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Unimolecular Decomposition of the FCO Radical

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The kinetics of the unimolecular decomposition of the FCO radical has been studied experimentally in a heated tubular flow reactor coupled to a photoionization mass spectrometer. Rate constants for the decomposition were determined in time-resolved experiments as a function of temperature (951−1051 K) and bath gas density ($(6-12) \times 10^{16}$ molecules cm^{-3}) in two bath gases—He and N_2. The rate constants are in the low-pressure limit under the conditions of the experiments and can be described by the following expressions: $k°_1(\mathrm{He}) = 10^{-8.74\pm0.28} \exp(-(14169 \pm 653\ \mathrm{K})/T)$ cm^3 molecule^{-1} s^{-1} (from the fitting of experimental data) and $k°_1(N_2) = 10^{-8.71} \exp(-14154\ \mathrm{K})/T)$ cm^3 molecule^{-1} s^{-1} (evaluated from comparison of data obtained in nitrogen and helium bath gases). The thermochemistry of the reaction was analyzed on the basis of the data available in the literature and those obtained in the current study. An upper limit estimate was obtained for the rate constant of the reaction of FCO radicals with O_2 at the temperature of 800 K: $k(\mathrm{FCO}+O_2\rightarrow\mathrm{products}) \leq 4 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}.

I. Introduction

FCO radicals are recognized as important intermediates in the oxidation of fluorinated hydrocarbons.[1,2] Unimolecular decomposition (together with the reaction with H atoms) is a major pathway of destruction of FCO radicals in the combustion environment. Recent extensive modeling studies[2] of detailed kinetics of the oxidation of fluorinated hydrocarbons (potential industrial flame suppressants) indicate the importance of the reaction

$$\mathrm{FCO} + \mathrm{M} \rightarrow \mathrm{F} + \mathrm{CO} + \mathrm{M} \qquad (1)$$

in the overall mechanism of combustion. It has been shown that the predicted flame-inhibiting ability of fluorinated hydrocarbons depends on the rate constant of reaction 1. At the same time, no experimental data are available on the rate constant of reaction 1.

The reverse reaction,

$$\mathrm{F} + \mathrm{CO} + \mathrm{M} \rightarrow \mathrm{FCO} + \mathrm{M} \qquad (-1)$$

has been studied only at room temperature,[3−5] and results of different groups differ by as much as a factor of 3. Values of k_1 estimated[2] from the thermochemistry of reaction (1,−1) with an assumed absence of an energy barrier in reaction −1 are highly uncertain due to a large uncertainty in the heat of formation of the FCO radical (refs 2 and 6, and references cited therein).

In the current study we present the first direct determination of the rate constants of the unimolecular decomposition of the FCO radical, reaction 1. Rate constants were measured at two densities of He ($[\mathrm{He}] = (6-12) \times 10^{16}$ atoms cm^{-3}) and one density of N_2 ($[N_2] = 9 \times 10^{16}$ molecules cm^{-3}) in the temperature range 951−1051 K. The thermochemistry of the reaction (1,−1) was analyzed on the basis of the data available in the literature. In addition, an upper limit estimate was obtained for the reaction of FCO radicals with O_2 at the temperature of 800 K.

II. Experimental Study

Details of the experimental apparatus[7] and procedures[8] used have been described before and so are only briefly reviewed here. FCO radicals were produced homogeneously at elevated temperatures in a heatable quartz tubular reactor by pulsed laser photolysis and their unimolecular decay subsequently monitored in time-resolved experiments using photoionization mass spectrometry. Pulsed unfocused 193- or 248-nm radiation (≈4 Hz) from a Lambda Physik EMG 201MSC excimer laser was directed along the axis of a heatable quartz reactor (1.05-cm i.d.) coated with boron oxide.[9] Gas flowing through the tube at ≈4 m s^{-1} contained the radical precursor (<3%) and the inert carrier gas (He or N_2) in large excess (>97%). The flowing gas was completely replaced between laser pulses.

FCO radicals were produced by the pulsed, 193- or 248-nm laser photolysis of acetyl fluoride:

$$\mathrm{CH_3COF} \xrightarrow{h\nu} \mathrm{CH_3} + \mathrm{FCO}$$
$$\rightarrow \text{other products}$$

Initial conditions (precursor concentration and laser intensity) were selected to provide low radical concentrations ($\leq 10^{11}$ molecules cm^{-3}, estimated from the observed appearance of a second-order contribution to the radical decay with an increased radical precursor concentration and laser intensity. The value of 10^{-11} cm^3 molecule^{-1} s^{-1} was taken as a lower limit for the radical−radical reaction rate constants). Under these conditions reactions between radical products (including FCO + FCO and FCO + CH_3) had negligible rates compared to that of the unimolecular decomposition of the FCO radicals.

Gas was sampled continuously through a conical hole (0.043-cm diameter at the inside of the reactor) in the side of the reactor and formed into a beam by a skimmer before the gas entered the vacuum chamber containing the photoionization mass spectrometer. As the gas beam traversed the ion source, a portion was photoionized and then mass selected by a quadrupole mass filter. FCO radicals were ionized using the light from an argon resonance lamp (11.6−11.9 eV) with a LiF window. While a lower-energy resonance lamp (hydrogen lamp, MgF_2 window, 10.2 eV) could be used to detect FCO radicals (IP-

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(FCO) = 9.3 ± 0.1 eV [6]), a sensitivity sufficient for kinetic measurements was achieved only with the higher-energy argon lamp. Temporal ion signal profiles (at $m/e = 47$, corresponding to FCO^+) were recorded on a multichannel scaler from a short time before each laser pulse up to 20 ms following the pulse. Data from 1000 to 6500 repetitions of the experiment were accumulated before the data were analyzed. The number of repetitions and, therefore, the sensitivity of FCO detection were limited by the rapid loss of the LiF window transparency due to the vacuum UV irradiation and exposure to the microwave discharge of the lamp.[10] This limited the range of bath gas densities used in these experiments, since the already poor sensitivity to FCO detection declined substantially outside the $6 \times 10^{16} \leq [\mathrm{He}] \leq 12 \times 10^{16}$ atoms cm^{-3} range.

The gases used were obtained from Aldrich (acetyl fluoride, 99%) and Matheson (He, >99.995%; N_2, >99.998%; O_2, >99.6%). Acetyl fluoride was purified by vacuum distillation prior to use. Helium, nitrogen, and oxygen were used as provided. Potential reactions of FCO with impurities contained in the bath gas could not significantly affect the kinetics of reaction 1 unless these reactions had rate constants higher than 10^{-12} cm^3 molecule^{-1} s^{-1}, which is unlikely considering the general low reactivity of FCO with stable molecules.[2]

The FCO ion signal profiles were fit to an exponential function ($[\mathrm{FCO}]_t = [\mathrm{FCO}]_0 e^{-k't}$) using a nonlinear least-squares procedure. Experiments were performed to establish that the decay constants did not depend on the concentration of precursor (provided that the concentration was kept low enough to ensure that radical−radical reactions had negligible rates) or the laser wavelength and intensity. The exponential decay constants depended only on temperature and bath gas density.

Unimolecular decay of FCO was observed only above 800 K. Below this temperature a slow decay of FCO is observed due to a first-order heterogeneous wall-loss process:

$$\mathrm{FCO} \rightarrow \text{heterogeneous loss} \qquad (2)$$

Above 800 K the decay constant increased rapidly with rising temperature due to the increasing importance of the thermal decomposition of FCO radical, reaction 1. The decay constants were analyzed assuming that FCO radicals were consumed only by two elementary reactions, (1) and (2). At low temperatures, only the heterogeneous loss is observed ($k' = k_2$). Above 800 K the sum of the two loss processes is observed ($k' = k_1 + k_2$).

Calculations of k_1 from measurements of k' require knowledge of k_2 above 800 K. While k_2 was directly determined below 800 K (18−49 s^{-1}, independent of temperature), it could not be measured above this temperature due to the additional loss of radicals by unimolecular decomposition. Values of k_2 above 800 K needed to determine k_1 from the measurements of k' were obtained by an extrapolation assuming that k_2 retains its temperature independence beyond 800 K up to the highest temperature of this study, 1051 K. To minimize possible errors in the determination of k_1 caused by this assumed temperature independence of k_2 above 800 K, experiments to obtain k_1 were conducted at temperatures sufficiently high to assure that $k' \geq 3k_2$. It was this criterion that established the lowest temperature used to determine k_1 at each bath gas density. The highest temperature used at each total gas density was determined by the fact that decay constants above 350 s^{-1} could not be measured accurately.

The results of all of the experiments and the conditions used to determine k_1 are given in Table 1. The unimolecular rate constants for reaction 1 obtained from these sets of experiments conducted at two different helium densities (6×10^{16} and 12×10^{16} atoms cm^{-3}) are shown in Figure 1. Estimated uncertainties in the k_1 determinations vary from ±10% in the middle of the temperature range to ±20% at the extreme temperatures used. The FCO detection sensitivity was lower when nitrogen was used as a bath gas and k_1 values in this case could be determined only under optimal conditions. Therefore, only a limited set of data at one density of nitrogen ($[N_2] = 9 \times 10^{16}$ molecules cm^{-3}) was obtained.

Experiments were performed to check for a possible high-temperature reaction of FCO radicals with molecular oxygen. At 800 K, addition of up to 3.5×10^{16} molecules cm^{-3} of O_2 yielded no significant increase in the apparent FCO decay constant, k', compared to the wall rate, k_2. This provided an

TABLE 1: Conditions and Results of Experiments To Measure the Unimolecular Rate Constants (k_1) of the Thermal Decomposition of FCO Radicals in He and N_2 as Bath Gases

10^{-16}[M] (molecules cm^{-3})	T (K)	10^{-14}[CH_3COF] (molecules cm^{-3})	I^a	k_2^b (s^{-1})	k_1 (s^{-1})
		He as Bath Gas			
6.12	951	5.2	32	18.3	41.6
6.12	971	5.2	32	18.3	52.4
6.11	1001	5.1	32	18.3	80.6
6.11	1011	12.1	34	43.7	99.4
6.12	1021	5.2	32	18.3	105.5
6.11	1051	12.1	34	43.7	159.1
12.23	951	4.9	38	23.5	68.7
12.25	971	4.9	38	23.5	105.7
12.25	981	29.4	18	40.3	120.6
12.25	981	29.4	7.4	34.5	104.6
12.28	981	12.5	6.5^c	48.6	110.8
12.25	991	4.9	38	23.5	151.6
12.24	991	5.2	35	20.1	119.0
12.20	1011	5.2	35	20.1	190.9
12.24	1021	29.3	18	40.3	181.8
12.25	1021	12.4	6.5^c	48.6	206.1
12.25	1031	5.2	35	20.1	247.9
12.23	1051	29.3	18	40.3	295.2
		N_2 as Bath Gas			
9.23	966	12.7	34	31.4	75.8
9.22	986	12.7	34	31.4	113.4
9.22	1006	12.7	34	31.4	136.2

[a] Photolyzing laser intensity (mJ cm^{-2} pulse^{-1}). [b] Determined experimentally at T = 800 K. [c] 193-nm photolysis was used (248-nm photolysis was used in all other experiments).

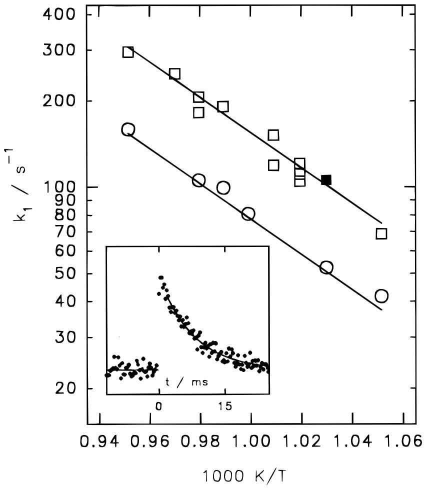

Figure 1. Plot of FCO unimolecular rate constants (k_1 vs (1000 K)/T) for two He densities: lines, result of the low-pressure-limit Arrhenius fit, formula I; circles, [He] ≈ 6×10^{16} atoms cm^{-3}; squares, [He] ≈ 12×10^{16} atoms cm^{-3}. The insert shows the recorded FCO decay profile for the conditions of the filled square: [He] = 12.25×10^{16} atoms cm^{-3}; T = 971 K; k' = 129.2 s^{-1}.

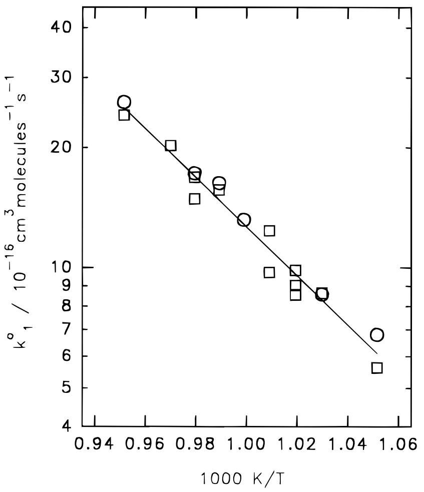

Figure 2. Same as Figure 1 displayed as bimolecular rate constants k_1/[He]. Symbols and line have the same meaning as those in Figure 1.

upper limit estimate for the rate constant $k(\mathrm{FCO}+\mathrm{O_2}\rightarrow\mathrm{products}) \le 4 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at $T = 800$ K.

III. Results and Discussion

The determinations of k_1 reported here provide the first direct measurements of this unimolecular rate constant. The results indicate that, under our experimental conditions, all measurements were in the second-order low-pressure-limit region. This can be seen in Figure 2, where the second-order rate constants $k^\circ_1 = k_1$/[He] are plotted. There is a good convergence of the k°_1 values obtained at two different helium densities used in the experiments: 6×10^{16} and 12×10^{16} atoms cm^{-3}. These second-order rate constants were fitted to the Arrhenius expression

$$k^\circ_1 = 10^{-8.74\pm0.28} \exp(-(14169 \pm 653\ \mathrm{K})/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \tag{I}$$

which provides values for the low-pressure-limit rate constant k°_1 in helium bath gas over the experimental temperature range of the current study, 951−1051 K. Error limits are 1σ and do not include possible systematic errors.

The experimental data on the rate constant of reaction 1 obtained with nitrogen as bath gas consist of only three values of k_1 measured at $[\mathrm{N_2}] = 9 \times 10^{16}$ molecules cm^{-3} and three temperatures, 966, 986, and 1006 K. This amount of data does not provide a reliable determination of the temperature dependence of k°_1 in N$_2$. Arrhenius parameters for reaction 1 in nitrogen can be obtained, however, by comparing the experimental values of k°_1 determined in helium (k°_1(He)) and nitrogen (k°_1(N$_2$)) bath gases within the framework of formula II for a low-pressure-limit rate constant in the case of a double-exponential model of the collisional energy transfer in the weak collision limit:[11]

$$k^\circ_1 \approx -\langle \Delta E\rangle_{\mathrm{all}} Z_0(T)\,\frac{\rho(E_0)}{Q(T)}\exp\left(-\frac{E_0}{RT}\right) \tag{II}$$

Here $\rho(E_0)$ is the density of states in active degrees of freedom of FCO at an energy equal to the barrier height E_0, $Q(T)$ is the partition function of the active degrees of freedom, $Z_0(T)$ is Lennard-Jones collision frequency, and $\langle \Delta E\rangle_{\mathrm{all}}$ is the average energy transferred per collision with bath gas in both upward and downward collisions (assumed here to be independent of temperature). Calculating $\rho(E)$ and $Q(T)$ using known geometry and vibrational frequencies[12] of FCO, one can obtain the values of $\langle \Delta E\rangle_{\mathrm{all}}$ and E_0 from fitting experimental data on $k^\circ_1(T)$. The results depend on whether all external rotational degrees of freedom are treated as adiabatic or one is treated as active. If only three vibrational degrees of freedom are considered as active, the obtained parameters are as follows: $E_0 = 125.3$ kJ mol^{-1}, $\langle \Delta E\rangle_{\mathrm{all}} = -279$ cm^{-1} ($\rho(E_0) = 6.6 \times 10^{-2}$ cm). If the active degrees of freedom include these three vibrations and one external rotation with the lowest moment of inertia, the obtained parameters are as follows: $E_0 = 129.5$ kJ mol^{-1}, $\langle \Delta E\rangle_{\mathrm{all}} = -191$ cm^{-1} ($\rho(E_0) = 2.6$ cm).

According to formula II,

$$\frac{k^\circ_1(N_2)}{k^\circ_1(He)} = \frac{\langle \Delta E\rangle_{\mathrm{all}}(N_2)\ Z_0(N_2)}{\langle \Delta E\rangle_{\mathrm{all}}(He)\ Z_0(He)}$$

Using the experimental k°_1(He) vs T dependence given by formula I, we can fit the experimental values of k°_1(N$_2$) to estimate $\langle \Delta E\rangle_{\mathrm{all}}(\mathrm{N_2}) = -407$ cm^{-1}, if only three vibrational degrees of freedom are considered as active, or $\langle \Delta E\rangle_{\mathrm{all}}(\mathrm{N_2}) = -279$ cm^{-1}, if one rotational degree of freedom is also treated as active. This results in the Arrhenius dependence of the low-pressure-limit rate constant of reaction 1 in nitrogen bath gas:

$$k^\circ_1(\mathrm{N_2}) = 10^{-8.71} \exp(-(14154\ \mathrm{K})/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

The density-of-states functions, $\rho(E)$, were calculated here using the modified Beyer−Swinehart algorithm[13] for harmonic oscillators and rigid rotors. Lennard-Jones collisional parameters for the FCO radical ($\sigma = 3.84$ Å, $\epsilon/k = 230$ K—taken to be the same as that for CF$_2$O) were calculated from boiling point and additive volume increments.[14] The values of $-\langle \Delta E\rangle_{\mathrm{all}}$ obtained here are noticeably higher than typical values obtained in other studies of unimolecular decomposition of free radicals (e.g., $\langle \Delta E\rangle_{\mathrm{all}}(\mathrm{He}) = -28$ cm^{-1} and $\langle \Delta E\rangle_{\mathrm{all}}(\mathrm{N_2}) = -40$ cm^{-1} for n-C$_4$H$_9$ decomposition,[15] $\langle \Delta E\rangle_{\mathrm{all}}(\mathrm{He}) = -74$ cm^{-1} and $\langle \Delta E\rangle_{\mathrm{all}}(\mathrm{N_2}) = -117$ cm^{-1} for C$_2$H$_3$ decomposition,[16] $\langle \Delta E\rangle_{\mathrm{all}}$(He and N$_2$) $= -45$ cm^{-1} for HCO decomposition,[17] see also ref 18 for other data on typical values of $\langle \Delta E\rangle_{\mathrm{all}}$). The values of $-\langle \Delta E\rangle_{\mathrm{all}}$ obtained here for FCO are likely to be overestimated due to not accounting for the effects of anharmonicity on the density-of-states function of FCO (e.g., Troe[19] has shown that including anharmonicity effects results in a factor of 3 increase in the calculated vibrational density of states of $\mathrm{NO_2}(\tilde{X}^2A_1)$ at an energy equal to the dissociation threshold). Taking anharmonicity into account is likely to increase the calculated density of states and, hence, result in lower fitted values of $-\langle \Delta E\rangle_{\mathrm{all}}$. These values of $\langle \Delta E\rangle_{\mathrm{all}}$ and E_0 can be treated only as approximate because formula II does not account for the effects associated with angular momentum conservation. The reverse reaction −1, addition of F atoms to CO, is, most probably, barrierless. High-level ab initio calculations[20] yield the energy of the "transition state" which is lower than the energy of reactants (F + CO) by 8 kJ mol^{-1} at the G2[21] level and 47 kJ mol^{-1} at the BAC-MP4[22] level. Therefore, a more rigorous treatment would include a variational selection of the transition state and explicit consideration of angular momentum conservation. Unfortunately, such a treatment requires detailed knowledge of the potential energy surface which is currently unavailable.

Reaction −1 has been studied at room temperature by three groups[3−5] who obtained significantly divergent values of k_{-1}. As checked by the simplified master equation[23] calculations conducted in the current study, the conditions of all three studies were close to the low-pressure limit. From the results of Appelman and Clyne,[3] Arutyunov et al.,[4] and Wallington et al.[5] the room temperature values of $k°_{-1} = k_{-1}/[M]$ (cm^6 molecule^{-2} s^{-1}) = 3.4×10^{-32} (He),[3] 6.3×10^{-32} (He),[4] 6.9×10^{-32} (N_2)[4], and 2.4×10^{-32} (N_2)[5] can be obtained (bath gas is indicated in parentheses). In all three studies high ($\geq 10^{14}$ atoms cm^{-3}) initial concentrations of F atoms were employed which resulted in potentially significant contributions of secondary reactions. Only Wallington et al.[5] applied kinetic modeling to account for these contributions. We, therefore, select the value of $k°_{-1}(N_2) = 2.4 \times 10^{-32}$ cm^6 molecule^{-2} s^{-1} obtained from the data of these authors for further use.

This information, together with the rate constant of reaction 1 extrapolated (via formula I) to room temperature ($\log(k°_1(\mathrm{He})/(\mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1})) = -29.38 \pm 1.33\ (2\sigma)$) can be used to estimate the enthalpy of reaction (1,−1). Neglecting the difference between the rate constants obtained in helium and nitrogen bath gases (compared to the large uncertainty of extrapolation), we obtain from the values of $k°_1$(He), $k°_{-1}(N_2)$, and the known entropies[12] of FCO, F, and CO

$$\Delta H°_{298}(\mathrm{FCO} \rightarrow \mathrm{F+CO}) = 130.1 \pm 7.6\ \mathrm{kJ\ mol^{-1}} \quad \text{(III)}$$

This value, together with the known thermochemistry of F and CO,[12] results in

$$\Delta H_f°_{298}(\mathrm{FCO}) = -161.2 \pm 8.1\ \mathrm{kJ\ mol^{-1}} \quad \text{(IV)}$$

Formulas III and IV were obtained using a linear extrapolation (in Arrhenius coordinates) of experimental values of $k°_1$ to room temperature. In reality, low-pressure-limit rate constants of unimolecular decomposition reactions are likely to exhibit a negative temperature dependence of the preexponential factor. The effect of such a dependence would be a lower extrapolated value of $k°_1$(298K), higher $\Delta H°_{298}(\mathrm{FCO} \rightarrow \mathrm{F+CO})$, and lower heat of formation of the FCO radical. Therefore, only the lowest possible value given by formula III and the highest possible value given by formula IV are meaningful, thus providing estimates of the lower limit of

$$\Delta H°_{298}(\mathrm{FCO} \rightarrow \mathrm{F+CO}) \geq 122.5\ \mathrm{kJ\ mol^{-1}} \quad \text{(V)}$$

and the upper limit of

$$\Delta H_f°_{298}(\mathrm{FCO}) \leq -153.1\ \mathrm{kJ\ mol^{-1}} \quad \text{(VI)}$$

These estimates are in agreement with the latest determination of the enthalpy of reaction (1,−1) by Buckley et al.[6] ($\Delta H°_{298}(\mathrm{FCO} \rightarrow \mathrm{F+CO}) = 121 \pm 12$ kJ mol^{-1}) and with BAC-MP4 ($\Delta H_f°_{298}(\mathrm{FCO}) = -182.9 \pm 7.4$ kJ mol^{-1})[24] and G2(MP2) ($\Delta H°_{298}(\mathrm{FCO} \rightarrow \mathrm{F+CO}) = 145.1$ kJ mol^{-1})[20] calculations.

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