Atmospheric Chemistry at 4.2 K: A Matrix Isolation Study of the Reaction between CF₃O₂ Radicals and NO

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A novel pathway is proposed for the reaction between CF₃OO radicals and NO to give carbonyl fluoride and nitryl fluoride. It has been shown in a series of matrix isolation experiments that unfiltered medium-pressure mercury lamp photolysis (λ > 265 nm) of trifluoronitrosomethane in 5% O₂-doped argon matrices at 4.2 K gives rise to the twin production of CF₂O and FNO₂ from a common intermediate. Although isotopic labeling experiments show that CF₃ONO₂ is produced, the observed chemistry can also be explained in terms of the decomposition of CF₃OONO. The overall reaction discussed in this work is exothermic and therefore contrasts with all other mechanisms hitherto suggested for the oxidation by molecular oxygen of ${}^{\bullet}CF_3$ radicals to CF_2O in the atmosphere.

Introduction

The fate of free radicals and atoms produced on photolysis of halogenated methanes has been the subject of many experimental studies over the past decade.¹⁻⁷ However, our understanding of the mechanism by which the halocarbon radicals are oxidized to carbonyl halide end products in the atmosphere is incomplete and contrasts with the well-documented gas-phase chemistry of atomic halogen species.⁸ Several laboratory investigations,^{6,7,9,10} have probed kinetic and mechanistic details for the oxidation by molecular oxygen of the trifluoromethyl radical, •CF₃, even though it is of less atmospheric significance than chlorofluoromethane radicals such as 'CF₂Cl. A pioneering study by Francis and Hazeldine¹¹ examined the gas-phase photooxidation of trifluoromethane, trifluorobromomethane, and trifluoroiodomethane. In each case, the primary product was carbonyl fluoride, CF_2O . These initial experimental observations were subsequently confirmed by Heicklen,¹² who suggested two mechanisms capable of explaining the results. The first proposal centers on a direct transformation of •CF₃ radicals:

$${}^{\bullet}CF_3 + O_2 \rightarrow CF_2O + OF (1)$$

The second postulated mechanism involves the intermediacy of peroxy- and oxyfluoromethyl radicals:

$$^{\bullet}\mathrm{CF}_{3} + \mathrm{O}_{2} \xrightarrow{\mathrm{M}} \mathrm{CF}_{3} \dot{\mathrm{O}}_{2}$$
 (2)

$$CF_3\dot{O}_2 + CF_3\dot{O}_2 \rightarrow CF_3\dot{O} + CF_3\dot{O} + O_2$$
 (3)

$$CF_3\dot{O} + CF_3\dot{O} \rightarrow CF_2O + CF_2O + F_2$$
 (4)

Both of these mechanisms, (1) and (2)-(4), are consistent with two recently measured quantum yield determinations for CF_2O production in which $\Phi_{COF_2}^{1843} = 1.02 \pm 0.10$ and $\Phi_{CF_2O}^{253.7} = 1.05 \pm 0.11$ for the photooxidations of CF₃Br¹³ and CF₃I,⁵ respectively. However, the two schemes above are subject to kinetic and thermochemical criticism. Process 1 appears to be of negligible importance in view of the mass spectrometry experiments by Ryan and Plumb,⁶ who have studied the reaction between °CF₃ radicals and molecular oxygen. It was shown that step 2 is an exclusive pathway and proceeds with a rate coefficient, k_2^{295} , of 8×10^{-12} cm³ molecule⁻¹ s⁻¹ at 295 K. A very recent low-pressure study of the temperature dependence of reaction 2 using laser photolysis and time-resolved mass spectrometry gives $k_2 = (1.9 \pm 0.2) \times 10^{-29} (T/298)^{(-4.7\pm0.4)}$ cm⁶ molecule⁻² s⁻¹ when M = N₂.¹⁰ Furthermore, thermochemical calculations indicate that reactions 3 and 4 are both endothermic: the former by 38 kJ mol⁻¹ and the latter by 39 kJ mol^{-1,14}

The importance of reaction 2 in the oxidation of trifluoromethyl radicals has been confirmed by the kinetic studies of Vedeneev et al.,⁹ who concluded that CF_2O is formed as a result of secondary reactions of the CF_3O_2 radical. In the stratosphere, it is believed that the principal reaction of the $CF_3\dot{O}_2$ radical is with NO rather than NO_2 or O_3 .⁷

$$CF_3\dot{O}_2 + NO \rightarrow CF_3\dot{O} + NO_2$$
 (5)

Over the temperature range 230-430 K, the rate coefficient for reaction 5, k_5 , has been evaluated as follows:

 $k_5 = (1.45 \pm 0.2) \times 10^{-11} (T/298)^{-(1.2\pm0.2)}$

It was suggested that the high value for k_5 and its negative temperature dependence indicate that reaction between CF_3O_2 radicals and nitric oxide does not proceed via direct oxygen atom transfer but that a trifluoromethylperoxynitrite adduct, CF₃OONO, is formed.7

The aim of the present research is to investigate the oxidation of CF₃ radicals by oxygen in the presence of nitric oxide using the matrix isolation technique to trap participating intermediates. The model used for this purpose was based on the photolysis of CF₃NO in oxygen-doped argon matrices at 4.2 K; Fourier transform infrared techniques were used to monitor products.

Experimental Section

The experimental procedure has been described in detail previously¹⁵ and is only briefly recounted here. Experiments were carried out employing an Air Products Heliplex Model CS-308 closed-cycle cryogenic refrigeration system coupled to a Digilab

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Figure 1. Absorbance vs. photolysis time profile for production of CF₃O₂ (\times), "z" (\bullet), CF₂O and FNO₂ (\odot) during medium-pressure mercury lamp photolysis of CF₃NO in a 5% ¹⁶O₂-doped argon matrix at 4.2 K $(MR = 1:10\,000).$

FTS-20V Fourier transform infrared spectrometer. Gas-phase matrix mixtures of total pressure 250 Torr were made up in a blackened, 2-L Pyrex bulb on a mercury-free vacuum line fitted with greaseless taps. Guest-host matrix ratios (MR) were calculated from pressure measurements obtained with an MKS Instrument Inc. Baratron capacitance monometer (Model 310) and a Wallace-Tiernan precision dial manometer (Model FA 141). Typically, 250 pulses of matrix sample of ca. 10-cm³ volume were deposited onto a CsI window maintained at 4.2 K. Photolyses at $\lambda > 265$ nm were carried out with an Applied Photophysics 250-W medium-pressure mercury lamp fitted with a quartz window and a quartz focusing lens. FTIR spectra were recorded at 0.5-cm⁻¹ resolution, boxcar apodized, and computed from the coaddition of 1000 interferograms.

Argon (Messer Griesheim GmbH, 99.999% stated purity), ¹⁶O₂ (Matheson, 99.999% stated purity), and ¹⁸O₂ (75% molecular isotopic purity, Amersham International) were used without further purification. CF₃NO (Peninsular Chem. Research, 97.99% stated purity) was thoroughly degassed at 77 K via a repeated freeze-pump-thaw cycle to remove traces of fluorine, followed by condensation on a column of BDH type 4A molecular sieve at 77 K to eliminate traces of water vapor. No impurities were revealed by subsequent analyses using FTIR, UV-visible absorption (Pve-Unicam SP8-500), and mass spectrometry (Spectrum Scientific Dataquad 200 M).

Results

The FTIR spectrum of CF₃N¹⁶O in a 5% ¹⁶O₂-doped argon matrix (MR = 1:10000) at 4.2 K was recorded and compared with FTIR spectra taken of the matrix after photolysis with an unfiltered medium-pressure mercury lamp ($\lambda > 265$ nm). Evidence was thereby obtained for the production of a variety of new species, which could be identified by comparison with previous assignments in matrices. The results demonstrate the formation of [CF₃...NO] cage radicals, CF₃ \dot{O}_2 radicals, ³ CF₂O, ¹⁶ and FNO₂¹⁷ (nitryl fluoride). Other product absorption bands were observed which could not be assigned to known species of general formula $C_w F_x N_y O_z$ (w, x, y, z = 0-6), e.g., the $CF_3 O$ radical,^{5,18,19} NO₂,²⁰ FONO,¹⁷ or CF₃OONO₂ (trifluoromethylperoxynitrate).²¹

A more detailed study of the absorbance-time behavior of the photoproducts was carried out by recording FTIR spectra after each of several successive photolysis periods from 15 to 150 min. the absorbance of each product infrared absorption band was measured as a function of photolysis time and normalized relative

TABLE I: Vibrational Frequencies (cm ⁻¹) of Product Absorptions
Which Appear upon Unfiltered Medium-Pressure Mercury Lamp ($\lambda >$
265 nm) Photolysis of CF ₃ NO ^a

CF3 ¹⁶ O ¹⁶ O	CF3 ¹⁸ O ¹⁸ Ó	"z"	"z _i "
1304.7	1302.0	1735.5	1722.0
1263.7	1262.6	1345.2	1344.8
1174.3	1164.1	1327.1	1315.3
1092.6	1040.1	1306.9 ^b	1287.2°
695.5	679.4	1260.8	1259.9
		1249.5	1248.1
		1142.5	1130.7, 1127.8
		924.1	901.2
		785.2	772.9
		752.9	738.9
		519.0	514.2
CF ₃ ¹⁶ O	CF218O	FN ¹⁶ O ¹⁶ O	FN ¹⁶ O ¹⁸ O
1941.9	1905.3	1800.1	1785.0
1911.9	1876.3	1312.7	1280.1
1236.3	1235.4	811.0	799.2
968.9	953.2	733.8	731.9
772.2	767.8	559.8	558.6
623.6	608.2		
583.5	578.1		

 a 5% $^{16}O_{2}$ - and $^{18}O_{2}$ -doped argon matrices at 4.2 K; MR = 1:10000. ^bCombination of 785.2- and 519.0-cm⁻¹ absorptions. ^cCombination of 772.9- and 514.2-cm⁻¹ absorptions.

to its maximum value. For species exhibiting more than one band, a mean value of its normalized absorbance was plotted against photolysis time. The unassigned absorptions referred to above were attributed to the same precursor "z", by this means since the bands exhibited a common temporal behavior. Figure 1 summarizes the data obtained for the photoproducts of the $CF_3NO/^{16}O_2/Ar$ matrix experiment.

The same photolysis conditions were applied to a $CF_3N^{16}O/Ar$ matrix (MR = 1:10000) with a 5% $^{18}O_2$ doping. Infrared evidence for the following ¹⁸O-labeled products was obtained: CF₃¹⁸O₂, CF2¹⁸O, and FN¹⁶O¹⁸O. Isotopically shifted infrared absorptions were also obtained for certain bands attributed to "z", as will be discussed below. Figure 2 illustrates the product infrared absorption peaks in the 2000-1650- and 1400-500-cm⁻¹ regions of the FTIR spectrum resulting from the difference between the absorbance spectrum of the $CF_3N^{16}O/^{18}O_2/Ar$ sample obtained after 3.5 h photolysis (upward peaks) and that of the deposited sample recorded prior to photolysis (downward peaks). Prominent infrared absorption bands due to CF2¹⁶O, CF2¹⁸O, FN¹⁶O¹⁶O, and FN¹⁶O¹⁸O, together with relatively much weaker features due to CF₃¹⁶O¹⁶O and CF₃¹⁸O¹⁸O, radicals are clearly evident.

The absorption frequencies attributed to the intermediate "z" in the ¹⁶O₂-Ar matrix were observed at 1735.5, 1327.1, 1142.5, 924.1, 785.2, 752.9, and 519.0 cm⁻¹. In an ¹⁸O₂-Ar-doped matrix the features shifted to 1722.0, 1315.3, 1130.7, 1127.8, 901.2, 772.9, 738.9, and 514.2 cm $^{-1}$ ("zi"). These data are of particular relevance to the gas-phase kinetic study of the reaction between CF_3O_2 radicals and nitric oxide in which a trifluoromethylperoxynitrite adduct was referred to.7

Table I summarizes the peak positions and assignments of the product infrared absorption bands shown in Figure 2 together with the corresponding data from the $CF_3NO/{^{16}O_2}/Ar$ experiment.

Discussion

Primary and Secondary Photochemistry of CF₃NO in O₂-Doped Argon Matrices at 4.2 K. The primary photochemical step for CF₃NO is C-N bond cleavage to produce a 'CF₃ radical.

$$CF_{3}NO + h\nu \frac{(\lambda > 265 \text{ nm})}{O_{2}/Ar/4.2 \text{ K}} [^{\circ}CF_{3} \cdots NO]$$
(6)

An analysis of the infrared spectra of [*CF₃...X] proximity (cage) radicals, where X = NO, I, and Br, will be the subject of a separate report.

The secondary chemistry leading to CF₂O and FNO₂ end products can be interpreted with the aid of the time-dependent photolysis experiments. It is evident from Figure 1 in the initial

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Figure 2. FTIR spectra of the products which appear upon medium-pressure mercury lamp photolysis of CF₃NO in a 5% ¹⁸O₂-doped argon matrix at 4.2 K (MR = 1:10000). (¹⁸O₂ was 75% isotopically pure.) A = CF₂¹⁶O; B = CF₂¹⁸O; C = FN¹⁶O¹⁶O; D = FN¹⁸O¹⁶O; E = CF₃¹⁸O¹⁸O; Z = species "z"; Z⁻ = species "z".

linear portions of the absorbance-time profiles that the change in absorbance, dA/dt, of the photoproducts observed during the CF₃NO/¹⁶O₂/Ar experiment varies in the following order:

$$CF_3O_2 > "z" > CF_2O = FNO_2$$

Furthermore, the behavior of $CF_3\dot{O}_2$ exhibits a temporal profile characteristic of a steady-state species. Indeed, the observation in the present experiments of extremely weak infrared absorption features due to $CF_3\dot{O}_2$ is in stark contrast to the very prominent bands which are observed in a series of $CF_3I/O_2/Ar$ experiments and discussed elsewhere.⁵ These observations suggest that reaction between $CF_3\dot{O}_2$ and NO in an argon matrix cage proceeds with little or no activation energy and explains the formation of "z". The twin formation of carbonyl fluoride and nitryl fluoride from a common molecular precursor is implied from the measurement that the production rate of CF_2O is equal to that of FNO₂.

Clearly, identification of the key intermediate, "z", is required before a precise mechanism can be put forward. The relatively large number of absorption bands listed in Table I and assigned to the single species, "z", is indicative of a moderate-sized molecule for which there are two obvious candidates. The first is CF_3O-ONO and the second is CF_3ONO_2 . The observed secondary chemistry in a matrix could then be described by a number of reactions.

$$[^{\bullet}CF_{3} \cdots NO] + O_{2} \rightarrow [CF_{3}\dot{O}_{2} + NO]$$
(7)

CF300N0 (8a)

$$CF_{3}O_{2} + NO_{3} -$$
 [CF₃O + NO₂] (8b)

$$CF_2OONO$$
 (9a)

$$F_{3}OONO - - - - - - - - [CF_{3}O + NO_{2}] (9b)$$

$$[CF_2 O + NO_2] \longrightarrow CF_2 O + FNO_2$$
 (10a)

$$F_{3} \cup + NO_{2} \cup - - - - CF_{3}ONO_{2}$$
 (10b)

$$CF_3ONO_2 \rightarrow CF_2O + FNO_2$$
 (11)

The formation of CF_2O from the decomposition of CF_3O_2 radicals

$$CF_3\dot{O}_2 \xrightarrow{(\Delta H_r^\circ = 131 \text{ kJ mol}^{-1})} CF_2O + \dot{O}F$$
(12)

or by the "direct" route

$$\dot{C}F_3 + O_2 \rightarrow CF_2O + \dot{O}F$$
 (1)

is of negligible importance, as no infrared evidence for $\dot{O}F$ radicals²² was obtained. No absorption features due to $F\dot{O}_2$ radicals²³ or O_3^{24} were observed, which rules out the production of free fluorine or oxygen atoms in the overall process.

Secondary photochemistry of "z" to produce CF_2O and FNO_2 was eliminated by means of an experiment in which a CF_3NO/Ar matrix (MR = 1:10000) at 4.2 K was photolyzed by the unfiltered medium-pressure mercury lamp to produce the [°CF₃...NO] proximity radical. Several pulses of ¹⁶O₂ were then deposited onto the matrix, which was subsequently annealed to 20 K for 5 min. It was observed that the [°CF₃...NO] absorption at 1247.1 cm⁻¹ was virtually destroyed and was accompanied by the growth of very weak features due to the most intense bands of CF₃O₂ radicals (1304.7 cm⁻¹), "z" (785.2 cm⁻¹), CF₂O (1941.9 and 1911.9 cm⁻¹), and FNO₂ (1800.1 cm⁻¹).

The question remains, Is it the decomposition of CF_3OONO via reactions 9a or 9b plus 10a which are responsible for the production of CF_2O and FNO_2 or is reaction 11 important?

The Vibrational Assignment of the Novel Species, "z". From an inspection of the data of Table I, three important statements may be made regarding "z".

1. The 1400–1100-cm⁻¹ region shows prominent absorptions at 1260.8 and 1249.5 cm⁻¹ which exhibit small isotopic shifts to 1259.9 and 1248.8 cm⁻¹, respectively, for " z_i ". In the present system these observations are consistent with vibrational frequencies largely associated with C-F stretching modes and are sufficient to characterize a CF₃ group.^{25,26}

2. In the 950–900-cm⁻¹ region, a weak absorption at 924.1 cm⁻¹ for the ${}^{16}O_2$ -Ar experiments was observed to shift to 901.2 cm⁻¹ in the ${}^{18}O_2$ -Ar-doped matrices. An isotopic shift of ca. 53 cm⁻¹ would be expected by calculation if this vibrational mode were identified with an -O-O- stretch; e.g., CF¹⁶O¹⁶O has $\nu_{O-O} = 1092$ cm⁻¹ whereas CF₃¹⁸O¹⁸O has $\nu_{O-O} = 1040$ cm⁻¹. The observed shift of 22.9 cm⁻¹ is consistent with a calculated

The observed shift of 22.9 cm⁻¹ is consistent with a calculated simple harmonic -C-O- stretching frequency of ca. 22 cm⁻¹ for $-C-^{16}O-$ to $-C-^{18}O-$.

3. The observed bands at 1735.5 and 1345.2 cm⁻¹ are consistent with the symmetric stretch of an $-NO_2$ group while the bands at 1327.1, 785.2, and 752.9 cm⁻¹ are all in appropriate regions for asymmetric $-NO_2$ stretching, -NO scissor, and $-NO_2$ out-of-plane bending modes, respectively.^{27,28} The observed isotopic shifts ($^{16}O^{-18}O$) for these bands are all of similar magnitude to those observed for ClONO₂ in a matrix assignment.²⁹

Alternatively, the band at 1735.5 cm⁻¹ could be assigned to the asymmetric stretching vibration of an -O-N=O group in a Y-ONO molecule since it is in the appropriate spectral region.

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However, this band then exhibits an anomolously large isotopic frequency shift to 1722.0 cm⁻¹ for " z_i " when compared to results obtained for F–ONO¹⁷ and Br–ONO.³⁰

It may be concluded that the most likely candidate for "z" is CF_3ONO_2 .

The Mechanism for the Photooxidation of CF_3NO in O_2 -Doped Argon Matrices at 4.2 K. The results discussed above provide the first direct spectroscopic evidence for the participation of CF_3OO radicals in the oxidation of the trifluoromethyl radical by molecular oxygen. However, the most surprising features of the experiments are (i) the twin formation of CF_2O and FNO_2 end products, as such a reaction has not been postulated before in atmospheric chemistry studies, and (ii) the absence of infrared absorption bands due to NO_2 , as reaction 8b with $\Delta H_r^{\circ} = -35$ kJ mol⁻¹ has been suggested to occur in recent gas-phase studies.

All of the data suggest that steps 6-11 can occur in a matrix. Such a mechanism would be consistent with the related study on the matrix photooxidation of ClNO by molecular oxygen. In these experiments ClONO₂ was identified as a product (although the formation of its isomer ClOONO could not be ruled out).²⁹

The absence of IR bands due to NO_2 could be quite simply explained by the efficiency of the highly exothermic reaction

$$\left[\operatorname{CF}_{3}\mathsf{O} + \operatorname{NO}_{2}\right] \xrightarrow[(\Delta H_{r}^{\circ} = -114 \text{ kJ mol}^{-1})]{} \operatorname{CF}_{2}\mathsf{O} + \operatorname{FNO}_{2}$$
(10a)

However, not all the $[CF_3\dot{O} + NO_2]$ cage sites would be expected to have the molecular pairs in an appropriate orientation for reaction and the side product "z", CF_3ONO_2 , could then be formed.

Finally, it is interesting to speculate on the structural nature of the intermediates that can result in the concurrent production of $CF_2O + FNO_2$. The photolysis of $CF_3N^{16}O/^{18}O_2/Ar$ at 4.2 K can be described from the results of Table I as follows:

$$CF_{3}N^{16}O \xrightarrow{n\nu} [^{\bullet}CF_{3}\cdots N^{16}O]$$
(6)

$$[^{\circ}CF_{3} \cdots N^{16}O] + {}^{18}O_{2} \rightarrow [CF_{3}{}^{18}O^{18}O + N^{16}O]$$
 (13)

$$[CF_{3}^{18}O^{18}O + N^{16}O] \rightarrow CF_{3}^{18}O^{18}ON^{16}O$$
(14)

$$CF_{3}^{18}O^{18}ON^{16}O \rightarrow CF_{2}^{18}O + FN^{18}O^{16}O$$
 (15)

$$CF_{3}^{18}O^{18}ON^{16}O \rightarrow CF_{3}^{18}ON^{16}O^{18}O$$
 (16)

$$CF_{3}^{18}ON^{16}O^{18}O \rightarrow CF_{2}^{18}O + FN^{16}O^{18}O$$
 (17)

A nonplanar $CF_3^{18}O^{18}ONO$ which could give rise to this specific isotopic chemistry is

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Cleavage across the C-F and ${}^{18}O{-}^{18}O$ bands allows formation of the observed products.

Alternatively, a unimolecular elimination process from CF_3O-NO_2 can be envisaged.



This cyclic intermediate can be proposed by analogy with the mechanism reported for CH_3ONO decomposition to give CH_2O and $HNO.^{31}$

The FTIR data obtained in these matrix experiments do not allow the relative importance of reactions 15 and 17 to be established (although CF₃ONO₂ was identified in this study whereas CF₃OONO was not). However, the important conclusion to be drawn from the results is that a novel pathway is observed in matrices to produce CF₂O and FNO₂ from the reaction between CF₃OO radicals and NO. This is an exothermic process (ΔH_r° = -152 kJ mol⁻¹), which contrasts with all other reactions hitherto suggested for the oxidation by molecular oxygen of °CF₃ radicals to carbonyl fluoride in the atmosphere.¹²

The results discussed in this paper are of particular importance in view of the recent report of the first stratospheric measurement of CF_2O by ATMOS.³²

Acknowledgment. We thank SERC for providing a studentship to K.C.C. We are both indebted to the late Edward K. C. Lee for his comments on this work earlier in the year and for his support on many other occasions.

Registry No. CF₃ONO₂, 334-99-6; CF₃OO[•], 17167-98-5; COF, 353-50-4; O₂NF, 10022-50-1; NO, 10102-43-9.

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