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The Gas-Phase Decomposition of CF_3OH with Water: A Radical-Catalyzed Mechanism

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CF_3OH is an atmospheric sink for hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs). Several new mechanisms, including catalyzation via H_2O and OH radical, for the decomposition of CF_3OH into HF and CF_2O are studied using ab initio methods. The present work demonstrates that the OH radical has a strong catalytic effect on the transition state for the decomposition of CF_3OH. The barrier is found to be reduced from 45.9 kcal mol^{-1} for the unimolecular decomposition to 11.0 kcal mol^{-1} for decomposition including H_2O and OH.

I. Introduction

Hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs) have recently replaced chlorofluorocarbons (CFCs) as industrial refrigerants and fire suppressants. They are believed to have fewer undesirable effects on the atmosphere as chlorine is the major contributor to ozone depletion.[1−3] Because of the current and future releases of HFCs and HFEs, an understanding of their environmental fate and degradation pathway is important.

Trifluoromethanol (CF_3OH) is a well-known byproduct of HFCs, such as HFC-23, HFC-125, and HFC-134a,[1,4] as well as HFEs such as $CF_2CFHCF_2OCF_3$.[5] CF_3OH is also formed in the oxidation of fluorotelomer alcohols[6,7] and fluorotelomer polymers, such as Teflon and K-fel.[8] It is known that at room temperature, trifluoromethanol quickly degrades into carbonyl fluoride and hydrofluoric acid.[9] However, the effects of trifluoromethanol in the atmosphere are not well-known. The photolytic lifetime of trifluoromethanol below 40 km in the atmosphere is on the million year scale and therefore insignificant.[10] Hydrogen abstraction reactions with reactive atmospheric species, such as OH radicals, which result in the formation of CF_3O radicals (reaction 1) were found to be slow and therefore also inconsequential.[11,12]

$$CF_3OH + OH \rightarrow CF_3O + H_2O \qquad (1)$$

The first suggested atmospheric mechanism, proposed by Francisco[4,13] for trifluoromethanol, is a unimolecular decomposition resulting in carbonyl fluoride (CF_2O) and hydrofluoric acid (HF) (reaction 2)

$$CF_3OH \rightarrow CF_2O + HF \qquad (2)$$

The activation barrier for this reaction is reported to be 45.1 kcal mol^{-1} by Francisco[13] and 42.1 kcal mol^{-1} by Schneider et al.[1] Dixon and co-workers[14] more recently reported a value of 44.1 kcal mol^{-1}. An alternative mechanism proposed by Francisco[13] and investigated by Schneider et al.[1] as well as Young and Donaldson[7] uses water as a catalyst (reaction 3); this utilizes the hydrogen bonding capability of water to bridge the hydrogen and the fluorine of CF_3OH. This process first forms a prereactive complex (reaction 4). The addition of water significantly lowers the activation energy to 17.2 kcal mol^{-1} reported by Schneider et al.[1] and 14.3 kcal mol^{-1} reported by Young and Donaldson[7] with respect to the reactants.

$$CF_3OH + H_2O \rightarrow CF_2O + HF + H_2O \qquad (3)$$

$$CF_3OH + H_2O \rightarrow CF_3OH \cdot H_2O \qquad (4)$$

This activation energy barrier is too large for the reaction to occur spontaneously in the lower atmosphere.

It has been shown by Vöhringer-Martinez et al.[17] that water can catalyze the decomposition reaction of a species with the aid of an OH radical. This study investigates OH radical catalysis to promote the decomposition of a reservoir species in the upper troposphere (reaction 5).

$$CF_3OH \cdot H_2O + OH \rightarrow CF_2O + HF + OH + H_2O \qquad (5)$$

This study also looks at the use of overtone pumping of the OH stretch to promote decomposition of a radical-molecule complex (reactions 6 and 7)

$$CF_3OH \cdot H_2O + OH \rightarrow CF_3OH \cdot OH \cdot H_2O \qquad (6)$$

$$CF_3OH \cdot OH \cdot H_2O + h\nu \rightarrow CF_2O + HF + OH + H_2O \qquad (7)$$

A mechanism involving the excitation of the water complex into an excited state followed by a collisional reaction with the OH radical is also studied (reactions 8 and 9)

$$CF_3OH \cdot H_2O + h\nu \rightarrow CF_3OH \cdot H_2O^* \qquad (8)$$

$$CF_3OH \cdot H_2O^* + OH \rightarrow CF_2O + HF + OH + H_2O \qquad (9)$$

The use of overtone pumping of the OH stretch local mode to promote a reaction has been shown by Vaida et al.,[18] Matthews et al.,[19] Low et al.,[20] as well as Young and Donaldson.[7]

In this article, ab initio studies are used to evaluate the catalytic role that water and OH radicals may play in the decomposition of trifluoromethanol. Overtone pumping as a possible photochemical route for the removal of atmospheric CF_3OH is also considered.

II. Methods

The geometries and frequencies of all of the reactants, transition states, and products are optimized with frozen core second-order Møller-Plesset perturbation theory (MP2), using the 6-31G(d) basis set. All calculations are performed using the GAUSSIAN 03 suite of programs.[21] On the basis of the optimized geometries, single-point energies are calculated using fourth-order Møller-Plesset perturbation theory (PMP4) and the

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TABLE 1: Relative Change in Enthalpy and Activation Barriers[a,b]

	$CF_3OH \rightarrow$ $CF_2O + HF$		$CF_3OH + H_2O \rightarrow$ $CF_2O + HF + H_2O$		$CF_3OH + H_2O + OH \rightarrow$ $CF_2O + HF + H_2O + OH$		$CF_3OH + H_2O + OH \rightarrow$ $CF_2O + HF + H_2O + OH$	
	ΔH_f	ΔE_a	ΔE_a (CX)	ΔE_a (TS)	ΔE_a (CX1)	ΔE_a (TS1)	ΔE_a (CX2)	ΔE_a (TS2)
MP2/6-31G(d)	11.1	43.8	−10.7	13.1	−19.8	3.5	−19.5	1.6
CCSD(T)/6-31G(d)	12.6	46.3	−10.0	16.8	−18.7	8.3	−18.5	5.6
PMP4/6-311++G(2d,2p)	1.6	42.7	−7.0	16.9	−13.2	9.0	−12.5	8.6
CCSD(T)/6-311++G(2d,2p)	3.3	45.4	−10.5	15.6	−16.6	8.0	−16.0	6.9
PMP4/6-311++G(2df,2p)	4.1	43.2	−7.0	17.5	−13.1	9.6	−12.6	9.0
CCSD(T)/6-311++G(2df,2p)	5.7	45.9	−6.9	19.9	−12.9	12.3	−12.4	11.0

[a] The heat of formation and activation barriers are given in units of kcal mol^{-1}. [b] All values are corrected for zero-point energy.

coupled cluster method with single and double excitations with perturbative correction of the triples (CCSD(T)) level of theory with the 6-311++G(2df,2p) basis set. The PMP4 method is used to correct for spin contamination, in addition to checking the convergence with the electron perturbation correction method, because PMP4 uses fourth-order and CCSD(T) uses fifth-order perturbation methods.

The calculation of the OH stretch overtone is achieved by fitting the potential energy curve of the OH stretch to a Morse oscillator. The potential energy curve is created by displacing the OH bond from a range of ±0.4 Å from the equilibrium point in steps of 0.05 Å. This was calculated using quadratic configuration interaction with single and double excitations (QCISD) with the 6-31+G(d,p) basis set. Since the oscillator is being approximated as a Morse oscillator, we can estimate the overtone frequencies as[19]

$$\upsilon = \upsilon\omega_e - (\upsilon^2 + \upsilon)\omega_e\chi_e \tag{10}$$

where υ is the vibrational level and ω_e and $\omega_e\chi_e$ are the vibrational frequency and anharmonicity, respectively. These values can be extracted from the potential energy curve using the following equations[19,20]

$$\omega_e = \frac{\omega_e}{2\pi c} = \frac{\sqrt{f_{ii}G_{ii}}}{2\pi c} \tag{11}$$

$$\omega_e\chi_e = \frac{\omega_e\chi_e}{2\pi c} = \frac{hG_{ii}}{72\pi^2 c}\left(\frac{f_{iii}}{f_{ii}}\right)^2 \tag{12}$$

where f_{ii} and f_{iii} are the second- and third-order force constants for the oscillator, respectively, G_{ii} is the inverse of the reduced mass of the oscillator, h is Planck's constant, and c is the speed of light. Finding the second- and third-order force constants of the potential energy curve is achieved by fitting the ab inito potential energy curve to a seventh-order polynomial and calculating the second- and third-order derivatives numerically. The overtone oscillator strength (f) and the absorption cross section (σ) are calculated from the following expressions[19]

$$f = 4.702 \times 10^{-7}\upsilon_{0\rightarrow\upsilon}|\mu_{0\rightarrow\upsilon}|^2 \tag{13}$$

$$\sigma = 8.85 \times 10^{-13} \times f \tag{14}$$

Here, $\upsilon_{0\rightarrow\upsilon}$ is the transition frequency in wavenumbers and $\mu_{0\rightarrow\upsilon}$ is the transition dipole moment matrix element. The equilibrium constant is calculated by using the thermodynamic data calculated by Gaussian at 298 K (ΔH, ΔS, and C_P). These values are corrected for temperature change using the following equations

$$\Delta H(T_2) = \Delta H(T_1) + \Delta C_p\Delta T \tag{15}$$

$$S(T_2) = S(T_1) + C_p \ln\left(\frac{T_2}{T_1}\right) \tag{16}$$

The rate constants are calculated using gas kinetic theory.[22]

III. Results and Discussions

A. Energetics. The unimolecular decomposition of CF_3OH occurs via a four-member ring transition state. Using the PMP4/6-311++G(2d,2p) level of theory, the activation energy found in this study, 42.7 kcal mol^{-1}, is consistent with the 42.1 kcal mol^{-1} finding by Schneider et al.[1] Computations are performed using larger basis sets and higher levels of theory, up to CCSD(T)/6-311++G(2df,2p), to converge the results, and the TS is found to be 45.9 kcal mol^{-1} (Table 1), which is in agreement with 44.1 kcal mol^{-1} reported by Nguyen et al.[14] at CCSD(T)/CBS. This energy barrier is too high for unimolecular decomposition to occur under lower atmospheric conditions.

The decomposition of CF_3OH with H_2O acting as a catalyst proceeds via a six-member ring transition state (Figure 1b). In this transition state, the oxygen in water abstracts the hydrogen of the alcohol group. Simultaneously, hydrogen from the water attacks the fluorine, yielding HF. The reaction barrier is calculated to be 16.9 kcal mol^{-1} at the PMP4/6-311++G(2d,2p) level of theory, which is consistent with the 17.2 kcal mol^{-1} reported by Schneider et al.[1] Further calculations, up to CCSD(T)/6-311++G(2df,2p), are performed to converge the energy; the transition state has an E_a of 19.9 kcal mol^{-1} (Table 1), which is agreeable with the value reported by Young and Donaldson[7] of 21.5 kcal mol^{-1}. The present work also finds a prereactive complex (Figure 1a) which has a binding energy of 6.9 kcal mol^{-1}. This is in agreement with Schneider et al.[1] as well as Young and Donaldson,[7] who found the complex to be bound by 8 and 7.2 kcal mol^{-1} respectively.

There are two possible configurations of reactants in which the OH radical can promote the decomposition of trifluoromethanol when complexed with water. Each of these configurations has its own respective prereactive complex (CX1,2) and transition state (TS1,2). In the first of these interactions, the hydroxyl radical approaches near the fluorine of the CF_3OH-water complex. The hydrogen on the OH radical interacts with the fluorine as the oxygen hydrogen bonds to water creating an eight-member ring like structure. Both the complex (CX1) and the transition state (TS1) can be seen in Figure 1c and d, respectively. The second configuration has the radical approaching the complex near the alcohol group with the oxygen of the radical hydrogen bonding with the hydrogen of the alcohol group and the hydrogen bonding with the oxygen of water. The prereactive complex (CX2) and the transition state (TS2) can be seen in Figure 1e and f, respectively. Creation of this eight-member ring appears to decrease the steric hindrance that causes the unimolecular and water-catalyzed decompositions to have such high activation energies. This can be seen in the OCF angle in the transition state. As this angle increases going toward the value of the prereactive complex, the activation energy decreases. The effective activation energy, at the CCSD(T)/6-311++G(2df,2p) level of the unimolecular decomposition, without the assistance of water or radical, is 45.9 kcal mol^{-1}.

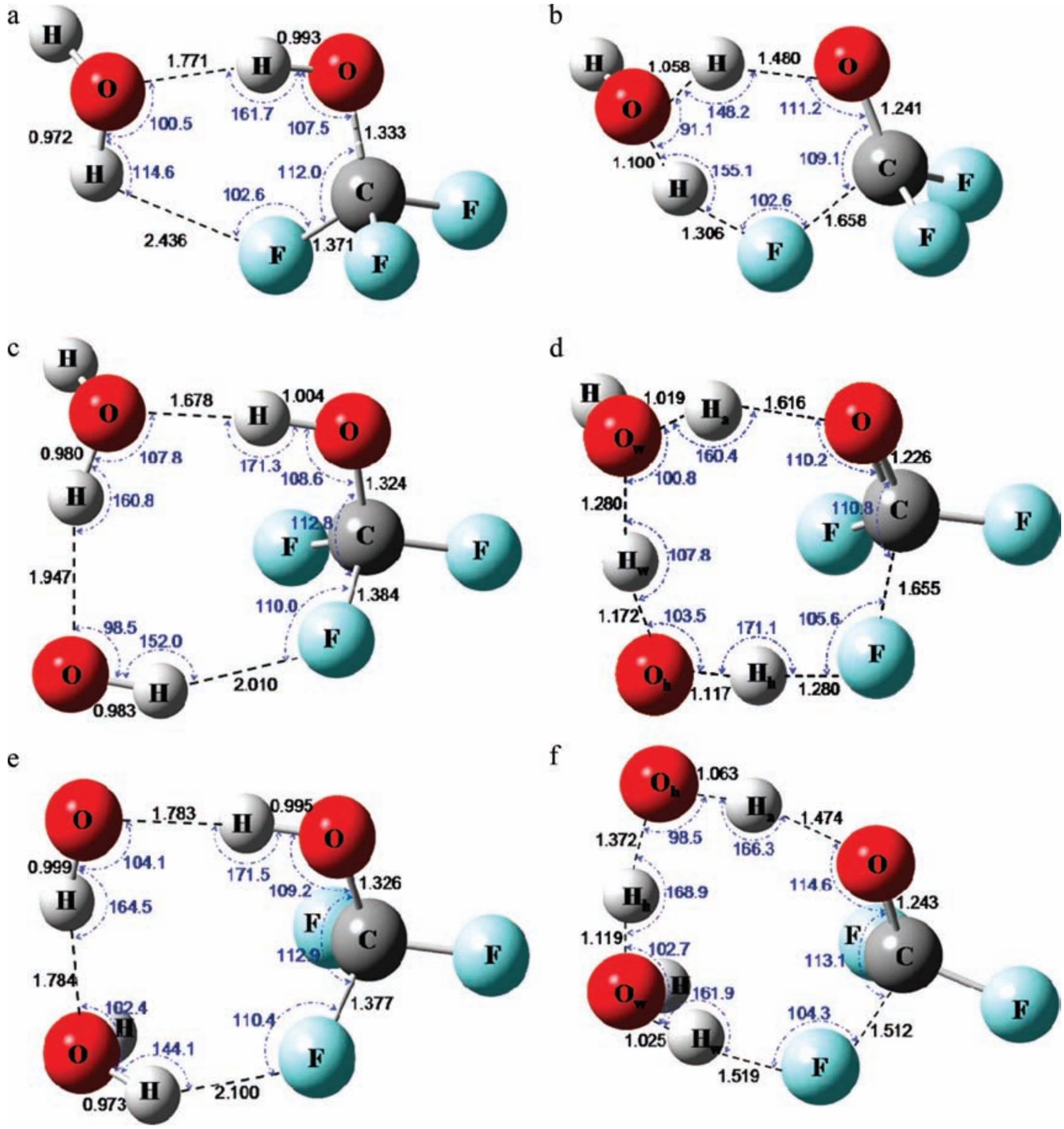

Figure 1. Optimized geometries, in angstroms and degrees, at the MP2/6-31G(d) level for CF_3OH decomposition via (a) the H_2O complex (CX), (b) H_2O catalysis (TS), (c) the H_2O and OH radical complex (CX1), (d) H_2O and OH radical catalysis (TS1), (e) the H_2O and OH radical complex (CX2), and (f) H_2O and OH radical catalysis (TS2). The "a" denotes the alcohol group, "h" denotes the hydroxyl radical, and "w" denotes water.

Adding the water reduces the energy to 19.9 kcal mol^{-1}, whereas the inclusion of the radical drops the energy even lower to 12.3 or 11.0 kcal mol^{-1} for TS1 or TS2, respectively, (Figure 2). This data suggests that a radical-catalyzed reaction is possible for decomposing trifluoromethanol.

B. Photochemistry and Atmospheric Implications. Experimental studies of Molina and co-workers[23] show that CF_3OH is transparent to UV radiation of wavelengths greater than 215 nm. Consequently, UV photodissociation is not an effective mechanism for dissociation of CF_3OH. Moreover, the short-wavelength UV radiation required for excitation and photodissociation is one reason why CF_3OH is environmentally persistent. This study finds the overtone excitation of the OH stretch for CF_3OH (see Table 2), with similar findings to that of Young and Donaldson.[7] It was found that the excitation needed in order to promote dissociation of CF_3OH was $\nu_{OH} = 5$. Young and Donaldson[7] suggest a photodissociation mechanism for the $CF_3OH \cdot H_2O$ complex by excitation into the $\nu_{OH} = 3$ level may be sufficient to induce dissociation. The findings here agree with this claim. However, if CF_3OH was excited to the $\nu_{OH} = 2$ level and subsequently collided with H_2O, sufficient energy would be available for the dissociation to occur as the overtone has a calculated energy of 19.8 kcal mol^{-1}. Another possible mechanism is the excitation of the water complex and subsequent reaction by a OH radical that would allow for dissociation through the $\nu_{OH} = 2$ level. An additional plausible photochemical route occurs via the $CF_3OH \cdot OH \cdot H_2O$ complex, which, at low temperatures, is stable. It is assumed that the difference in excitation energy between $CF_3OH \cdot H_2O$ and the $CF_3OH \cdot OH \cdot H_2O$ will be similar to that between CF_3OH and $CF_3OH \cdot H_2O$. This suggests that the same overtone, $\nu_{OH} = 3$, must be reached to promote dissociation of the $CF_3OH \cdot OH \cdot H_2O$ complex. This vibrational overtone transition suggests that the complex can be excited in the atmosphere by long wavelength solar radiation.[24] More importantly, the complex provides an avenue by which CF_3OH can be decomposed by sunlight-induced photochemistry via vibrational overtone pumping.

To determine atmospheric significance, equilibrium constants have been calculated. From these constants, the percentage of

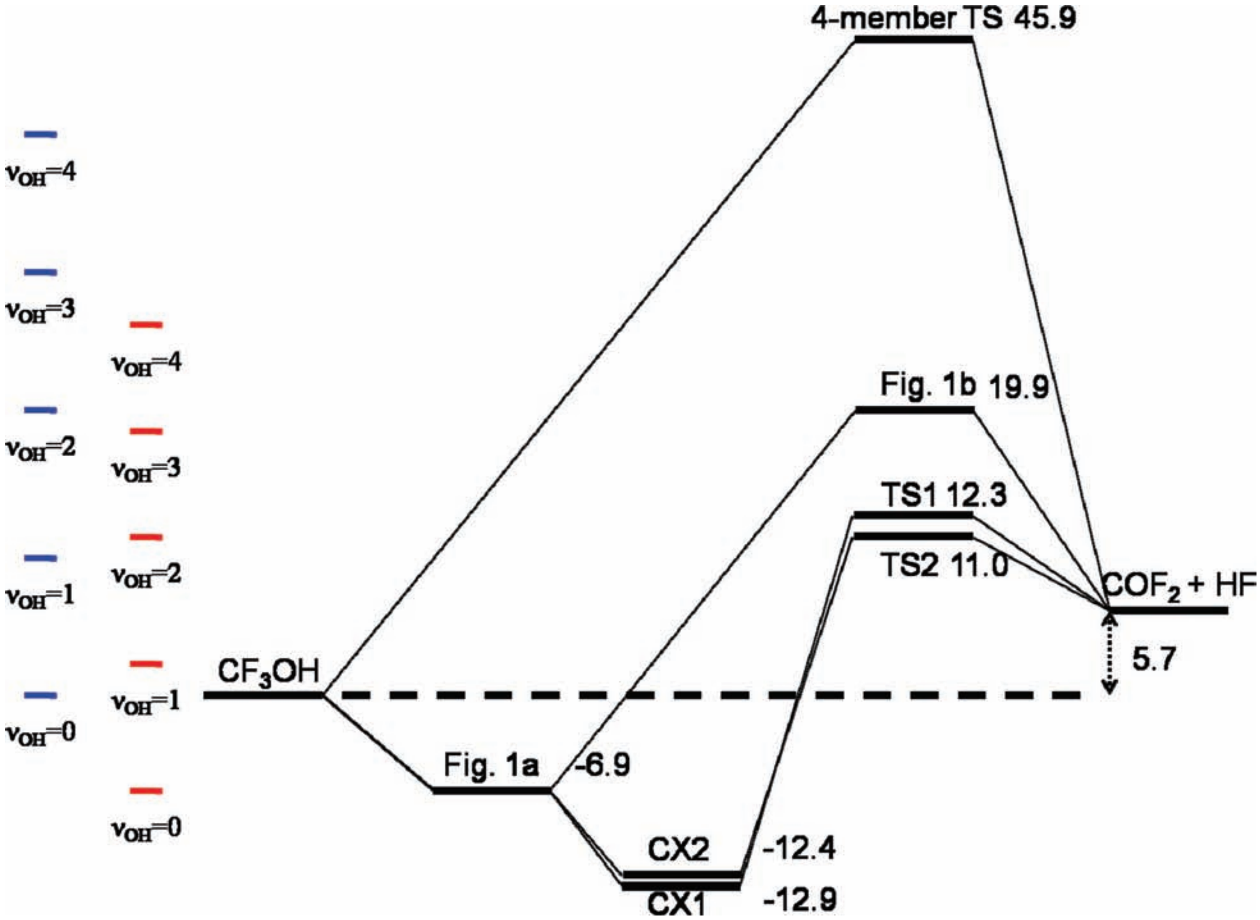

Figure 2. Potential energy diagram for CF_3OH decomposition (energies in kcal mol^{-1} from the CCSD(T)/6-311++G(2df,2p) level of theory; blue denotes CF_3OH overtones calculated at QCISD/6-31+G(d,p), and red denotes $CF_3OH \cdot H_2O$ overtones taken from ref 7).

TABLE 2: OH Stretching Overtones

	CF_3OH					$CF_3OH \cdot H_2O$	
ν	ν_{OH} (cm^{-1})[a]	energy (kcal mol^{-1})	ν_{OH} (cm^{-1})[b]	energy (kcal mol^{-1})	σ (cm^2 $molecule^{-1}$)[c]	ν_{OH} (cm^{-1})[a]	energy (kcal mol^{-1})
1	3669	10.5	3560	10.2	1.8×10^{-5}	3325	9.5
2	6858	19.6	6928	19.8	9.6×10^{-7}	6080	17.4
3	10047	28.7	10104	28.9	5.8×10^{-8}	8835	25.2
4	13075	37.4	13088	37.5	7.7×10^{-9}	11401	32.6

[a] Taken from ref 7. [b] Calculated with QCISD/6-31+G(d,p). [c] Calculated using the overtones calculated in this study[b].

all CF_3OH that will exist in the complex form of $CF_3OH \cdot H_2O$ was also calculated. A previous investigation has shown that 4.4% of all CF_3OH is in the complex form in a tropical setting (303 K and 80% relative humidity), and 1.5% is in an arctic setting (273 K and 50% relative humidity).[7] The smaller binding energy observed with the higher level of theory is consistent with the reported values of Young and Donaldson.[7] In this study, further calculations are carried out to investigate the significance of the newly found complex of $CF_3OH \cdot H_2O \cdot OH$. Given the low concentration of OH radical along with a small binding energy, little or no complex is formed; hence, the photochemistry contribution is minimal, making the $CF_3OH \cdot H_2O \cdot OH$ complex atmospherically insignificant. The species of atmospheric significance is the $CF_3OH \cdot H_2O$ complex.

The plausible mechanisms for CF_3OH decomposition are the overtone excited $CF_3OH \cdot H_2O$ complex subsequently reacting with a OH radical and the overtone excited CF_3OH reacting with water. To better understand the impact that mechanisms involving CF_3OH and H_2O may have on the atmospheric removal of CF_3OH, several factors need to be addressed, specifically, the predissociation of the $CF_3OH \cdot H_2O$ complex after excitation, as well as vibrational and collisional relaxation of both excited CF_3OH and $CF_3OH \cdot H_2O$. Predissociation of the $CF_3OH \cdot H_2O$ complex is not expected to occur as excitation in the OH stretching mode of CF_3OH will be localized, as seen in excitation of the OH stretch in water.[25,26] The rate of collisional reactions are expected to be much faster than the rate of vibrational relaxation of the OH stretch. The estimated rates of the collisional reactions are $k_{CF_3OH+H_2O} = 1.05 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} and $k_{CF_3OH \cdot H_2O+OH} = 1.89 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 303 K. The rate of vibrational relaxation in the OH stretch has been estimated to be the same as the relaxation of the $\nu_{OH} = 2$ stretch of $H_2{}^{18}O$ with argon, $(4.2 \pm 0.9) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}.[27] This will allow sufficient time for a collisional reaction with either water or the OH radical to occur, and neither mechanism will be out competed by vibrational relaxation. Collisional relaxation of the OH stretch excitation is another factor in determining the atmospheric influence of each of these mechanisms. In the upper troposphere, both O_2 and N_2 will provide collisional relaxation for the excited species. The rate constant on the collisional relaxation are estimated to be similar to that of the OH radical stretch, which is known to be $k_{O_2} = (1.1 \pm 0.3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} for relaxation by collisions with O_2 and $k_{N_2} = (6 \pm 2) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} for relaxation by collisions with N_2.[28] These rate constant are several orders of magnitude lower than the rate constant of the collisional reactions. However, the overall rates will not only depend on the rate constants but also on the concentration of reactants O_2 and N_2 competing with H_2O and OH radicals. The number densities of O_2 and N_2 in the upper troposphere are on the order of 10^{18} molecules cm^{-3} compared to the H_2O number density, which is on the order of 10^{14} molecules cm^{-3}; because the reaction rate is several orders of magnitude faster than the relaxation rate, the reaction mechanism will be competitive with the relaxation mechanism. Conversely, the OH radical number density is on the order of 10^6 molecules cm^{-3} with such a small amount of OH radical in the atmosphere; it appears that this photochemical route (reaction 8 and 9) is not significant. However, the photochemical route of excitation of CF_3OH and the subsequent reaction by water is plausible. Since Molina and Molina[23] have shown that the atmospheric photochemical removal of CF_3OH due to UV excitation is small, the significant finding in this study is a potential photodecomposition route for CF_3OH involving long-wavelength radiation, as well as the demonstration of the potential for a radical-catalyzed reaction.

IV. Conclusions

This study shows the catalytic potential of atmospheric radicals. The reduction in the activation energy barrier for the decomposition of CF_3OH is notable. Results from this study suggest a new mechanism for the photochemical decomposition of CF_3OH, the overtone induced excitation of CF_3OH, and subsequent collisional reaction with water. These findings have important ramifications in the atmospheric removal of longer chained perfluorinated alcohols that result from the atmospheric oxidation of extremely persistent perfluorinated materials.[7]

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Supporting Information Available: Complete table of energetics, table of vibrational frequencies, and complete ref 21. This material is available free of charge via the Internet at http://pubs.acs.org.

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