pont de Nemours and Co., Eastman Kodak Co., and Minnesota Mining and Manufacturing Inc. Additional support was provided by the Irvine Foundation, the Chevron Corp., a Dreyfus Newly Appointed Faculty Award, an AT&T Special Purpose Grant, and a Department of Education Graduate Fellowship (C.M.N.).

References and Notes

(1) Farman, J. C.; Gardiner, B. G.; Shankin, J. D. *Nature* **1985**, *315*, 207.

(2) Anderson, J. G.; Toohey, D. W.; Brune, W. H. *Science* **1991**, *251*, 39.

(3) Solomon, S.; Garcia, R. R.; Rowland, F. S.; Wuebbles, D. J. *Nature* **1986**, *321*, 755.

(4) Atkinson, R.; Tuazon, E. C.; MacLeod, H.; Aschmann, S. M.; Winer, A. M. *Geophys. Res. Lett.* **1986**, *13*, 117.

(5) Atkinson, R.; Aschmann, S. M.; Tuazon, E. C.; Goodman, M. A.; Winer, A. M. *J. Atmos. Chem.* **1987**, *5*, 83.

(6) Molina, L. T.; Molina, M. J.; Stachnik, R. A.; Tom, R. D. *J. Phys. Chem.* **1985**, *89*, 3779.

(7) Molina, L. T.; Molina, M. J. *J. Phys. Chem.* **1987**, *91*, 433.

(8) Solomon, S. *Rev. Geophys.* **1988**, *26*, 131.

(9) McElroy, M. B.; Salawitch, R. J. *Science* **1989**, *243*, 763.

(10) Leu, M. T. *Geophys. Res. Lett.* **1988**, *15*, 17.

(11) Tolbert, M. A.; Rossi, M. J.; Golden, D. M. *Geophys. Res. Lett.* **1988**, *15*, 847.

(12) Tolbert, M. A.; Rossi, M. J.; Malhotra, P.; Golden, D. M. *Science* **1987**, *238*, 1258.

(13) Rossi, M. J.; Malhotra, R.; Golden, D. M. *Geophys. Res. Lett.* **1987**, *14*, 127.

(14) Leu, M. T.; Moore, S. B.; Keyser, L. F. *J. Phys. Chem.* **1991**, *95*, 7763.

(15) Wofsy, S. C.; Molina, M. J.; Salawitch, R. J.; Fox, L. E.; McElroy, M. B. *J. Geophys. Res.* **1988**, *93*, 2442.

(16) Yang, X.; Zhang, X.; Castleman, A. W., Jr. *Int. J. Mass Spectrom. Ion. Processes* **1991**, *109*, 339. Yang, X.; Castleman, A. W., Jr. *J. Geophys. Res.* **1991**, *96*, 2573.

(17) Bohringer, H.; Fahey, D. W.; Fehsenfeld, F. C.; Ferguson, E. E. *Planet Space Sci.* **1983**, *31*, 185.

(18) Schmeisser, M. *Inorg. Synth.* **1967**, *9*, 127.

(19) Levine, R. D.; Bernstein, R. B. *Molecular Reaction Dynamics and Chemical Reactivity*; Oxford Press: New York, 1987; pp 37–38.

(20) Lau, Y. K.; Ikuta, S.; Kebarle, P. *J. Am. Chem. Soc.* **1982**, *104*, 1462.

(21) *CRC Handbook of Chemistry and Physics*; Lide, D. R., Ed.; CRC Press: Boston, 1990; pp 6–11.

(22) Lee, T. J.; Rice, J. E. *J. Phys. Chem.* **1992**, *96*, 650.

(23) Schultz, R. H.; Armentrout, P. B. *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 29.

(24) Cacace, F.; Attina, M.; de Petris, G.; Speranza, M. *J. Am. Chem. Soc.* **1990**, *112*, 1014.

(25) Molina, M. J.; Tso, T. L.; Molina, L. T.; Wang, F. C. Y. *Science* **1987**, *238*, 1253.

(26) Abbatt, J. P. D.; Molina, M. J. *J. Geophys. Res.* **1992**, *19*, 461.

(27) Prather, M. J. *Nature* **1992**, *355*, 534.

(28) Abbatt, J. P. D.; Beyer, K. D.; Fucaloro, A. F.; McMahon, J. R.; Woolridge, P. J.; Zhang, R.; Molina, M. J. *J. Geophys. Res.*, in press.

FTIR Spectroscopic Study of the Reaction of CF_3O with NO: Evidence for $CF_3O + NO \rightarrow CF_2O + FNO$

J. Chen, T. Zhu, and H. Niki*

Centre for Atmospheric Chemistry and Department of Chemistry, York University, 4700 Keele Street, North York, Ontario, Canada M3J 1P3 *(Received: April 2, 1992)*

A long-path FTIR-based product study was made in the visible ($\lambda > 400$ nm) photolysis of mixtures containing CF_3NO and NO in the millitorr range in 700 Torr of O_2–N_2 diluent at 298 ± 1 K. In the early stage of the photolysis CF_2O, FNO, and NO_2 were detected as products in stoichiometric amounts of the CF_3NO reacted. The additions of CH_4 at sufficiently high concentrations to scavenge F atoms, if present, did not alter the product distribution. These results are consistent with the occurrence of the following elementary reactions: $CF_3NO + h\nu$ ($\lambda > 400$ nm) $\rightarrow CF_3 + NO$ (1); $CF_3 + O_2$ (+ M) $\rightarrow CF_3OO$ (+ M) (2); $CF_3OO + NO \rightarrow CF_3O + NO_2$ (3); and $CF_3O + NO \rightarrow CF_2O + FNO$ (4).

Introduction

The oxidation of the trifluoromethoxy (CF_3O) radical is one of the major uncertainties in the mechanism of tropospheric degradation of hydrofluorocarbons (HFC) and hydrochlorofluorocarbons (HCFC).[1] This radical is formed in the degradation of CF_3 via CF_3OO.[1,2] According to current thermochemical knowledge, the elimination of an F atom either thermally or by reaction with O_2 appears too endothermic to be of major importance in the atmosphere,[3,4] i.e.

$$CF_3O + M \rightarrow CF_2O + F + M \quad (\Delta H = +96 \text{ kJ mol}^{-1}) \qquad (1)$$

$$CF_3O + O_2 \rightarrow CF_2O + FO_2 \quad (\Delta H = +42 \text{ kJ mol}^{-1}) \qquad (2)$$

Thus, although no quantitative kinetic and mechanistic data seem to be available at present, its reactions with other reactive species such as NO_x, O_3, or HOO are likely to be operative in the atmosphere. Presented here are the results from an FTIR-based product study on the $CF_3O + NO$ reaction.

There are two thermochemically feasible channels for the $CF_3O + NO$ reaction. Namely, analogously to the mechanism known for the RO (R = alkyl) radicals,[5,6] reaction 3 leading to the

$$CF_3O + NO\ (+\ M) \rightarrow CF_3ONO\ (+\ M) \qquad (3)$$

$$CF_3O + NO \rightarrow CF_2O + FNO \qquad (4)$$

formation of CF_3ONO is to be expected. The other reaction (eq 4) has been estimated to be exothermic by 142 kJ mol^{-1}.[3,4] Francisco et al. recently reported the detection of FNO attributable to reaction 4 in the multiphoton infrared dissociation of CF_3OOCF_3 to CF_3O radicals in the presence of NO.[7] In the present study, the visible ($\lambda > 400$ nm) photolysis of CF_3NO was used as a convenient source for the CF_3 radicals. Namely, CF_3NO is sufficiently stable in the dark but readily photodissociates to CF_3 and NO upon irradiation in the visible (500–750 nm) region.[8] Also, the use of a visible photolytic source greatly minimized the possible mechanistic complications arising from the secondary photochemical reactions of the expected products.

Experimental Section

The long-path FTIR/photochemical reactor facility has been described in detail elsewhere.[5,6] In brief, the main IR cell/photochemical reactor was a Pyrex glass cylinder (2 m long; 30-cm diameter; 180-m path length) surrounded by 26 visible fluorescent lamps (GE F40CW, $\lambda > 400$ nm). IR spectra in the 500–3700-cm^{-1} range were recorded typically at $^1/_{16}$ cm^{-1} resolution with a Ge-coated KBr beam splitter and a liquid He cooled Cu–Ge detector.

CF_3NO (>95%, PCR) was purified by liquid N_2 trap-to-trap distillation to remove its major impurity, CF_3NO_2. Trace amounts of SiF_4 were also observed during the slow decay of CF_3NO stored in a glass bulb, but when highly diluted in N_2, freshly purified CF_3NO was stable up to 1 week. The reactant mixtures used for

0022-3654/92/2096-6115$03.00/0

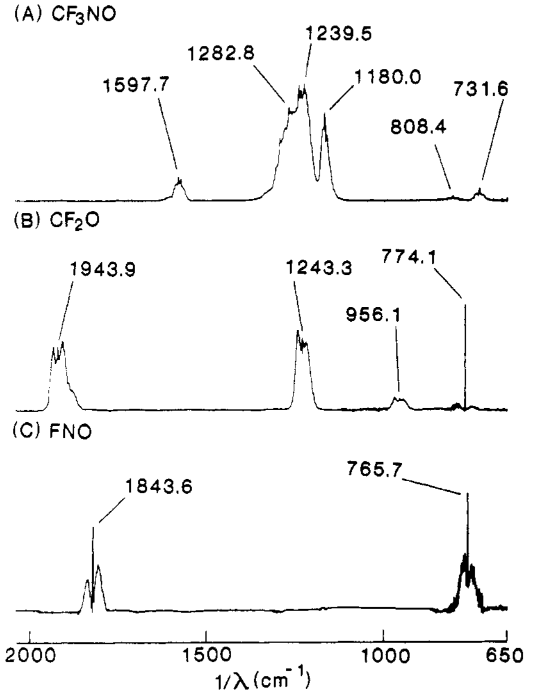

Figure 1. Absorbance spectra of CF$_3$NO, CF$_2$O, and FNO.

the photochemical experiment contained CF$_3$NO (<15 ppm; 1 ppm = 0.76 mTorr) and NO (<5 ppm) in 700 Torr of air or in a O$_2$ (1–5 Torr)–N$_2$ (700 Torr) mixture. The product spectra were typically recorded every minute during 3 min irradiation and 5 min aging in the dark.

The concentrations of the reactants and products were determined using the library of standard reference spectra recorded in this laboratory. To illustrate, the absorbance spectra of CF$_3$NO, CF$_2$O, and FNO are shown in Figure 1. CF$_3$NO had the absorptivities of 9.9 (±0.4) × 10^{-4} and 3.4 (±0.2) × 10^{-4} ppm^{-1} m^{-1} (base 10) for the Q-branch maxima at 1597.7 cm^{-1} (N–O stretch) and at 1180 cm^{-1} (C–F sym stretch), respectively. CF$_2$O was quantitatively produced in situ in the photolysis of mixtures containing known concentrations of HCClF$_2$ and Cl$_2$ in 700 Torr of air.[6] The observed band frequencies for the CF$_2$O spectrum shown in Figure 1 are in agreement with those of previous studies.[9] The peaks at 1943.9, 1243.3, 956, and 774.1 cm^{-1} correspond to the C═O stretch, CF$_2$ asym and sym stretch, and CF$_2$O out of plane, respectively. The absorptivities thus determined were 1.6 (±0.1) × 10^{-3} and 1.9 (±0.1) × 10^{-3} ppm^{-1} m^{-1} for the Q branch maxima at 1943.9 cm^{-1} (C═O stretch) and at 1243.3 cm^{-1} (C–F asym stretch), respectively. A quantitative absorbance spectrum of FNO was derived in the present experiment from the product spectra recorded in the photolysis of CF$_3$NO–NO mixtures in air. Namely, in the early stage of the photolysis of such mixtures, FNO and NO$_2$ were the only nitrogen-containing products detected, and the concentration of FNO could be determined based on the nitrogen balance. The two peaks at 1843.6 and 765.7 cm^{-1} have been previously assigned to the N–O stretch and NF stretch.[10] The absorptivity determined for the Q branch maximum at 1843.6 cm^{-1} (N–O stretch) was 2.7 (±0.3) × 10^{-3} ppm^{-1} m^{-1}.

Results and Discussion

After 3 min of the visible irradiation, approximately 5% of the reactant CF$_3$NO was consumed, and the product yields could be measured quantitatively. The absorbance spectra recorded in a typical run are illustrated in Figure 2. For clarity, only the most conspicuous portion of the spectra in the 650–2100-cm^{-1} region is displayed in this figure. Parts A and B of Figure 2 correspond to the spectra recorded before and after 3-min irradiation, and Figure 2C, is the difference spectrum, i.e., (B) − (A), with the absorbance scale expanded by a factor of 8. All the bands observed in these spectral data could be assigned to those belonging to the reactants and the products CF$_2$O, FNO, and NO$_2$. Values in parentheses in Figure 2C are concentrations in ppm. In this figure the consumption of the CF$_3$NO is seen to have led to the formation of stoichiometric amounts of CF$_2$O and NO$_2$. On the other hand, the observed yield of FNO was less than unity, but it was noted that the FNO decayed rapidly (τ < 5 min) in the dark with concomitant increase in NO concentration. The product yields have been determined as a function of the conversion of CF$_3$NO. The results of three runs were combined and are plotted in Figure 3. Nearly stoichiometric yields of CF$_2$O, FNO, and NO$_2$ are seen in this figure in the early stage of the photolysis. Values of the ratios Δ[CF$_2$O]/Δ[CF$_3$NO], Δ[NO$_2$]/Δ[CF$_3$NO], and Δ[NO]/Δ[FNO] were determined, based on six runs, to be 0.98 (±0.05), 1.08 (±0.06), and 1.12 (±0.09), respectively, where the

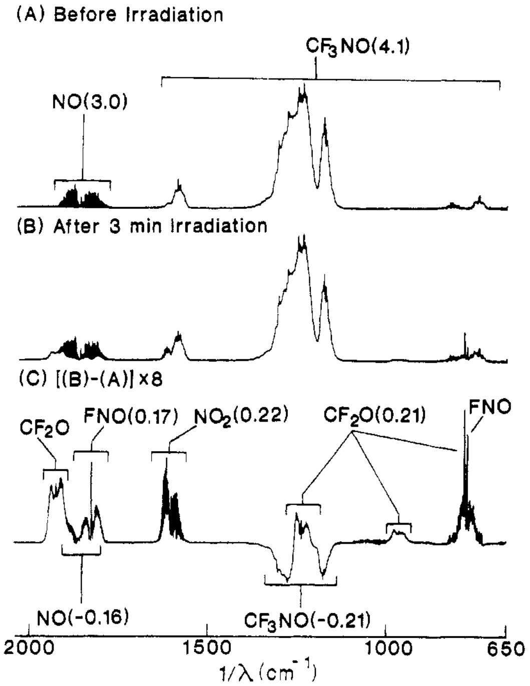

Figure 2. Spectral data in the frequency region 650–2000 cm^{-1} obtained from the photolysis of a mixture containing 4 ppm of CF$_3$NO and 3 ppm of NO in 700 Torr of air. The spectra were recorded (A) before irradiation, (B) after 3-min visible irradiation, and (C) difference spectrum = (B) − (A) scale expanded by 8 times. Values in parentheses are concentrations in ppm.

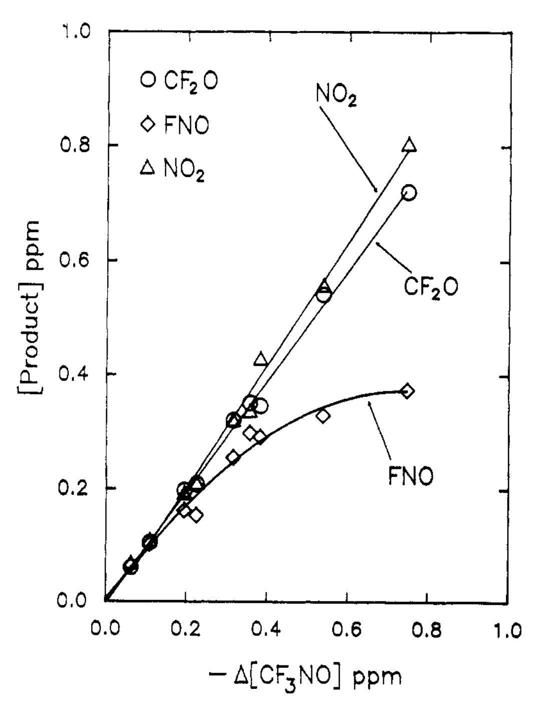

Figure 3. Product yields plotted as a function of the conversion of CF$_3$NO.

indicated uncertainties were 1 standard deviation.

The above observed results are consistent with the occurrence of the following series of elementary reactions. The only channel observed for the reaction between CF_3O and NO was reaction 4 rather than reaction 3:

$$CF_3NO + h\nu\ (\lambda > 400\ \text{nm}) \rightarrow CF_3 + NO \quad (5)$$

$$CF_3 + O_2\ (+ M) \rightarrow CF_3OO\ (+ M) \quad (6)$$

$$CF_3OO + NO \rightarrow CF_3O + NO_2 \quad (7)$$

$$CF_3O + NO \rightarrow CF_2O + FNO \quad (4)$$

Literature values of the rate constants, for reactions 6 and 7, are 1.9×10^{-29} cm^6 $molecule^{-2}$ s^{-1} and 1.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, at 298 K, respectively.[11,12] It is interesting to note that Sugawara et al.[18] have detected CF_2O and FNO in the reaction of CF_3 + NO_2. These authors have proposed a four-center decomposition of the intermediate CF_3ONO^* to yield CF_2O and FNO. In the present study, attempts to detect IR signals attributable to CF_3ONO were not successful. Apparently, this compound has never been observed previously. However, in comparison with the infrared spectrum of CX_3ONO type molecules such as CH_3ONO, the vibrational modes associated with the N–O stretch and C–O stretch of CF_3ONO should be located in the frequency regions around 1700 and 1000 cm^{-1}, respectively.[13] In addition, on the basis of the IR band of the CF_3-group-containing molecules such as CF_3NO,[14] the vibrational bands for C–F stretch should occur in the frequency region 1100–1300 cm^{-1}. No IR bands attributable to CF_3ONO were observed above the detection limit of 0.02 ppm which was estimated based on the absorbance of CH_3ONO. This observation suggests that CF_3ONO, if formed as the sole product of the CF_3O + NO reaction, has a dissociative lifetime of 10 s. Thus, it is highly unlikely that CF_3ONO is an important product of reaction 4 in the atmosphere.

The occurrence of another series of reactions, i.e., reaction 2 followed by reaction 8, 9, or 10, cannot be ruled out a priori

$$FOO\ (+ M) \rightleftarrows F + O_2\ (+ M) \quad (8)$$

$$F + NO\ (+ M) \rightarrow FNO\ (+ M) \quad (9)$$

$$FOO + NO \rightarrow FNO + O_2 \quad (10)$$

because of the presence of high concentration of O_2 in the above experiment. The equilibrium constant for reaction 8 at 300 K has been reported as 0.21 Torr by Pagsberg et al.[17] There is no literature information on the occurrence of reaction 10. These reactions can form the products identical to those of reactions 4–7. The possible contribution of these reactions to the present system was ruled out based on the results of two sets of experiments. One of these experiments was designed to test the effect of O_2 pressure on the product distribution. The use of O_2 (1 Torr) + N_2 (700 Torr) and O_2 (5 Torr) + N_2 (700 Torr) as the diluents exhibited no observable difference from those carried out in 700 Torr of air. The calculated ratios [F]/[FOO] are 21%, 3%, and 0.15% at 1, 5, and 140 Torr of O_2, respectively. Thus, if the fate of F and FOO is governed solely by reactions 9 and 10, the above change in the ratio [F]/[FOO] would not have altered the product distribution. In the second experiment, attempts were made to scavenge F atoms, if present. Namely, if F atoms were produced from reaction 8, they could be scavenged by adding CH_4 to the reaction mixture:

$$CH_4 + F \rightarrow CH_3 + HF \quad (11)$$

The rate constants of reactions 9 and 11, at 298 K, have been reported as 1.3×10^{-12} and 8×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively.[15,16] The addition of up to 1000 ppm of CH_4 to the system neither altered the product distribution not yielded an expected product CH_2O (i.e., $CH_3 + O_2 + (M) \rightarrow CH_3OO + (M)$, $CH_3OO + NO \rightarrow CH_3O + NO_2$, $CH_3O + O_2 \rightarrow CH_2O + HOO$) above the detection limit of 0.005 ppm. Thus, these results indicate that the reaction series 2, 8, 9, and 10, if it occurred, would account for at most 10% of the decay of CF_3O in the above experiment and that the CF_2O and FNO observed were formed predominantly via reaction 4.

Acknowledgment. We thank NSERC and AFEAS for financial support and Dr. J. Francisco and reviewers for their helpful discussion.

References and Notes

(1) Atkinson, R.; Cox, R.; Lesclaux, R.; Niki, H.; Zellner, R. An Assessment of Potential Degradation Products in the Gas-Phase Reactions of the Alternative Fluorocarbons in the Troposphere. World Meteorological Organization, Global Ozone Research and Monitoring Project; AFEAS Report 20, 1991; Vol. II.

(2) Dognon, A. M.; Caralp, F.; Lesclaux, R. *J. Chim. Phys. Phys. Chim. Biol.* **1982**, *82*, 349.

(3) Li, Z.; Francisco, J. S. *J. Am. Chem. Soc.* **1989**, *111*, 5660.

(4) Francisco, J. S.; Williams, I. H. *Int. J. Chem. Kinet.* **1988**, *20*, 455.

(5) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Mol. Struct.* **1980**, *59*, 1.

(6) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *Chem. Phys. Lett.* **1979**, *61*, 100.

(7) Li, Z.; Francisco, J. S. *Chem. Phys. Lett.* **1991**, *186*, 336.

(8) Mason, J. *J. Chem. Soc.* **1963**, 4537.

(9) Nielsen, A. H.; Burke, T. G.; Woltz, P. J. H.; Jones, E. A. *J. Chem. Phys.* **1952**, *20*, 596.

(10) Jones, L. H.; Asprey, L. B.; Ryan, R. R. *J. Chem. Phys.* **1967**, *47*, 3371.

(11) Caralp, F.; Lesclaux, R.; Dognon, A. M. *Chem. Phys. Lett.* **1986**, *129*, 433.

(12) Felder, P.; Ha, T. K.; Dwivedi, A. M.; Gunthard, H. H. *Spectrochim. Acta* **1981**, *37A*, 337.

(13) Demore, W. B.; Sander, S. P.; Hampson, R. F.; Kurylo, M. J.; Golden, D. M.; Howard, C. J.; Ravishankara, A. R.; Molina, M. J. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, NASA Report, JPL Publication 90-1, 1990.

(14) Demuth, R.; Burger, G.; Paweker, G.; Willer, H. *Spectrochim. Acta* **1978**, *34A*, 113.

(15) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F.; Kerr, J. A.; Troe, J. *J. Phys. Chem. Ref. Data* **1989**, *18*, 881.

(16) Demore, W. B.; Sander, S. P.; Hampson, R. F.; Kurylo, M. J.; Golden, D. M.; Howard, C. J.; Ravishankara, A. R.; Molina, M. J. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, NASA Report, JPL Publication, 1987; p 1.

(17) Pagsberg, P.; Ratajczak, E.; Sillesen, A. *Chem. Phys. Lett.* **1987**, *141*, 88.

(18) Sugawara, K.; Nakanaga, T.; Takeo, H.; Matsumura, C. *J. Phys. Chem.* **1989**, *93*, 1894.