Making Sure That Hydrofluorocarbons Are "Ozone Friendly"

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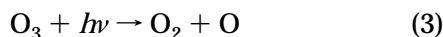*Department of Chemistry, Purdue University, West Lafayette, Indiana 47907*
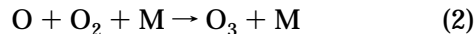
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I. Introduction

The discovery of the Antarctic ozone hole in 1985 by Farman et al.[1] reawakened the public to a danger that had been detected a decade earlier by Rowland and Molina,[2] namely, that emissions of man-made chlorofluorocarbon compounds (CFCs) could lead to significant depletion of the ozone layer. This layer, a broad region of the stratosphere located at an altitude of about 24 km, shields the earth's surface from solar ultraviolet (UV) radiation that is harmful to life. Stratospheric ozone exists in a dynamic equilibrium, described in its simplest form by the Chapman mechanism:

$$O_2 + h\nu \rightarrow 2O \tag{1}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{2}$$

$$O_3 + h\nu \rightarrow O_2 + O \tag{3}$$

$$O_3 + O \rightarrow 2O_2 \tag{4}$$

Rowland and Molina[2] pointed out that the very stability of CFCs that makes them so useful in a vast variety of refrigeration, foam blowing, cleaning, and other applications also represents a liability. Because they are chemically inert, CFCs have exceedingly long atmospheric lifetimes. Therefore, they can act as vehicles to transport chlorine to stratospheric altitudes. Above the protective ozone layer, solar UV radiation photolyzes the CFCs, releasing chlorine atoms that catalytically destroy ozone molecules

$$Cl + O_3 \rightarrow ClO + O_2 \tag{5}$$

$$ClO + O \rightarrow Cl + O_2 \tag{6}$$
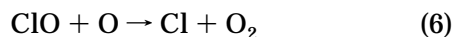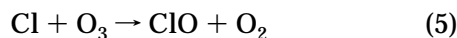
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potentially leading to large perturbations of the ozone equilibrium.

The harmful consequences of ozone depletion, such as a higher incidence of skin cancer, sparked in the 1970s a momentary concern over the widespread use of CFCs. Some limitations in their use were introduced, and possible alternatives were identified; however, by the early 1980s the concern had languished.[3] The appearance of the ozone hole revitalized the debate over limiting CFC production by dramatically illustrating the impact that human activity can have on the ozone layer. In 1987 the Montreal Protocol was signed calling for a worldwide reduction of CFCs by 50%; by 1988 the major CFC manufacturers had agreed to a complete phaseout of CFC production. This accelerated the implementation of suitable replacements. In some cases, such as cleaning applications, non-halocarbon substitutes were employed. For other applications, including refrigeration and air conditioning, hydrochlorofluorocarbon (HCFC) and hydrofluorocarbon (HFC) compounds were endorsed on the basis that their physical and chemical properties were suitable for the task.

Aside from having the appropriate physical attributes, HFCs and HCFCs were considered viable alternatives because they contain hydrogen. In principal, this makes them susceptible to chemical attack by OH radicals present in the troposphere and, thereby, renders the HFCs and HCFCs ineffective as vehicles to transport chlorine to the stratosphere. Concern over the environmental impact of these replacement compounds inspired a research effort of unprecedented scope into the atmospheric chemistry of these alternatives.[4] Having indicted the CFCs as harmful to the atmosphere, it would be unacceptable to replace them with compounds posing perhaps some other potential hazard. Of the conclusions to emerge from this research, one is that most HCFCs react slowly with hydroxyl radical, thus bestowing them sizable atmospheric lifetimes and significant ozone depletion potentials (ODPs). Accordingly, they too

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(2) Molina, M. J.; Rowland, F. S. *Nature* **1974**, *249*, 810.

(3) Roan, S. *Ozone Crisis: The 15-Year Evolution of a Sudden Global Emergency*; Wiley: New York, 1989.

(4) Much of the data on the atmospheric chemistry of HFCs and HCFCs are summarized in the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS), *Proceedings of the Workshop on the Atmospheric Degradation of HCFCs and HFCs*, Boulder, CO, November 1993; *Proceedings of the STEP-HALOCSIDE/AFEAS Workshop*, Dublin, March 1993.

have been conscripted for phaseout. By the 1995 Vienna amendments HCFC consumption will be reduced gradually, with its production in developed countries terminating by year 2030.

The HFCs, on the other hand, were not supposed to pose a danger to the ozone layer; they contain no chlorine. However, the atmospheric degradation of HFCs leads to unique intermediate fluorocarbon radicals whose atmospheric chemistry could not be anticipated from hydrogen- or chlorine-containing analogs. CF_3O provides one example. Unlike hydrogen- or chlorine-containing alkoxy radicals, it does not react with O_2 or undergo bond fission. Another example is $FC(O)O$, which by analogy with its hydrogen and chlorine counterparts should not exist as a stable radical; yet it has a lifetime of seconds at room temperature, and considerably longer at stratospheric temperatures. Theoretical work suggested that CF_3O, as well as $FC(O)O$, could behave chemically like a chlorine atom; in particular, each could potentially remove ozone via a catalytic cycle similar to reactions 5 and 6.[5,6] After preliminary experimental evidence seemed to confirm this theoretical possibility,[7] and in the absence of known CF_3O removal pathways, concern over the use of HFCs as CFC alternatives mounted substantially. Fortunately, subsequent experiments showed these molecules to react too slowly with ozone to register anything but a negligible ODP, and the HFCs remain "ozone friendly".

The present Account examines the question of the environmental acceptability of HFCs from the perspective of the roles played by a handful of key intermediate species formed during the atmospheric degradation process, namely, those of CF_3O, $FC(O)O$, $CF_3C(O)O_2$, and FNO. It focuses on the chemistry of these species relevant to assessing the impact of HFCs on the ozone layer. The reader interested in a comprehensive treatment of the atmospheric degradation processes of HFCs and HCFCs is referred to a recent review of this field.[8]

II. CF_3O

The trifluoromethoxy radical is an intermediate species formed during the atmospheric degradation of HFCs having the form CF_3CHX_2, where X_2 represents a combination of H and F atoms. The reaction pathways leading to CF_3O formation are summarized in Figure 1. The initial OH attack, which is temperature dependent, occurs with a rate constant on the order of 10^{-15} cm^3 s^{-1}. Since the tropospheric OH concentration is roughly 10^6 cm^{-3}, this implies that HFCs have atmospheric lifetimes on the order of years, long enough for some to reach the stratosphere.[9] There they undergo the same degradation process as shown in Figure 1, except that the concentrations of the reactants differ from the troposphere to the stratosphere.

(5) Francisco, J. S.; Williams, I. H. *Proc. 16th Annu. Meet. Natl. Org. Black Chem. Chem. Eng., Chicago* **1989**, *16*, 59.

(6) Francisco, J. S.; Goldstein, A. N.; Li, Z.; Zhao, Y.; Williams, I. H. *J. Phys. Chem.* **1990**, *94*, 4791.

(7) Biggs, P.; Canosa-Mas, C. E.; Shallcross, D. E.; Wayne, R. P.; Kelly, C.; Sidebottom, H. W. *Proceedings of the STEP-HALOCSIDE/AFEAS Workshop*, Dublin, March 1993.

(8) Francisco, J. S.; Maricq, M. M. *Adv. Photochem.* **1995**, *20*, 79.

(9) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*; JPL Publication 94-26, 1994.
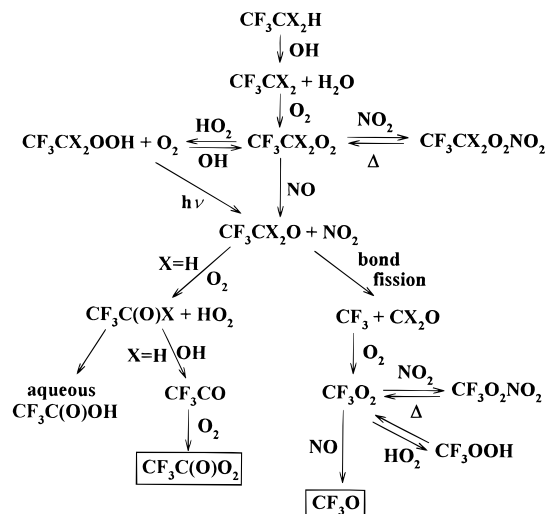
Figure 1. Atmospheric degradation pathways for HFCs of the form CF_3CHX_2, with X = F or H.

Peroxy radicals formed by hydrocarbon oxidation react with trace atmospheric species, predominantly NO, NO_2, and HO_2. Because reactions with the latter two species are largely reversible for HFC-derived peroxy radicals, the most important degradation pathway is the reaction with NO:

$$CF_3CX_2O_2 + NO \rightarrow CF_3CX_2O + NO_2 \qquad (7)$$

Rate constants for this reaction typically lie in the range of 1×10^{-11} to 2×10^{-11} cm^3 s^{-1} and are expected to be relatively insensitive to temperature;[8] thus, the peroxy radical has approximately a 1 min lifetime with respect to reaction with NO at an altitude of 24 km.

The alkoxy radical formed by reaction 7 has two possible fates. If the alkoxy radical contains hydrogen, it can react with molecular oxygen

$$CF_3CXHO + O_2 \rightarrow CF_3CXO + HO_2 \qquad (8)$$

to form a trifluoroacetyl halide and the hydroperoxy radical. Alternatively, it can undergo C−C bond fission

$$CF_3CX_2O + M \rightarrow CF_3 + CX_2O + M \qquad (9)$$
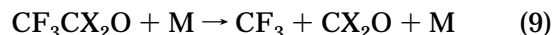
to produce the CF_3 radical and a carbonyl halide. Under atmospheric conditions, the branching ratio, $k_8[O_2]/k_9[M]$, varies from about 0.2 at sea level to 3.5 at 12 km.[10]

The CF_3 radical produced in reaction 9 is mainly converted to CF_3O (see Figure 1). Unlike other alkoxy radicals, bond cleavage and reaction with O_2 are not feasible for this molecule. Furthermore, the C−F bond strength of 23 ± 3 kcal/mol[11] is too strong to permit thermal dissociation at atmospheric temperatures. It is the lack of apparent pathways for rapid removal that prompted concern that CF_3O, like chlorine atoms,
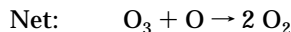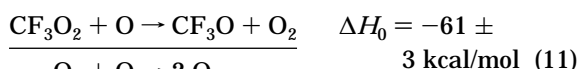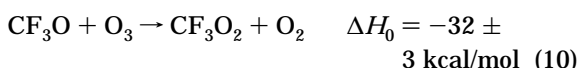
(10) Wallington, T. J.; Hurley, M. D.; Ball, J. C.; Kaiser, E. W. *Environ. Sci. Technol.* **1992**, *26*, 1318.

(11) Unless otherwise stated, heats of formation for CF_3O_x, CF_2O, etc. are from Schneider, W. F.; Wallington, T. J. *J. Phys. Chem.* **1994**, *98*, 7448; **1993**, *97*, 12783. The remainder are taken from ref 9. The indicated errors arise predominantly from uncertainties in the theoretical values.
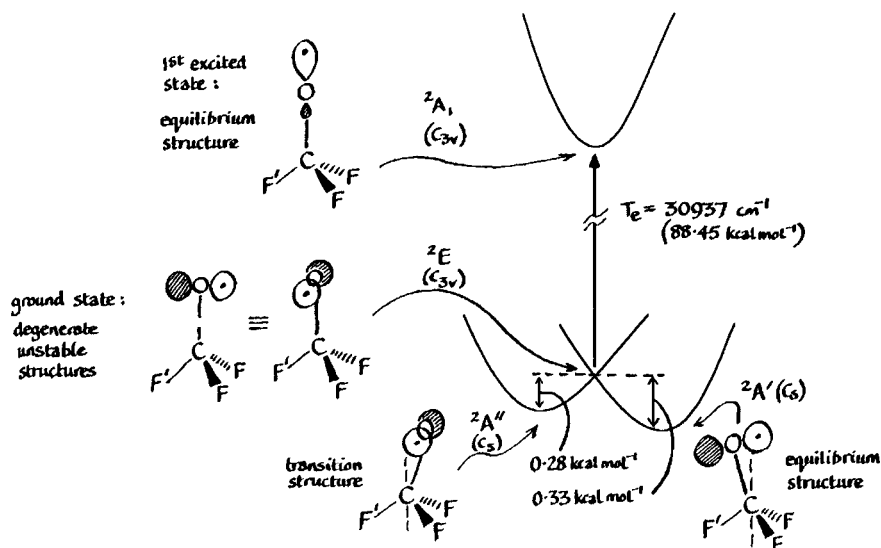
Figure 2. *Ab initio* geometries and energies of CF_3O. Shown are the excited state and the Jahn−Teller distorted ground electronic states.
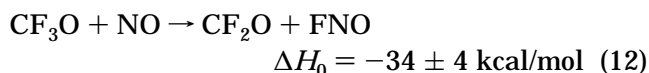
could catalytically remove ozone:

$$CF_3O + O_3 \rightarrow CF_3O_2 + O_2 \quad \Delta H_0 = -32 \pm$$
$$3 \text{ kcal/mol} \quad (10)$$

$$\underline{CF_3O_2 + O \rightarrow CF_3O + O_2 \quad \Delta H_0 = -61 \pm}$$

Net: $\quad O_3 + O \rightarrow 2 \, O_2 \qquad 3 \text{ kcal/mol} \quad (11)$

The CF_3O radical was first examined theoretically by Francisco and Williams.[12] *Ab initio* structures and energies were calculated for the $^2A_1$ excited state, the ^2E ground state of C_{3v} symmetry, and the Jahn−Teller distorted C_s ground state geometries, as illustrated in Figure 2. These calculations helped identify this radical in the laboratory via its laser-induced fluorescence (LIF) spectrum.[13] The spectrum has subsequently been obtained in high resolution by Tan et al.,[14] who found that the Jahn−Teller effect is too weak to permanently distort the ground state from C_{3v} symmetry. They measured a rotational constant of $B = 0.198 \, 21 \text{ cm}^{-1}$ that is in good agreement with the theoretical value of $0.201 \, 88 \text{ cm}^{-1}$.

The efficacy of CF_3O as an ozone destruction catalyst rests on the relative rate of its reaction with ozone, eq 10, as compared to its removal from the atmosphere. The initial report of a rate constant $k_{10} = 1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ by Biggs et al.[7] spurred a series of studies showing, in contrast, that the reaction of CF_3O with ozone has an upper limit of $k_{10} < {\sim}5 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$.[15] Subsequent measurements (see Table 1) have refined the rate constant to the range $k_{10} = (1.5-2.5) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ at 295 K.

The possibility that CF_3O could be removed by reaction with NO

$$CF_3O + NO \rightarrow CF_2O + FNO$$
$$\Delta H_0 = -34 \pm 4 \text{ kcal/mol} \quad (12)$$

Table 1. Selected CF_3O Reactions

reaction	A (or k(298 K)) (cm³ s⁻¹)	activation energy[a]	ref
$CF_3O + O_3$	$<10 \times 10^{-14}$		15c
	$<3 \times 10^{-14}$		15b
	$<5 \times 10^{-14}$		15a
	$<4 \times 10^{-14}$		18
	$2.5 \, (+0.7/-1.5) \times 10^{-14}$		19
	$(1.5 \pm 0.5) \times 10^{-14}$		20
	1×10^{-12}		7
$CF_3O + NO$	$(4.7 \pm 0.3) \times 10^{-11}$		21
	$(5.2 \pm 2.7) \times 10^{-11}$		22
	$(3.3 \pm 0.7) \times 10^{-11}$	-160 ± 45	19
	$(4.1 \pm 0.6) \times 10^{-11}$	-60 ± 120	23
	$(4.4 \pm 1.5) \times 10^{-11}$	-100 ± 88	17
$CF_3O + CH_4$	$(3.1 \pm 0.5) \times 10^{-12}$	1470 ± 250	23
	$(1.9 \pm 0.3) \times 10^{-12}$	1370 ± 85	24
	3.3×10^{-12}	1430	25
$CF_3O + H_2O$	$<1 \times 10^{-16}$		26
	$<7 \times 10^{-18}$ (at 277 K)		
	$(0.2-40) \times 10^{-17}$		27

[a] Given in kelvin as E_A/R. When it is given, $k = A \exp(-E_A/(RT))$.

or by hydrogen atom abstraction from hydrocarbons, e.g.

$$CF_3O + CH_4 \rightarrow CF_3OH + CH_3$$
$$\Delta H_0 = -15 \pm 3 \text{ kcal/mol} \quad (13)$$
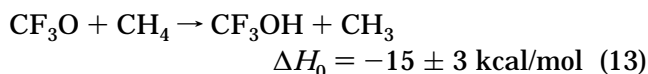
was demonstrated by the product studies of Chen et al.[16] Subsequently, a number of groups took advantage of LIF detection of CF_3O to measure rate constants for reactions 12 and 13 (see Table 1). Transient diode laser measurements of the CF_2O formation rate confirmed the LIF determinations of k_{12} and demonstrated that reaction 12 represents the dominant pathway for the reaction between CF_3O and NO.[17]

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Table 2. Atmospheric Lifetime of CF_3O with Respect to Various Removal Pathways

altitude (km)	T (K)	species	concn[a] (cm^{-3})	lifetime (min)
		Troposphere		
1	277	NO	5×10^8	0.5
1	277	CH_4	4×10^{13}	0.03
1	277	H_2O	3×10^{17}	0.01[b]
1	277	O_3	1.5×10^{12}	0.6[c]
		Stratosphere		
24	215	NO	1.3×10^9	0.18
24	215	CH_4	2×10^{12}	2.6
24	215	H_2O	5×10^{12}	500[b]
24	215	O_3	6×10^{12}	0.14[c]

[a] Obtained for local noon conditions from ref 9. [b] Lower limit of the lifetime assuming the rate constant equals the upper limit of 7×10^{-18} cm^3 s^{-1}. [c] Based on a rate constant of 2×10^{-14} cm^3 s^{-1} at 295 K.

This eliminates the possibility that CF_3O is converted by NO to the temporary reservoir species CF_3ONO, the photolysis of which would regenerate the alkoxy radical. The reaction with NO, therefore, irreversibly removes CF_3O from the atmosphere. However, in so doing it generates FNO (see below), which plays an important role in the atmospheric fluorine cycle.

CF_3O has the ability to abstract hydrogen atoms from a variety of hydrocarbons. Its reactivity in this regard is less than that of fluorine atoms, but comparable to those of Cl and OH. As with the latter radicals, the rate coefficient of the reaction of CF_3O with RH increases with the size of the R group; thus, $k_{CF_3O-CH_4} < k_{CF_3O-C_2H_6} < k_{CF_3O-C_3H_8}$.[24] Because the atmospheric concentration of methane greatly exceeds those of other hydrocarbons, however, it is the reaction with CH_4 that is the most important with respect to the fate of CF_3O. The abstraction reaction exhibits a strong dependence on temperature and, therefore, altitude. This coupled with the decrease in methane concentration as altitude increases implies that removal of CF_3O by CH_4 is important in the troposphere, but not the stratosphere (see Table 2).

Due to the high concentration of water vapor in the troposphere, the gas phase reaction of CF_3O with H_2O represents a possible removal mechanism in this region of the atmosphere. The product study by Wallington et al.[27] gave a room temperature rate constant of 0.2×10^{-17} cm^3 s^{-1} < $k_{CF_3O-H_2O}$ < 40×10^{-17} cm^3 s^{-1}. A subsequent investigation by Turnipseed et al.[26] failed to reveal a measurable reaction, yielding instead upper limits of 1×10^{-16} and 2×10^{-16} cm^3 s^{-1} at 298 and 381 K, respectively. Combining the latter limit with the theoretical activation energy, the authors suggest that the actual upper limit is less than 7×10^{-18} cm^3 s^{-1} at 277 K, the weighted global mean temperature for OH reactions with HFCs. In the extreme case that the rate constant equals this limit, the tropospheric removal of CF_3O by H_2O is comparable to its removal by CH_4.
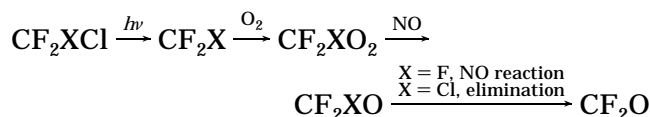
Owing primarily to differences in the relative concentrations of the reactants, the fate of CF_3O differs in the troposphere versus the stratosphere, as il-

lustrated by Table 2. CF_3O formed in the lower atmosphere, where methane and water vapor are in relatively high concentrations, is converted to CF_3OH by reaction with these species. The effectiveness of removal by H_2O is highly variable owing to the strong variation of atmospheric water vapor with time and location. It also awaits a better determination of the $CF_3O + H_2O$ rate constant.

In contrast, CF_3O formed in the stratosphere reacts primarily with NO and O_3; removal by CH_4 represents a minor pathway, and the reaction with H_2O is negligible. At 24 km, where the ozone concentration peaks, the rate of ozone loss by reaction with CF_3O is comparable to the rate of CF_3O removal by NO. The simple relative rate analysis provided in Table 2 indicates that the chain propagation and termination rates are similar and, thus, suggests that CF_3O will be considerably less efficient at catalytic ozone destruction than Cl or Br atoms. This conclusion is born out by the atmospheric modeling performed by Ravishankara et al.,[18] which incorporates the appropriate CF_3O kinetic data.

III. FC(O)O

The (fluoroformyl)oxyl radical is an intriguing intermediate formed in the atmospheric degradation of HFCs and HCFCs as well as of CFCs. The preceding section showed how CF_3O arises from the degradation of compounds of the form CF_3CHX_2 and how its reaction with NO produces CF_2O. Other HFCs also yield carbonyl fluoride; for example, the degradation of CF_2HCHX_2 leads to the formation of, among other products, CF_2HO by pathways analogous to those of Figure 1. This alkoxy radical subsequently reacts with O_2 to produce CF_2O and HO_2. Even CFCs lead to carbonyl fluoride as per the following pathway:

$$CF_2XCl \xrightarrow{h\nu} CF_2X \xrightarrow{O_2} CF_2XO_2 \xrightarrow{NO}$$
$$CF_2XO \xrightarrow[\text{X = Cl, elimination}]{\text{X = F, NO reaction}} CF_2O$$

Short-wavelength UV radiation, found in the middle to upper stratosphere, photolyzes carbonyl fluoride (also CFClO) and leads to formation of the (fluoroformyl)oxyl radical via

$$CF_2O \xrightarrow{h\nu} FCO \xrightarrow{O_2} FC(O)O_2 \xrightarrow{NO} FC(O)O$$

FC(O)O is a fascinating radical, being essentially a carbon dioxide molecule with a fluorine atom attached to it. Analogous species are not stable. HC(O)O has recently been shown to have a negative C–H bond energy, and XC(O)O molecules, with X = Cl, Br, or I, exist as van der Waals complexes with C–X bond energies of 0.5–1 kcal/mol.[28]

FC(O)O, however, is stable. It has been formed in the gas phase both from the photolysis of F_2 in the presence of CO and O_2 and by the photolysis of (FC(O)O)$_2$ and detected via the visible absorption spectrum arising from the $B^2A_1 \leftarrow X^2B_2$ transition.[29,30]

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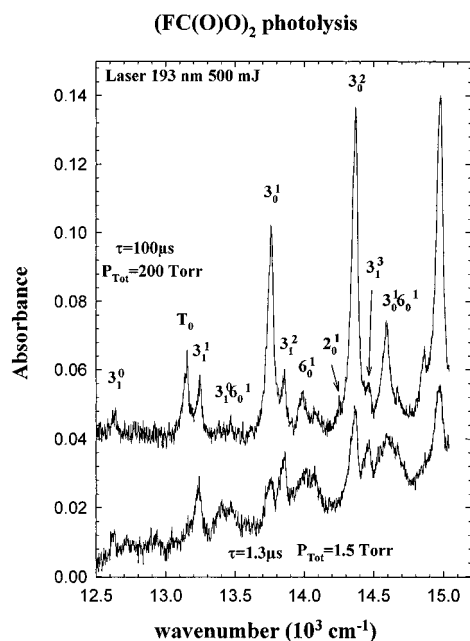
Figure 3. Visible absorption spectrum of FC(O)O obtained from the 193 nm photolysis of (FC(O)O)$_2$. The lower trace represents a nearly nascent spectrum. The upper trace shows a 298 K spectrum. The peaks are labeled by their spectral assignments.

Figure 3 displays a spectrum of vibrationally hot FC-(O)O produced from the 193 nm photolysis of (FC-(O)O)$_2$, as well as a thermalized spectrum. Both spectra are dominated by progressions of 610 cm^{-1}, corresponding to the frequency of the bending vibration in the excited B^{2}A$_1$ state. FC(O)O has subsequently been observed by the photoelectron spectroscopy[28] of FC(O)O$^-$ and by matrix isolation,[31] yielding vibrational frequencies for the ground electronic state.

The calculation of the structure and properties of FC(O)O by *ab initio* techniques turns out to be notoriously difficult. If one assumes a C_{2v} geometry, calculations at the UMP2 level lead to quite good structural parameters. Yet the vibrational frequencies of the asymmetric in-plane modes are unphysical; for example, ω_4, the asymmetric C−O stretch, is predicted to have a frequency of 3401 cm^{-1} at the UMP2 level.[29] Worse, if the C_{2v} constraint is relaxed, an unphysically asymmetric ground state structure is predicted with widely different C−O bond lengths. These difficulties are caused by symmetry breaking of the Hartree−Fock wave function. It originates from the three valence bond resonance structures that describe FC(O)O: the unpaired electron is localized on one or the other oxygen atom, or it is delocalized. Although most properly attacked by multireference methods, single-reference correlation techniques, when used carefully, have been found to provide accurate vibrational frequencies; thus, using the QRHF-CCSD-(T) approach,[34] a value of $\omega_4 = 1049$ cm^{-1} is obtained, in good agreement with the experimental frequency of 1098 cm^{-1}.

Given that FC(O)O is sufficiently stable to react with trace atmospheric species, one can hypothesize

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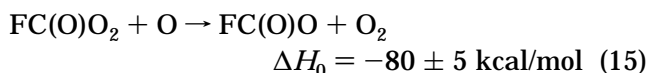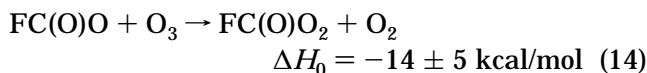(34) Schneider, W. F.; Maricq, M. M.; Francisco, J. S. *J. Chem. Phys.* **1995**, *103*, 6601.

Table 3. FC(O)O Reactions

reaction	A (or k(298 K)) (cm^3 s^{-1})	exponent[a]	ref
FC(O)O + O$_3$	$<3 \times 10^{-15}$		30
	$<2.5 \times 10^{-14}$		32
	$<6 \times 10^{-14}$		33
FC(O)O + NO	$(3.6 \pm 0.5) \times 10^{-11}$	0.1 ± 0.5	30
	$(3.8 \pm 0.5) \times 10^{-11}$	0.0	32
	$(1.3 \pm 0.7) \times 10^{-10}$		33
FC(O)O + NO$_2$	$(7.5 \pm 1.1) \times 10^{-12}$	3.1 ± 1.1	30
	$(5.3 \pm 1.2) \times 10^{-12}$	2.5 ± 1.0	32
FC(O)O + HO$_2$	$(1.2 \pm 0.2) \times 10^{-11}$	1.2 ± 0.2	30
FC(O)O + CH$_4$	$<4 \times 10^{-18}$		32

^{a} When the exponent n is given, $k = A(T/300)^{-n}$.

an ozone depletion cycle consisting of[35]

$$FC(O)O + O_3 \rightarrow FC(O)O_2 + O_2$$
$$\Delta H_0 = -14 \pm 5 \text{ kcal/mol} \quad (14)$$

$$FC(O)O_2 + O \rightarrow FC(O)O + O_2$$
$$\Delta H_0 = -80 \pm 5 \text{ kcal/mol} \quad (15)$$

or with other FC(O)O regeneration steps in lieu of reaction 15. The efficiency of the cycle rests on the competition between reaction 14 and termination pathways, including chemical removal of FC(O)O as well as its photolysis.

FC(O)O has been found to react rapidly with a number of atmospheric species; thus, the reactions

$$FC(O)O + NO \rightarrow FNO + CO_2$$
$$H_0 = -41 \pm 5 \text{ kcal/mol} \quad (16)$$

$$FC(O)O + NO_2 \rightarrow FNO_2 + CO_2$$
$$\Delta H_0 = -37 \pm 5 \text{ kcal/mol} \quad (17)$$

$$FC(O)O + HO_2 \rightarrow HF + CO_2 + O_2$$
$$\Delta H_0 = -71 \pm 4 \text{ kcal/mol} \quad (18)$$
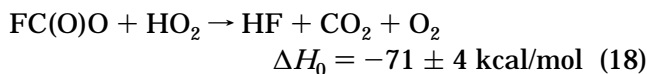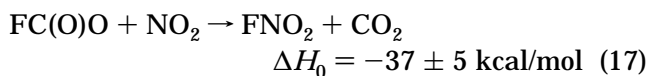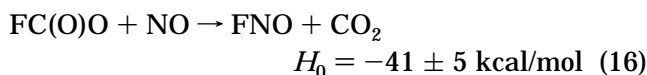
represent viable removal mechanisms. The reaction with NO was examined in detail by Dibble and Francisco[36] using *ab initio* methods. They characterize the reaction as proceeding through the FC(O)ONO adduct; however, the adduct has sufficient internal energy to overcome the barrier for rearrangement into the FNO and CO$_2$ products. The fact that reaction 16 has been found experimentally to be fast and nearly independent of temperature supports this mechanism.[30,32] Likewise, the reactions of FC(O)O with NO$_2$ and HO$_2$ are fast (see Table 3). Both exhibit a negative temperature dependence and presumably proceed via adduct formation and subsequent rearrangement and dissociation. In contrast to CF$_3$O, the (fluoroformyl)oxyl radical does not appear to react with simple hydrocarbons. The rate constant for the reaction with methane has an upper limit of $<4 \times 10^{-18}$ cm^3 s^{-1},[32] whereas for ethane the upper limit is $<5 \times 10^{-15}$ cm^3 s^{-1}.[30]

Table 4 summarizes the fate of FC(O)O in the upper stratosphere (40 km) and at the ozone maximum (24 km). At both altitudes chemical FC(O)O loss is primarily by reaction with NO. The HO$_2$ reaction plays a negligible role owing to its comparably low

(35) The FC(O)O$_2$ heat of formation was estimated by Antonik, S. *Bull. Soc. Chim. Fr.* **1982**, *I*, 83. That of FC(O)O is from ref 34. Those for the other species are from ref 9.
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Table 4. Stratospheric Lifetime of FC(O)O with Respect to Various Removal Pathways

| altitude (km)	T (K)	species	concn[a] (cm^{-3})	lifetime (min)
24	215	NO	1.3×10^9	0.4
24	215	NO$_2$	2×10^9	0.4
24	215	HO$_2$	1×10^7	90
24	215	O$_3$	6×10^{12}	0.9[b]
40	250	NO	7×10^8	0.6
40	250	NO$_2$	2×10^8	6
40	250	HO$_2$	1×10^7	110
40	250	O$_3$	8×10^{11}	7[b]

[a] Obtained for local noon conditions from ref 9. [b] Assuming the value of the rate constant to be the upper limit of 3×10^{-15} cm^3 s^{-1}.

concentration in the stratosphere. At 24 km a significant fraction of FC(O)O is removed by reaction with NO$_2$; however, this contribution decreases with increasing altitude owing to the falloff in NO$_2$ concentration. The rate constant for the chain propagation reaction of FC(O)O + O$_3$ is very small. Combined with the typical stratospheric ozone concentration, this implies an upper limit for the fraction of FC(O)O radicals reacting with ozone that varies between 10% and 20%. This fraction becomes substantially smaller when the photolytic loss[32] of FC(O)O is taken into account. Consequently ozone depletion by the cycle of reactions 14 and 15 is negligible.

IV. CF$_3$CO$_x$

Among the stable products from the atmospheric degradation of HFCs are a variety of halogenated carbonyl compounds of the form CF$_3$C(O)X, where X = F or H (see Figure 1).[37] The degradation of HFC-134a leads to the formation of CF$_3$C(O)F, whereas CF$_3$C(O)H is a degradation product of HFC-143a (CF$_3$-CH$_3$). Analogous chlorinated carbonyl compounds derive from the atmospheric reactions of HCFCs. These carbonyl compounds are lost from the atmosphere by uptake into cloud water, photolysis, or reaction with OH (if they contain hydrogen atoms).

Francisco[38] explored a key step in the ability of cloud water to remove carbonyl compounds, namely, hydrolysis. The initial step involves the addition of H$_2$O across the carbonyl bond, forming a four-center transition state complex leading to the formation of CF$_3$CX-(OH)$_2$, which decomposes to trifluoroacetic acid; thus

$$CF_3C(O)X + H_2O \rightarrow CF_3CX(OH)_2 \rightarrow$$
$$CF_3C(O)OH + HX \quad (19)$$
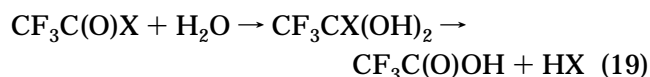
The limiting step in this process is the addition of water. Calculated activation energies are 54.6, 35.5, and 50.1 kcal mol^{-1} for CF$_3$C(O)H, CF$_3$C(O)F, and CF$_3$C(O)Cl, respectively. The calculations also predict that trifluoroacetic acid is more likely to be produced from the hydrolysis of CF$_3$C(O)F and CF$_3$C(O)Cl than from CF$_3$C(O)H. It is possible that some of the water droplets evaporate prior to raining out, releasing gas phase CF$_3$C(O)OH. In this case the acid can react with OH radicals[39] with a rate constant ranging from

1.2×10^{-13} to 7.4×10^{-13} cm^3 s^{-1}. Other than this, there is no known removal mechanism for trifluoroacetic acid.

Aside from hydrolysis, CF$_3$C(O)Cl is also removed by photolysis[40]

$$CF_3C(O)Cl + h\nu(193, 248 \text{ nm}) \rightarrow CF_3 + CO + Cl \quad (20)$$

with the absorption of the photon leading to the fission of both the C–Cl and C–C bonds. This process releases a chlorine atom, which partakes in ozone destruction, as well as a CF$_3$ radical, which is rapidly converted to CF$_3$O, as discussed in section II. By contrast, homogeneous removal of CF$_3$C(O)H occurs by reaction with OH:

$$CF_3C(O)H + OH \rightarrow CF_3CO + H_2O \quad (21)$$

The trifluoroacetyl radical that is produced has two possible fates: dissociation into CF$_3$ and CO or the addition of molecular oxygen to form the (trifluoroacetyl)peroxy radical.

The existence of CF$_3$CO was first postulated by Tucker and Whittle[41] as an intermediate in photochemical reactions involving Br$_2$ and Cl$_2$ in the presence of hexafluoroacetone. Spectroscopic characterization of CF$_3$CO came from infrared absorption studies by Kozuka and Isobe.[42] They observed the CO stretching mode (1574 cm^{-1}) and two CF$_3$ stretching modes (1115 and 1338 cm^{-1}). These vibrations were confirmed by *ab initio* predictions.[43] The laser-induced fluorescence spectrum of the CF$_3$CO, recorded by Li and Francisco[44] using IR multiphoton dissociation of CF$_3$C(O)Cl, revealed a progression at 1525 cm^{-1} involving the CO stretching mode in the ground state, consistent with the work of Kozuka and Isobe.[42]

The question of the stability of the trifluoroacetyl radical remained uncertain for some time. Product studies by Kerr and Wright[45] yielded an activation energy for dissociation of 19.8 kcal mol^{-1}; in contrast, Amphlett and Whittle[46] found a barrier of about 10 kcal mol^{-1}. Subsequent *ab initio* studies[43] predicted the activation energy to be 11.4 kcal mol^{-1}, quite close to the results of Amphlett and Whittle. Recent experiments have explored the dissociation reaction in real time by probing the rate of CO production.[47] The results indicate an activation barrier of 12.4 $\pm$ 1.0 kcal mol^{-1} for C–C bond dissociation, confirming theoretical predictions and the experimental value of Amphlett and Whittle.[46] Yet even the lower activation energy is sufficiently high that at atmospheric temperatures the predominant fate of CF$_3$CO is to add O$_2$ and form CF$_3$C(O)O$_2$.[47,48]

(Trifluoroacetyl)peroxy radicals react with a variety of atmospheric species. In analogy with other RO$_2$ radicals, the reaction with NO yields the correspond-
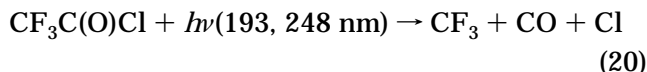
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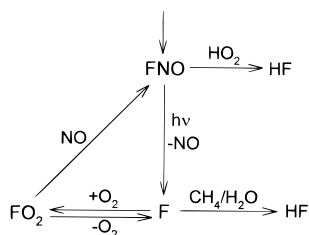(43) Francisco, J. S. *Chem. Phys. Lett.* **1992**, *191*, 7.
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Figure 4. Schematic of the atmospheric inorganic fluorine cycle.

ing RO molecule. Theoretical considerations[43] indicated that the C−C bond of $CF_3C(O)O$ is substantially weaker than the F−C bond in $FC(O)O$ (section III); thus, the $CF_3C(O)O$ radical formed by this reaction is expected to dissociate into CF_3 and CO_2. This prediction was confirmed experimentally by Wallington et al.[48] and more recently by Maricq et al.[49] $CF_3C(O)O_2$ can also add NO_2 to form the corresponding peroxyacetyl nitrate ($k = 6.6 \times 10^{-12}$ cm^3 s^{-1} at 295 K).[50] However, the nitrate acts as a temporary reservoir; the peroxy radical is regenerated by thermal decomposition or photolysis of the $CF_3C(O)O_2NO_2$. The reaction of $CF_3C(O)O_2$ with HO_2 has not been studied; however, its reaction with NO is fast[49] ($k = 4.0 \times 10^{-12}e^{536/T}$ cm^3 s^{-1}). Thus, with the possible exception of remote areas, where the [HO$_2$]/[NO] ratio is relatively high, the major atmospheric fate of $CF_3C(O)O_2$ is the reaction with NO, yielding $CF_3C(O)O$. This radical dissociates into CO_2 and a CF_3 radical that reacts with O_2 and then NO to produce CF_3O (see section II).

V. FNO

There is an important difference between the atmospheric fates of CFCs and HCFCs on one hand versus that of HFCs on the other. The former compounds liberate free chlorine atoms, either by photolysis of the parent halocarbon or during the degradation process by C−Cl bond fission of chlorine-containing alkoxy radicals. Except for the photolysis of $FC(O)O$, HFCs do not directly liberate free fluorine atoms owing to the strength of the C−F bond. Instead, inorganic fluorine appears in the form of FNO, which is produced by the reactions of CF_3O and $FC(O)O$ with NO and becomes a cornerstone of the atmospheric fluorine cycle.

The cycle is shown in Figure 4. FNO does not react at a significant rate with O_3, O(^{3}P), or HCl.[51] It does absorb UV radiation in the 260−335 nm region, producing a predissociative state that yields F atoms and NO. The fluorine atoms[52] that are liberated rapidly add molecular oxygen to form FO_2. This compound either dissociates or reacts with NO to regenerate FNO. The cycle can be broken at two points on the triangle: those marked F and FNO. Fluorine atoms are lost from the cycle primarily by reaction with CH_4 and H_2O as well as ozone. FNO is removed from the cycle by the reaction[53]

$$FNO + HO_2 \rightarrow HF + NO + O_2 \qquad (22)$$
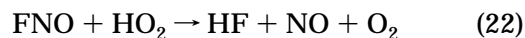
The rate constant for reaction 22 is relatively large, $k = 2.7 \times 10^{-13}e^{742/T}$ cm^3 s^{-1}, making this termination step competitive with the loss of F atoms. Employing the presently known rate constants, approximately 10−20% of the fluorine loss from the cycle at stratospheric altitudes occurs via reaction 22; however, this fraction is sensitive to the F + O$_2$ equilibrium constant, which is not very precisely known at present.[53]

Via either termination process, atmospheric fluorine is eventually converted into HF and one of the NO molecules expended during the halocarbon's degradation is regenerated. The high stability of HF ensures that this is an effective fluorine atom sink. The principal difference between the two mechanisms for fluorine removal is that reaction 22 consumes an HO_2 radical whereas the loss of F atoms by reaction with RH or H_2O generates either a peroxy radical or OH. It is at present unclear to what extent this competition affects the HO$_x$ balance of the upper atmosphere.

VI. Conclusion

The Montreal Protocol on Substances that Deplete the Ozone Layer started a global political process based on accumulated scientific data and aimed at eliminating the industrial use of CFCs. From the environmental standpoint, the substances identified as replacements had to satisfy two criteria: they could not destroy ozone, nor could they introduce some other hazard. Thus began an intensive research effort to understand the atmospheric chemistry and environmental implications of the replacements, namely, the HCFCs and HFCs. This endeavor was aided by the timely interplay between theoretical and experimental approaches to elucidating the degradation mechanisms of these compounds. As a result the HFCs, in particular HFC-134a, which replaces CFC-12 in mobile refrigeration systems, have been shown to be "ozone friendly"; that is, they do not contribute to ozone depletion either directly or via their degradation products. As sometimes happens in science, the need to solve a practical problem introduced us to something new, in this case chemical species such as the CF_3O, $FC(O)O$, CF_3CO, $CF_3C(O)O_2$, and FNO molecules that have been the principal subjects of this Account. These molecules are of interest in the broader scientific context and exhibit physical properties and chemistry, many aspects of which remain to be explored.

What is the outlook regarding HFCs' long-term use? Unlike their cousins the HCFCs, which are slated for phaseout, HFCs do not adversely impact the ozone layer. Apart from a nagging, but in our current understanding a minor, concern about trifluoroacetic acid, for which no removal pathway is currently known, HFC degradation products are not environmentally detrimental. HFCs do contribute to global warming, but with global warming potentials a fraction of the CFC values, because of their significantly shorter atmospheric lifetimes. It is likely that the extent to which global warming is perceived to be a threat, and the extent to which HFCs contribute, will ultimately dictate the long-term fate of HFC use.

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