$CF_3CFHO^\bullet$ Radical: Decomposition vs. Reaction with O_2

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Two puzzles are associated with reactions of the CF_3CFHO alkoxy radical: first, the ratio of *A*-factors for the reaction with O_2 and that for decomposition is about 500 times greater than expected; second, decomposition is more favored when the alkoxy radicals are produced by the reaction of peroxy radicals (RO_2) with NO, compared to when they are produced by RO_2 radical disproportionation. Recent experimental evidence suggests that a major fraction of the exothermicity of the reaction RO_2+NO is deposited into vibrational excitation of the alkoxy radical product. A combined electronic structure and kinetic modeling study has been conducted to examine these issues. The results reported here implicate the reaction with O_2 as responsible for the surprisingly large *A*-factor ratio. They also support the notion that significant numbers of vibrationally excited CF_3CFHO alkoxy radicals are produced in the reaction of peroxy radicals with NO and that the radicals subsequently decompose promptly on a nanosecond time scale.

Introduction

Recognition of the adverse effect of chlorofluorocarbon (CFC) release into the atmosphere [1] has led to an international effort to replace CFCs with environmentally acceptable alternatives. While the atmospheric chemistry of such substitutes is generally well established, a few uncertainties remain.

Hydrofluorocarbon 134a (1,1,1,2-tetrafluoroethane) is an important CFC replacement used in automotive air conditioning and domestic refrigeration systems. It is well established that HFC-134a has no impact on stratospheric ozone [2] and has only a modest Global Warming Potential [3]. However, questions have been raised concerning the environmental impact of trifluoroacetic acid that is formed from HFC-134a in the following reaction sequence:

$$CF_3CFH_2 + OH \rightarrow CF_3CFH + H_2O \qquad (1)$$

$$CF_3CFH + O_2 + M \rightarrow CF_3CFHO_2 + M \qquad (2)$$

$$CF_3CFHO_2 + NO \rightarrow CF_3CFHO + NO_2 \qquad (3)$$

$$CF_3CFHO + O_2 \rightarrow CF_3COF + HO_2 \qquad (4)$$

Reaction (4) produces CF_3COF which is hydrolyzed to CF_3COOH after uptake in cloud or groundwater. The concentrations of CF_3COOH expected in rainwater from the degradation of HFC-134a have no known ecological impact. However, at high concentrations ($>5\times10^{-4}$ Molar) CF_3COOH is phytotoxic [4]. It has been suggested that in seasonal wetlands CF_3COOH could accumulate over several decades to levels where ecological impacts may be felt [5]. However, CF_3COOH production is reduced if CF_3CFHO radicals undergo thermal decomposition:

$$CF_3CFHO + M \rightarrow CF_3 + HC(O)F + M \qquad (5)$$

In recent experiments, the competition between reactions (4) and (5) has been investigated and two puzzles have emerged. First, measurements of the k_4/k_5 reaction rate constant ratio obtained in several laboratories are gratifyingly consistent, as long as the CF_3CFHO radicals are produced in the same way, but the ratio differs dramatically when the radicals are produced via disproportionation, rather than via reaction (3):

$$CF_3CFHO_2 + CF_3CFHO_2 \rightarrow 2\,CF_3CFHO + O_2 \qquad (6)$$

This puzzle can be explained if a non-negligible fraction of the nascent CF_3CFHO radicals from reaction (3) possess sufficient internal excitation to undergo prompt decomposition, while radicals produced via reaction (6) do not. Reaction (3) is exothermic by about 17 kcal mol^{-1} based on the calculated heats of formation [6]. Such an exothermicity is consistent with those estimated for the corresponding reactions of other fluorinated peroxy radicals with NO, namely CF_3O_2 (–16.3 kcal mol^{-1} [7]) and CH_2FO_2 (–18.1 kcal mol^{-1} [8, 9]). The barrier to C-C bond scission has been estimated to be only 8–10 kcal mol^{-1} [10–15]. Recent experimental evidence suggests

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that about 60% of the nascent CF_3CFHO radicals have sufficient energy to decompose promptly [16], i.e. sufficiently rapidly that the bimolecular reaction (4) cannot compete. The remaining 40% are thermalized and either react with O_2 via reaction (4), or undergo thermal decomposition via reaction (5).

The effect of prompt decomposition is most easily appreciated by modifying the mechanism consisting of reactions (1–5) by replacing reaction (3) with (3′) and introducing two additional reactions (7) and (8):

$$\mathrm{CF_3CFHO_2 + NO \rightarrow CF_3CFHO^* + NO_2} \qquad (3')$$

$$\mathrm{CF_3CFHO^* \rightarrow CF_3 + HC(O)F} \qquad (7)$$

$$\mathrm{CF_3CFHO^* + M \rightarrow CF_3CFHO + M} \qquad (8)$$

Instead of reaction (3′), concerted decomposition via reaction (3″) might also explain the prompt appearance of decomposition products:

$$\mathrm{CF_3CFHO_2 + NO \rightarrow CF_3CFHO_2NO^* \rightarrow CF_3 + HC(O)F + NO_2} \qquad (3'')$$

However, it seems unlikely that the excited nascent $CF_3CFHO_2NO^*$ will undergo simultaneous fission into three separate fragments: the sequential process involving reactions (3′), (7), and (8) appears to be more likely.

That approximately 60% of the nascent CF_3CFHO radicals may undergo prompt decomposition rather than collisional relaxation is of interest for two reasons. First, current assessments of the yield of $CF_3C(O)F$, and hence CF_3COOH, from the atmospheric degradation of HFC-134a do not account for prompt decomposition and thus may overestimate the CF_3COOH yield by a factor of ≈ 2.5. Second, the conventional wisdom is that chemical excitation of alkoxy radicals formed in the reaction of peroxy radicals with NO does not play a role in atmospheric chemistry. If nascent CF_3CFHO radicals do undergo prompt decomposition, then our view of the atmospheric chemistry of alkoxy radicals may need to be changed fundamentally. To shed light on this issue we use a collision/reaction master equation model to investigate the prompt decomposition pathway for CF_3CFHO radicals under conditions typical of the lower atmosphere. The results are consistent with a significant fraction of the CF_3CFHO radicals produced in reaction (3) decomposing promptly via reaction (7).

The second puzzle is that the k_4/k_5 reaction rate constant ratio for the thermalized radicals is about 500 times larger than expected, based on analogous reactions by other alkoxy radicals. In this work, we use ab initio calculations to show that the transition state for reaction (5) is rather ordinary and we argue that reaction (4) is responsible for the unusual rate constant ratio. If our conclusion is correct, other halogenated alkoxy radicals may react surprisingly rapidly with O_2.

Rate Constants k_4 and k_5 for Thermalized Radicals

The rate constant ratio k_4/k_5 for thermalized CF_3CFHO radicals has been measured by several groups [10–16] and is well described by:

$$\frac{k_4}{k_5} = \left(2.1^{+1.4}_{-0.8}\right) \times 10^{-25} \exp\left(3625 \pm 140/T\right) \mathrm{cm}^3 \qquad (9)$$

The pre-exponential factor in this expression is the ratio of the *A*-factors for reactions (4) and (5), which are known for a number of alkoxy radicals. For non-halogenated alkoxy radicals, A_5, the *A*-factor for reaction (5) is in the range 3×10^{12} to 10^{14} s^{-1}, which is appropriate for a simple bond-fission [17]. For non-halogenated alkoxy radicals, the *A*-factor for reaction (4) is of the order of $A_4 \approx n^H \times 2\times10^{-14}$ cm^3 s^{-1}, where n^H is the number of H-atoms bonded to the carbon adjacent to the alkoxy oxygen atom [18]. Thus, the expected range for A_4/A_5 for the CF_3CFHO radical is 7×10^{-27} to 2×10^{-28} cm^3, which is two to three orders of magnitude smaller than the measured value. Because the rate constants have not been measured individually, it is not possible to identify which reaction is more responsible for the deviation of the measured ratio from the expected one.

Reaction (4) for non-halogenated alkoxy radicals has been suggested to be more complicated than a simple metathesis: the *A*-factor is far too low [19, 20]. Recently, Jungkamp and Seinfeld [21] reported calculations on the reaction of methoxy radicals with O_2 and concluded that the reaction probably occurs via an addition-elimination process:

$$\mathrm{CH_3O + O_2 \leftrightarrow CH_3OOO^*} \qquad (10, -10)$$

$$\mathrm{CH_3OOO^* \rightarrow CH_2O + HO_2} \qquad (11)$$

The lower *A*-factor is the result of the low efficiency of the over-all process. By using the pseudo-steady-state approximation for the intermediate, the over-all rate constant for the reaction with O_2 can be written

$$k = k_{10}\,\frac{k_{11}}{k_{-10} + k_{11}} = \varepsilon k_{10} \qquad (12)$$

where ε is the efficiency of the process. The relative rates of reactions (–10) and (11) depend sensitively on the relative barrier heights, which are small. For CH_3O (and presumably for other nonhalogenated alkoxy radicals), reaction (–10) is much faster than reaction (11) and ε is small [21].

A similar reaction scheme is possible for reaction (4). If halogen substitution lowers or eliminates the barrier for reaction (11) relative to reaction (–10), the efficiency ε will be increased. However, halogen substitution leads to lower efficiencies in some cases [22]. If the *A*-factor for reaction (5) is of the order of 5×10^{13} s^{-1}, then the *A*-factor ratio in Eq. (9) gives $A_4 = 10^{-11}$ cm^3 s^{-1} for the *A*-factor of reaction (4). This value is about what is expected for a simple metathesis reaction and in this case the efficiency must be near unity.

The ab initio calculations reported by Jungkamp and Seinfeld for the CH_3O_3 system were very demanding and yet still have significant error bars. Comparable calculations for the much larger CF_3CFHO_3 system would be far more demanding. The relative rate constants depend sensitively on small differences in energy barriers. It is unlikely that even the highest quality electronic structure calculations possible for CF_3CFHO_3 can determine the energy barriers sufficiently accurately. Thus, we turned our attention to reaction (5) as a candidate for calculations. If the *A*-factor for reaction (5) is within the expected range, then reaction (4) is implicated as responsible for the unusual rate constant ratio.

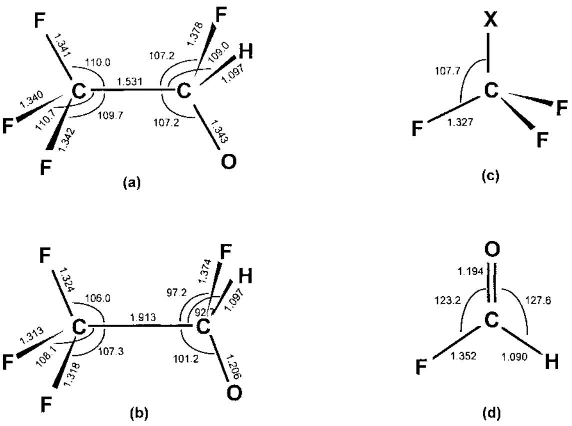

Fig. 1
MP2/6-31G(d,p) optimized structures of CF_3CFHO (a), $[CF_3CFHO]^\ddagger$ (b), CF_3 (c), and HC(O)F (d)

Electronic Structure Calculations

Single reference calculations were performed using the ACESII electronic structure program [23]. The ground-state structures of CF_3CFHO, CF_3, HC(O)F, and of the transition state connecting these, $[CF_3CFHO]^\ddagger$, were determined at the unrestricted Hartree-Fock (HF) and second-order Møller-Plesset (MP2) levels [24] using a 6-31G(d,p) basis set [25]; the MP2 results are reported in Fig. 1. The reactant and product geometries differ little at the HF and MP2 levels and are consistent with those reported previously for related molecules [7, 26, 27]. The structure of the transition state $[CF_3CFHO]^\ddagger$ is expected to be more sensitive to inclusion of electron correlation, although the only notable difference in the HF and MP2 structures is an increase by 0.10 Å in the C–C separation. The approximate spin multiplicty of the MP2 result is 2.091, indicating that spin contamination is not a serious problem. To further ensure that the MP2 results reasonably describe $[CF_3CFHO]^\ddagger$, CASSCF [28, 29] calculations were performed at the MP2 geometry, using the COLUMBUS code [30]. With a 7 electrons in 7 orbitals active space, the HF reference was found to account for 93% of the final CASSCF wavefunction, with no other configuration contributing more than 2%. This result shows that resonance is not important in the transition state, and that the HF reference is adequate for further correlated electron treatments. In addition, the largest contributing configurations outside the HF reference included only single and double excitations into the same orbital, which are adequately dealt with in an MP2 correlation treatment. We conclude that the MP2 structure and potential energy surface of $[CF_3CFHO]^\ddagger$ are sufficiently reliable for providing input parameters to the kinetic models.

Formation of the transition state is accompanied by a lengthening of the C–C bond by almost 0.4 Å and a slight flattening of both the CF_3 and HC(O)F fragments. Vibrational frequencies were determined by two-point numerical differentiation of the MP2 analytical gradients and are reported in Table 1. The presence of a single imaginary frequency (905i cm^{-1}) confirms the identity of the transition state. Rotational constants were calculated from the CF_3CFHO and $[CF_3CFHO]^\ddagger$ MP2 optimized structures, and the reduced moments of internal rotation about the C–C bonds were estimated using standard formulas [31].

Because of the large size and absence of symmetry in CF_3CFHO, an approximate basis set additivity scheme similar to that employed previously [26, 32] was used to improve the calculated energetics of reaction (5). Single-point coupled cluster calculations [CCSD(T), [33]] were performed using a double zeto plus polarization (DZP) basis set [34], and MP2 calculations were performed at the same geometries using the same DZP basis and a larger, triple zeta plus two polarization (TZ2P) basis [35]. The approximate CCSD(T)/TZ2P electronic energies were then constructed using the formula:

$$\begin{aligned} E\,[\mathrm{CCSD(T)/TZ2P}] &\approx E\,[\mathrm{CCSD(T)/DZP}] \\ &+ \{E\,[\mathrm{MP2/TZ2P}] - E\,[\mathrm{MP2/DZP}]\} \end{aligned} \tag{13}$$

The error made in this approximation is –0.3 kcal mol^{-1} for CF_3 and HC(O)F; the error is expected to scale roughly with system size and largely cancel in application to reaction (5). Table 1 contains the relative energies of CF_3CFHO, $[CF_3CFHO]^\ddagger$, and CF_3+HC(O)F at the various levels of theory considered here. Using Eq. (13) and with the inclusion of zero point energy, reaction (5) is found to be slightly endothermic (–0.3 kcal mol^{-1}), in good agreement with available measured [36] and computed [6, 26] heats of formation. The barrier to reaction is estimated to be 10.7 kcal mol^{-1}, slightly larger than that reported in previous, lower-level calculations [27] and than the activation energy inferred from experimental kinetic measurements [10–16]. The final calculated barrier is relatively insensitive to the transition state geometry, e.g. varying by <1 kcal mol^{-1} from the UHF to the MP2 geometry. The barrier calculated here provides a reasonably conservative estimate of the true barrier to reaction (5), and is used directly in the master equation calculations reported below.

Table 1
MP2/6-31G(d,p) rotational and vibrational spectral parameters (cm^{-1}), and relative electronic energies (kcal mol^{-1})

	CF_3CFHO			$[CF_3CFHO]^‡$			CF_3	HC(O)F
Harmonic vibrational frequencies	76.6	222.2	240.5	905.3i	56.7	170.1	504.2	662.8
	372.2	409.4	520.2	205.2	286.7	347.1	504.2	1056.6
	576.7	594.7	708.6	522.4	537.0	626.6	704.5	1122.0
	859.3	1077.1	1153.1	657.0	887.2	1054.7	1126.3	1431.4
	1214.9	1279.8	1330.6	1148.7	1338.0	1376.1	1317.7	1887.0
	1340.6	1396.3	3096.2	1392.5	1673.8	3092.6	1317.7	3211.7
Rotational constants	0.1226	0.0836	0.0690	0.1226	0.0768	0.0648		
Red. internal rotation constant		1.5188			0.6916			
ZPE		23.54			21.98		7.83	13.40
Relative electronic energies								
(1) MP2/DZP		0			+18.12		–3.41	
(2) CCSD/DZP		0			+17.33		+4.56	
(3) CCSD(T)/DZP		0			+15.30		+3.50	
(4) MP2/TZ2P		0			+15.09		–4.89	
(3)+(4)–(2)		0			+12.27		+2.02	
+ZPE		0			+10.7		–0.3	

From the calculated molecular frequencies and moments of inertia presented in Table 1, the rate constant in the high pressure limit for reaction (5) was calculated using canonical transition state theory. Partition functions were calculated using the usual statistical mechanics formulas based on separable vibrations and rigid rotors. The classical barrier height and zero point energies were taken directly from the ab initio results. Scaling of the vibrational frequencies would have little effect on the results, which give

$$k_5 = 4.8 \times 10^{13} \exp(-11.4 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}. \quad (14)$$

This calculated A-factor is completely consistent with experimental results for other alkoxy radical decomposition reactions. Combining with the k_4/k_5 ratio from Eq. (9) scaled (by a factor of 1.4) to the high pressure limit [10, 16], we obtain an unusually large $A_4 \approx 1.4 \times 10^{-11}$ cm^3 s^{-1} and activation energy for reaction (4) of approximately 4 kcal mol^{-1}. Therefore, reaction (4) rather than reaction (5) is implicated as the source of the surprisingly large k_4/k_5 ratio. The likely error ranges of the calculated barrier height, transition state structural parameters, and vibrational frequencies for this level of calculation do not affect this conclusion.

Master Equation Calculations

From the electronic structure calculations and a few auxiliary assumptions, we can construct a model for the unimolecular decomposition of the CF_3CFHO radical. The auxiliary assumptions are needed to account for collisional energy transfer and for the energy distribution of excited radicals produced in reaction (3).

The energy-dependent microcanonical unimolecular rate coefficients, $k(E)$, were calculated according to conventional RRKM theory [37–39] and based on the vibrational model parameters summarized in Table 1. Variations in the vibrational parameters of $\approx 10\%$ (a generous estimate of the uncertainty in the MP2 results) has a negligible impact on the rate coefficients. Densities and sums of states needed for the RRKM rate coefficients and collision step-size probabilities were calculated by exact counts using the Stein-Rabinovitch [40] version of the Beyer-Swinehart algorithm [41] with a grain size of 25 cm^{-1}. The calculations were performed using the stochastic time-dependent Master Equation code described previously [42–45]. Briefly, the Master Equation is solved by the Gillespie Exact Stochastic method [46], which is exact in the limit of an infinite number of stochastic trials. For a finite number of trials, the precision of the calculated result is proportional to $N^{-1/2}$, where N is the number of trials. For each datum in Fig. 2, 1000 trials were used, resulting in statistical imprecision less than the size of the data points.

In the Master Equation code, collisional energy transfer obeys detailed balance and microscopic reversibility. Lennard-Jones parameters for the radical are needed for calculating collision frequencies. In addition, the collision step-size distribution, $P_c(T,E,E')$, must be specified. For this system, the actual energy transfer parameters are unknown and must be estimated. Detailed experimental data and previous master equation simulations are available for deactivation of several benzene and toluene isotopomers [47, 48], as well as for azulene [49] and pyrazine [50, 51]. Considering the free rotor in the CF_3CFHO free radical, it seemed appropriate to use toluene energy transfer parameters for collisions with N_2 [47, 52] to provide an estimate for the step-size distribution function (Table 2).

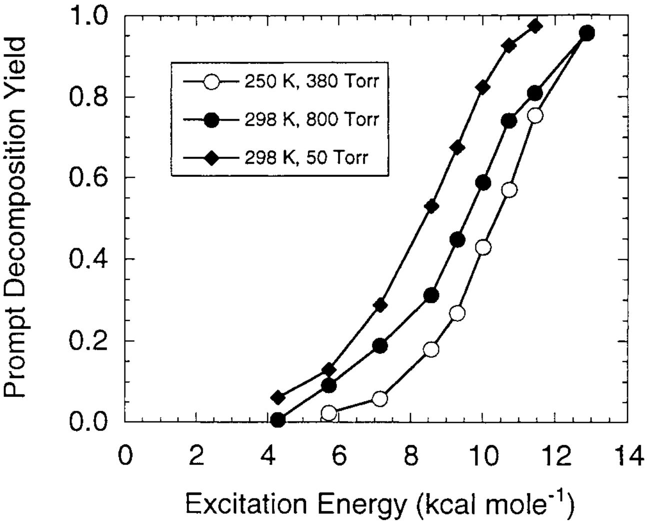

Fig. 2
Calculated fraction of nascent CF_3CFHO radicals that undergo prompt decomposition versus the excitation energy of the nascent CF_3CFHO radicals at: 250 K in 380 Torr total pressure of N_2 (○); 298 K in 800 Torr of N_2 (●); and 298 K in 50 Torr of N_2 (◆)

For present purposes, we used a conventional "exponential" model, because it has been shown to give good descriptions of data from both unimolecular rate coefficient studies [39, 53–55] and relatively "direct" experiments on energy transfer [47, 55–57]. Because the collision parameters are only crudely estimated, we arbitrarily assumed that the Lennard-Jones parameters for CF_3CFHO are $\sigma = 5.5$ Å and $\varepsilon/k = 250$ K, similar to other species of about the same size (Table 2).

The energy distribution of excited CF_3CFHO radicals produced in reaction (3) is unknown, although the exothermicity is about 17 kcal mol^{-1}. In the transition state for reaction (3), there are 27 vibrational degrees of freedom, while there are only 18 vibrations in the CF_3CFHO radical. If energy is distributed according to the ratio of 18/27, then two thirds of the exothermicity, or about 11 kcal mol^{-1}, will be deposited in the nascent radical. Furthermore, there should be a distribution of energies deposited in the radicals. Because the tabulated thermochemical data are probably uncertain by several kcal mol^{-1} and the distribution of energy deposited in the CF_3CFHO radicals is unknown, we adopted the following approach. We assumed that the distribution of excited radicals is described by a Boltzmann distribution at the ambient temperature, but displaced to higher energy due to the partitioning of energy between the CF_3CFHO radical and NO_2 in reaction (3). We considered using a delta function for the population distribution, but the thermal model is probably somewhat more realistic. We investigated the prompt dissociation yield by arbitrarily varying the nominal amount of vibrational excitation energy in the radical. We could have also varied the dissociation threshold, but the calculated threshold energy (i.e. transition state barrier) is already roughly consistent with experiments [16]. Adjusting the threshold energy within reasonable bounds results in small quantitative changes but does not alter our qualitative results and conclusions.

Table 2
Collision parameters

Estimated Lennard-Jones Parameters	σ (Å)	ε/k (K)
N_2	3.74	82
CF_3CFHO	5.5	250
net:	4.62	143
Collision Rate Constant (298 K)	4.39×10^{-10} cm^3 s^{-1}	
Exponential Model Parameters	$a(E) = 39.3 + 0.0159E - 2.63\times10^{-7}E^2$ [Based on Toluene+N_2; Ref. [52]]	

Decomposition yields were calculated for various assumed combinations of temperature, pressure, and excitation energy. Representative curves are presented in Fig. 2. The curves corresponding to 298 K show the sensitivity of the calculated decomposition yields to a sixteen-fold change in pressure. As seen in Fig. 2, the calculated yields are moderately sensitive to temperature. At 5.5 km altitude in the US Standard Atmosphere the temperature is 250 K and the pressure is 380 Torr. As seen from Fig. 2, the calculated prompt decomposition yields are similar for conditions representative of the surface and 5.5 km altitude.

It should be stressed here that the prompt decomposition yields given in Fig. 2 are the calculated fractions of excited CF_3CFHO radicals that decompose promptly. For example, given an initial excitation energy of 10 kcal mol^{-1} the calculations suggest that 60% of the CF_3CFHO radicals decompose promptly. The remaining 40% are thermalized by collisions with the bath gas (N_2). The thermalized radicals either react with O_2 via reaction (4) or undergo thermal decomposition via reaction (5). The overall fraction of CF_3CFHO radicals that decompose is determined by those that undergo prompt decomposition plus those that undergo thermal decomposition. Those radicals that undergo prompt decomposition do so on a time scale less than 10^{-9} s: they experience few if any collisions prior to decomposition. The lifetime of the thermalized CF_3CFHO radicals is much longer (on the order of 10^{-3} to 10^{-4} seconds [58, 59]).

From the HC(O)F and $CF_3C(O)F$ product yields observed after UV irradiation of HFC-134a/Cl_2/O_2/N_2/NO mixtures, Wallington et al. [16] inferred that in 800 Torr of N_2, at 243, 263, and 295 K, the fraction of alkoxy radicals from reaction (3) that undergo prompt decomposition is 0.57±0.05, 0.59±0.05, and ($0.64^{+0.12}_{-0.23}$), respectively. Variation of the total pressure over the range 120–1100 Torr at 243 and 263 K had little (0–15%) effect on the fraction of alkoxy radicals that undergo prompt decomposition [16]. As seen from Fig. 2, the calculated yields agree with the experimental yields, when the excitation energy is in the range of about 9 to 11 kcal mol^{-1}, in good agreement with simple statistical partitioning of the exothermicity of reaction (3). Since the calculated bond threshold energy is only approximate and the energy transfer parameters are only rough estimates, the good quantitative agreement with simple statistical energy partitioning may be fortuitous, but it clearly demonstrates the plausibility of the physical model.

The model results are slightly more sensitive to temperature and total pressure than the experimental observations. However, given the experimental uncertainties and assumptions inherent in the models we believe that these small differences are not significant. If the assumed threshold energy was lowered (closer to experimentally inferred values) the excited free radicals would have a shorter average lifetime and the sensitivities would be reduced. In summary, the theoretical calculations are consistent with the available experimental data which suggest that prompt decomposition of excited nascent CF_3CFHO radicals is important [16].

Implications for Atmospheric Chemistry

The modeling results reported here support two main conclusions. First, thermalized CF_3CFHO radicals react with O_2 at rates considerably higher than expected on the basis of non-halogenated alkoxy radicals. Second, vibrational excitation in CF_3CFHO radicals produced in reaction (3) is likely sufficient to open up a prompt decomposition channel. When combined with the experimental observations reported elsewhere [16], we believe that there is compelling evidence that prompt decomposition of excited nascent CF_3CFHO radicals limits the formation of $CF_3C(O)F$, and hence CF_3COOH, in the atmospheric degradation of HFC-134a. This effect is substantial: assessments of the yield of CF_3COOH which ignore the prompt decomposition of excited nascent CF_3CFHO radicals overestimate the yield of CF_3COOH by a factor of 1.8–4.0 [16].

The atmospheric oxidation of all organic compounds proceeds via the formation of peroxy radicals. Chemical activation of alkoxy radicals formed from reactions of peroxy radicals with NO may be an important consideration in the degradation mechanism of some of these organic compounds. For chemical activation to impact the atmospheric fate of an alkoxy radical there must be at least two competing loss mechanisms for the alkoxy radical, one of which must be a unimolecular decomposition reaction with a modest barrier. Experimental evidence has been presented suggesting that chemical activation is important in the atmospheric fate of CF_3CF_2CFHO [60], CBr_2ClO [61], $HOCH_2CH_2O$ [62] and CH_2ClO [63] radicals. Further experimental and computational work is needed to clarify and quantify the role of chemical activation in the atmospheric chemistry of non-halogenated alkoxy radicals.

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