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The reaction of atomic fluorine with formyl fluoride: An experimental and theoretical study

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The rate coefficient for the reaction of F + HFCO has been determined over the temperature range 298-368 K by monitoring the appearance rate of HF infrared chemiluminescence using the infrared multiphoton dissociation-infrared chemiluminescence technique. Results, expressed in the Arrhenius form $k(T) = 4.4 \pm 2.6 \times 10^{-11} \exp[-1800 \pm 400/RT]$ cm³ molecule⁻¹ s⁻¹, are compared with the barrier height calculated using *ab initio* molecular orbital theory. The rate coefficient is theoretically discussed with the aid of essential features of the potential energy surface for the F + HFCO system and the potential importance of the reaction is considered. A rate coefficient for deactivation of excited HF by HFCO is reported as $1.2 \pm 0.2 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.

INTRODUCTION

Our laboratory has undertaken a detailed theoretical survey of mechanisms of oxidation of trihalomethyl radicals, the fragment resulting from UV photodissociation of chlorofluorocarbons, in order to understand possible implications for stratospheric chemistry. Our previous work suggested that oxidation of trihalomethyl radicals results in the formation of stable halocarbonyl compounds CX₂O and the release of additional halogen atoms;^{1,2} consistent with previous laboratory studies.³⁻⁵ Recent in situ measurements have confirmed the presence of CF₂O and CCl₂O in the stratosphere,^{6,7} thus providing indirect support of these views. Examination of oxidation pathways of CX₂O (where X = F or Cl) compounds had led to the suggestion that FC(0)O, intermediates are possibly involved in catalytic cycles for ozone destruction and formation.⁸⁻¹⁰ The existence of catalytic cycles involving carbon-containing species has not been demonstrated, but we suggested that the relative stability of FCO permits this intermediate to participate in various processes of possible significance. As a prelude to understanding the role of FCO radicals in stratospheric processes, we have experimentally examined the reaction of fluorine atoms with formyl fluoride as a source of such radicals

$$\mathbf{F} + \mathbf{HFCO} \rightarrow \mathbf{HF} + \mathbf{FCO}.$$
 (1)

The reaction of fluorine atoms, resulting from degradtion of chlorofluoromethanes, with hydrogenated species also plays an important role in stratospheric chemistry by suppression of fluorine initiated catalytic ozone depletion cycles. Reactions of fluorine atoms with stratospheric H₂, CH₄, and CH₂O are well recognized as a chain termination step for fluorine atom depletion of O₃.^{11,12} Consequently, it is of interest to know how effectively formyl fluoride consumes additional fluorine atoms by reaction (1). To assess this point quantitatively, the rate coefficient for this reaction must be known.

Although the reaction of fluorine with formyl fluoride has been studied by McDonald and Sloan¹³ with the view of understanding the energy disposal in the products, no measurements of the rate coefficient have been reported. However, by observing the relative flows required to produce a given HF signal, the authors concluded that the F + HFCO rate constant was nearly an order of magnitude slower than that the $F + H_2CO$ rate coefficient. Using infrared multiphoton dissociation (IRMPD) chemiluminescence technique, the rate coefficient for the reaction of fluorine atoms with formyl fluoride has been measured, by following the chemiluminescence of HF, over a range of different pressures and temperatures. In order to understand details of the reaction dynamics and mechanism, *ab initio* calculations have been performed to determine relative thermodynamics and activation energies for pathways which result in the formation of HF.

II. METHODOLOY

A. Computational methods

All calculations were performed with the GAUSSIAN 86 system of programs.¹⁴ All equilibrium geometries and transition structures were fully optimized with Schlegel's analytical gradient method¹⁵ of unrestricted Hartree-Fock (UHF) level employing 6-31G(d) and 6-311G(d,p)bases,¹⁶ whereas only the former bases were used for optimizations at the UHF level for transition state searches; however, both bases were used for optimizations at the secondorder unrestricted Møller-Plesset (UMP2) levels with all orbitals active. The geometries were optimized to better than 0.001 Å for bond distances and 0.1° for bond angles. With a convergence of at least 10^{-7} on the density matrix, the rootmean-square (rms) force was less than 10^{-4} a.u. for the optimized structures. Single point calculations were performed for UMP2-optimized geometries using Møller-Plesset perturbation theory up to fourth order, including single, double, and quadruple excitation (MP4SDQ, frozen core).¹⁷ The effects of spin contamination were examined by annihilation of the next highest spin component in the unrestricted wave function.¹⁸ Vibrational frequencies and zero point energies were obtained at the UHF/6-31G(d) optimized geometry from analytical second derivatives.¹⁹

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B. Experimental methods

The laser photolysis/infrared chemiluminescence apparatus is schematically depicted in Fig. 1. A Laser Science PRF 150 CO₂ TEA laser was focused by an antireflection coated Ge lens of 38.1 cm focal length into a cell containing mixtures of SF₆, HFCO, and a buffer gas (He or Ar). The laser was operated at 5 Hz with typical output energies of 100 mJ/pulse. Multiphoton dissociation of SF_6 with the CO_2 laser using the P(22) line at 10.6 μ m (942.383 cm⁻¹) was used to generate fluorine atoms for reacton with HFCO. The rate of reaction was monitored by observing the time-dependent emission from the reaction using a liquid nitrogen cooled HgCdTe detector (Judson-Infrared, Inc.). Emission was observed at right angles to the CO_2 laser beam and was observed through a sapphire window which blocked scatter CO2 radiation. For observation of HF chemiluminescence, a Corion RS-3500-F filter which passed 1.75–3.2 μ m was used. Chemiluminescence was collected using a CaF₂ focusing lens (25.4 mm diameter, 63.0 mm focal length). Signals from the detector were amplified by a low noise preamplifier, and digitized and averaged (Tektronix 2430A digital Oscilloscope) before being transmitted to an IBM personal compute ATTM (Everex System, Inc.) for storge and subsequent analysis. Signals were averaged over 256 laser pulses.

A variable temperature sample cell was used for these experiments. It consisted of an inner Pyrex tube 50 cm in length which was fitted with an O-ring connector on each end that sealed, by pressing, NaCl windows against Viton O rings. Liquid connection tubes allowed the flow of a constant temperature heat exchange fluid through the outer tube to establish the cell temperature. For temperatures in the range of 298–368 K antifreeze was used. The fluid was circulated through a heated water bath which was regulated to control the temperature in the cell. For temperatures in the range from 228–298 K, acetone was used as the heat exchange fluid. Its temperature was controlled by flowing it through a bath cooled by dry ice and ethanol.

Typical pressures used in these experiments were 0.1– 1.8 Torr of HFCO, 0.2–0.3 Torr SF₆, and 4–30 Torr of argon. Pressures were measured by a MKS capacitance manometer (ranging from 0.01 to 100 Torr full scale). Mixtures were allowed to mix for 10 min before irradiation with the CO₂ laser and data recorder. After 256 laser pulses, the



FIG. 1. The experimental setup for the infrared multiphoton dissociationinfrared chemiluminescence technique.

cell was emptied and refilled before the next run was performed.

SF₆ (Matheson, 99.8%) was purified and degased, before use, by repeated freeze-pump-thaw cycles in liquid nitrogen, Argon (Cryogenic Gases, Inc., 99.996%) was also degased using the freeze-pump-thaw procedure. Samples of SF₆ and argon were withdrawn from a bulb immersed in a bath of liquid nitrogen. HFCO was prepared from potassium fluoride, HCOOH, and benzoyl chloride in accord wih the method reported by Morgan and co-workers.¹⁷ The resulting formyl fluoride was purified by vacuum distillation and the sample purity was checked by Fourier transform-infrared (FT-IR) scans. No absorption due to any compound other than HFCO was observed.

Additionally, FT-IR spectra of several mixtures of HFCO, SF₆, and Ar were taken with a Nicolet Model 5DXCFT-IR spectrometer (2 cm^{-1} resolution) before and after irradiation with CO₂ laser pulses. The spectra were used for final product identification in the irradiated samples.

III. EXPERIMENTAL RESULTS

A. Emission characterization

Several control experiments were performed in order to characterize the nature of the observed emission. Without the HF filter in, a sample of 5 Torr HFCO and 5 Torr helium was excited with the P(22) 10.6 μ m CO₂ laser line used to dissociate the SF_6 . No emission was observed from the sample. Also, with just 5 Torr SF_6 no emission was observed. Irradiation of a mixture of 1.0 Torr HFCO and 0.3 Torr SF_6 and 5 Torr argon led to observed emission. A Corion RS-3500-F filter which passed 1.75–3.2 μ m radiation was used to isolate emission in the 2.3–3.0 μ m region due to vibrationally excited HF*. Insertion of the filter above the observation window reduced the signal from the HFCO/SF₆/Ar mixture by one-fourth. A Corning RL-3000-F Corion filter which passed 3.3-6.0 μ m was inserted and the signal was reduced by three-fourths. This suggested that one-fourth of the observed emission resulted not from HF emission, but is due to vibrationally excited HFCO*. It has peaks at 3.4, 4.8, and 5.4 μ m which correspond to vibrations of the CH stretching mode (v_1) , the CF stretching overtone mode $(2\nu_4)$ and the CO stretching mode (ν_2) , respectively.²⁰ The presence of emission due to vibrationally excited HFCO suggests that collision of excited SF₆ molecules during and shortly after the laser pulse transfers energy to the reactant which is not directly excited by the laser. The question of whether the excited formyl fluoride contributed to the observed HF emission via reaction (2) was addressed

$$HFCO^* \to HF^* + CO. \tag{2}$$

To investigate this possibility, experiments were performed where several sample mixtures of 5 Torr HFCO and 1 Torr SF_6 were irradiated with 3000 CO₂ laser pulses of 150 mJ per pulse energy. In FT-IR scans of the final mixtures, no evidence for CO resulting from the dissociation of HFCO* was found. Consequently, although collisions of excited SF_6 activate the HFCO leading to infrared emission, there is insufficient energy to dissociate HFCO to produce HF and CO. Characterization of the final products following irradiation using FT-IR revealed the presence of CF_2O with characteristic infrared frequencies²¹ at 1928, 1242, and 792 cm⁻¹. The presence of CF_2O results from the recombination of fluorine atoms and fluoroformyl radicals viz.

$$F + FCO + M \rightarrow F_2CO + M \tag{3}$$

could also be evidence of the formation of FCO radicals from the F + HFCO reaction.

B. HF rates of formation and relaxation

The concentration of vibrationally excited HF molecules formed by reaction (1), under the condition of $[HFCO]_0 \ge [F]_0$, as a function of time is given by

$$[HF^*] = \frac{k [HFCO]_0[F]_0}{k [HFCO]_0 - k_d[M]} [exp(-k_d[M]t) - exp(-k [HFCO]_0t)]$$
(4)

where k is the rate constant for reaction (1) and k_d [M] is the collisional decay rate. In our experiment, the HF chemiluminescence signal was accurately represented by a double exponential of the form

signal = amplitude ×
$$[\exp(t/\tau_d) - \exp(-t/\tau_r)],$$
(5)

where τ_d and τ_r are the decay and rise times, respectively. The term $\tau_d^{-1} = k_d [M]$ describes the decay of the signal due to vibrational relaxations of HF* by a third body (He, Ar, HFCO, or SF₆). The term $\tau_r^{-1} = k [HFCO]_0$ describes the rise of the signal due to the formation of HF* molecule. Figure 2 shows a typical HF chemiluminescence signal curve fitted by a double exponential of the abovementioned form. An examination of the decay of HF* shows that with 5 Torr Ar, the decay time is ~30 μ s. This corresponds to ~10⁻¹³ cm³ molecule⁻¹ s⁻¹ for the deactivation rate of HF*. Literature values for deactivation of HF (v = 0-1) by Ar are about ~1.9×10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ which is two orders of magnitude slower.²² Consequently, deactivation of the HF* may be due mainly to relaxation via collision with HFCO which is a major collision partner. A plot of the



FIG. 2. HF chemiluminescence signal resulting from 0.5 for HFCO, 0.3 Torr SF_6 and 5 Torr Ar.

decay time τ_d^{-1} with pressure of HFCO allows a better determination of the relaxation rate of HF by HFCO (see Fig. 3). The deactivation rate is determined as $1.2 \pm 0.2 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ over the pressure range of 0.1–1.0 Torr with a fixed pressure of 0.2 Torr SF₆ and 10 Torr argon. It is interesting to note that the observed rate of $1.2 \pm 0.2 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ is in good agreement with an ealier estimate for the deactivation of 1.7×10^{-12} cm³ molecule⁻¹ s⁻¹ obtained by Amimota.²³

A plot of the rise time τ_r^{-1} with pressure of HFCO gives a straight line whose slope is the total rate constant for the production of HF by the reaction of F + HFCO via reaction (1). It is also noticed that the initial concentration of the F atom will only affect the amplitude, but not the rise time of the signal. Consequently, fluctuations in the F atom concentrations produced from multiphoton dissociation of SF₆ as a result of pulse-to-pulse energy variation will not contribute to fluctuations in the measured total rate constant.

Moreover, variation in the number of laser pulses per gas fill showed no significant differences in total rate constant, which suggests that reaction of F atoms with secondary photoproducts are minor. The issue of secondary reactions has been explored further for two reasons: (1) the products resulting from secondary reactions could emit and consequently obscure the measured signals; (2) the removal of F atoms by secondary reactions may affect the validity of Eq. (4) and hence the measured total rate constant. The most probable secondary reaction in the cell is reaction (3); as indeed F_2CO does not emit at wavelengths that will pass through the filter and therefore emission from it should not interfere with emission resulting from excited HF. In order to study the effects of removal of F atom by secondary reaction, computer simulations on the reaction system has been performed:

$$\mathbf{F} + \mathbf{HFCO} \rightarrow \mathbf{HF} + \mathbf{FCO}; \tag{1}$$

$$\mathbf{F} + \mathbf{F}\mathbf{C}\mathbf{O} + \mathbf{M} \rightarrow \mathbf{F}_2\mathbf{C}\mathbf{O} + \mathbf{M}; \tag{3}$$

$$HF^* + M \rightarrow HF + M. \tag{6}$$

Reactions (1), (3), and (6) are mainly considered. Under



FIG. 3. Inverse decay time for HF chemiluminescence as a function of HFCO pressure for the condition 298 K, $[SF_6] = 0.2$ Torr and [Ar] = 1.0 Torr.

the conditions of these experiments, the focusing Ge lens has a beam width of $\omega_0 = 0.04$ cm. The typical pulse energy used in photolysis is 100 mJ/pulse; thus, a maximum fluence at the focal point $\sim 20 \text{ J/cm}^2$. From SF₆ fractional decomposition as a function of fluence data for dissociation in a focused beam system,²⁴ the decomposition of SF_6 is expected to be at most 0.01%. Under these conditions, this suggests that the initial concentration of F atoms resulting from IRMPD of 0.3 Torr SF₆ is 1.0×10^{12} atoms cm⁻³. The rate constant for reaction (3) is not available in the literature, but a reasonable value for the rate of a third body radical-radical reaction is 2.0×10^{-27} cm⁻⁶ molecule⁻² s⁻¹. The decay rate of 1.2×10^{-12} cm⁻³ molecule⁻¹ s⁻¹ is used for reaction (6). The time evolution of the HF* concentration calculated with or without considering reaction (3) are almost identical. Using a larger rate constant does not change the results. The computer simulations show that the extent of the removal of F atoms by secondary reaction is negligible. The validity of discounting the effect of secondary reaction can be thus understood by observing two facts: one, reaction (3) involves a third body for which under the conditions of these experiments, such a process is slow; two, the radical concentrations are not high enough for secondary reactions to be important.

C. Pressure and temperature dependences

Figure 4 shows representative plots of the rise time in the presence of varying pressure of HFCO for fixed pressures of SF₆. The slopes of the straight lines in Fig. 4 shows that in the presence of the excess reactant [HFCO]₀ \gg [F]₀, pseudo-first order kinetics are observed for concentrations of SF₆ between 0.2–0.3 Torr. (Note that SF₆ is the source of F atoms from dissociation.) Signals were unmeasurably low







FIG. 5. Inverse rise time for HF chemiluminescence as a function of argon pressure for the conditions: \Box 298 K, [SF₆] = 0.3 Torr, [HFCO] = 0.5 Torr; (\blacktriangle) 228 K, [SF₆] = 0.3 Torr, [HFCO] = 0.5 Torr.

with pressures of <0.2 Torr SF₆. Line C in Fig. 4 shows results from following the rise time for various HFCO pressures with helium as a buffer gas. Compared with the rate obtained with argon (line A), the total rate constant is found to be independent of the nature of the buffer gas. The total rate constant at room temperature for the appearance of HF from the average of all the data in Fig. 4 is

$$k = (2.3 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
.

The error is given as twice the standard deviation. Additionally, we have explored the behavior of the rate as a function of the buffer gas pressure. Figure 5 shows the results of the chemiluminescence signal rise time measurements at several pressures of the buffer gas. Fluctuation of the rise time is within our experimental uncertainty which is about 10% at 2σ as can be seen in Table I. Results of the pressure dependence study imply that no stable intermediate species is involved in the reaction that results in the formation of HF that would be collisionally stabilized at room temperature or very low temperature. The absence of such species suggests that the reaction of F with HFCO results in the direct formation of HF, i.e., reaction (1).

Figure 6 shows several plots for data taken at various temperatures. The plots are linear and the temperature-dependent total rate constants are summarized in Table I. The error limits indicated are two times the standard error obtained from a linear least-squares fit to the data.

TABLE I. Total rate constant as a function of temperature derived for the kinetics of F with HFCO.

<i>T</i> (K)	k(T) (cm ³ molecule ⁻¹ s ⁻¹)
298	$2.3 \pm 0.2 \times 10^{-12}$
313	$2.6 + 0.2 \times 10^{-12}$
328	$3.1 \pm 0.4 \times 10^{-12}$
343	$3.4 \pm 0.3 \times 10^{-12}$
368	$3.9 \pm 0.5 \times 10^{-12}$

=

The measured value of the total rate constants obtained from the slopes of the lines in Fig. 6 are plotted as a function of the inverse temperature T^{-1} in the Arrhenius plot shown in Fig. 7. The temperature range of this study was from 298– 368 K. The best lines through the data given

$$k(T) = (4.4 \pm 2.6) \times 10^{-11} \exp[-(1800 \pm 400)/RT] \operatorname{cm}^{-3} \operatorname{molecules}^{-1} \operatorname{s}^{-1}.$$

The indicated error limits are the 94% confidence limits.



IV. COMPUTATIONAL RESULTS

A. Mechanisms for the formation of HF in the F + HFCO reaction

In the reaction of fluorine atoms with formyl fluoride, the observed major product is HF. There are several channels for the production of HF. One route involves direct abstraction of hydrogen to produce HF. Another, involves fluorine addition to produce chemically activated difluoromethoxy radical which can be collisionally stabilized or revert to reactants, or react further to yield HF. Other possibilities are summarized in Scheme I.

Scheme I

From the above scheme, the difluoromethoxy radical can undergo 1,1 elimination to form HF (reaction III), or it could decompose to hydrogen atoms and carbonyl difluoride (reaction IV). The hydrogen atoms could then react with either the carbonyl difluoride to produce HF (reaction V), or with formyl fluoirde to produce HF and formyl radical (reaction VI). In order to assess the relative importance of reactions I–VI in determining the overall rate constant, extensive *ab initio* calculations on the F + HFCO potential surface were performed. Particularly of interest is to determine activation barriers and relative thermodynamic stabilities of each of these channels.

B. Potential energy surfaces for the F+HFCO reaction

1. Structures and vibrational frequencies

The optimized equilibrium geometries and transition structures are collected in Table II. Corresponding total energies are given in Tables III. We note that Hartree–Fock bond lengths for all the equilibrium structures are grossly underestimated by 0.02 Å (rms), however, inclusion of electron correlation improves the agreement between calculated and experimental geometries. At the MP2/6-311G(d,p) level of theory, the agreement between predicted and experimental structures are within ± 0.008 Å (rms); moreover, the bond lengths of F₂CO predicted at this level are in excellent agreement with the experimental values.



FIG. 6. Inverse rise time for HF chemiluminescence as a function of HFCO pressure parametric in temperature.



FIG. 7. Plot of $\ln k$ as a function of inverse temperature. The solid line is the linear-least-squares fit to the Arrhenius expression.

TABLE II. Optimized bond lengths (Å) and angles (degrees) for reactant, products and transition states.
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Species	State	Coordinate	UHF/6-31G(d)	UMP2/6-31G(d)	UMP2/6-311G(<i>d</i> , <i>p</i>)	Experiment
HF	¹ Σ _g	<i>r</i> (H–F)	0.911	0.934	0.912	0.917ª
нсо	² A′	r(C-H) r(C-O) θ(HCO)	1.105 1.159 126.3	1.124 1.191 123.4	1.123 1.182 123.8	1.125 ^b 1.175 125.0
FCO	${}^{2}A_{1}$	r(C-F) r(C-O) θ(FCO)	1.304 1.153 128.3	1.340 1.181 128.1	1.329 1.170 128.2	1.334° 1.169 127.3
F ₂ CO	¹ A 1	r(C–F) r(C–0) θ(FCO)	1.290 1.157 125.9	1.326 1.186 126.3	1.316 1.175 126.2	1.317 ^d 1.170 126.2
нгсо	¹ A'	r(C-H) r(C-F) r(C-O) θ(HCO) θ(FCO)	1.081 1.314 1.164 126.9 123.0	1.094 1.352 1.194 127.6 123.2	1.094 1.345 1.183 127.9 123.2	1.100° 1.341 1.183 129.0 122.7
HF₂CO	² <i>A</i> '	r(C-O) r(C-H) r(C-F) θ(HCO) θ(FCO) θ(FCH)	1.346 1.080 1.327 106.9 111.1 110.3	1.352 1.098 1.357 105.6 111.9 110.3	1.342 1.098 1.349 105.0 112.3 110.1	
[F + HFCO→HF + FCO] [‡]	² <i>A</i> ′	r(C-O) r(C-H) r(C-F) r(F'-H) θ(HCO) θ(FCO) θ(F'HC)	1.153 1.262 1.296 1.163 124.3 127.4 173.1	1.185 1.170 1.334 1.315 125.5 126.4 162.1	1.176 1.153 1.329 1.343 126.1 126.0 170.9	
[F + HFCO→HF₂CO] [‡]	² <i>A</i>	r(CO) r(C-H) r(C-F) r(C-F') θ(HCO) θ(FCO) θ(F'CO) θ(F'CH) θ(F'CF)	1.230 1.074 1.309 1.795 123.5 119.8 92.6 97.3 101.9	1.215 1.091 1.331 1.781 126.0 122.1 84.1 98.6 102.4	1.208 1.090 1.321 1.771 125.7 121.9 85.6 97.7 102.6	
[HF₂CO→H + F₂CO] [‡]	² A'	r(C-O) r(C-H) r(C-F) θ(HCO) θ(FCO) θ(FCH)	1.198 1.591 1.303 93.0 123.3 99.7	1.204 1.449 1.342 92.3 124.3 100.1	1.192 1.451 1.333 92.2 124.5 99.5	
[H + F₂CO→HF + FCO] [‡]	² <i>A'</i>	r(C-O) r(C-F) r(C-F') r(H-F') θ(FCO) θ(F'CO) θ(HF'C)	1.149 1.290 1.694 1.267 128.8 125.1 179.8	1.174 1.325 1.649 1.197 128.8 125.9 179.6	1.162 1.309 1.631 1.181 129.8 125.1 179.4	
[H + HFCO→HF + HCO] [‡]	² <i>A'</i>	r(C-O) r(C-H) r(C-F) r(H'-F) θ(HCO) θ(FCO) θ(H'FC)	1.150 1.091 1.752 1.259 131.0 122.0 180.4	1.172 1.107 1.714 1.190 131.0 123.1 180.8	1.160 1.104 1.697 1.174 133.0 122.2 180.9	

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Species	State	UHF /6-31G(d)	UMP2 /6-31G(d)	UMP2 /6-311G(<i>d</i> , <i>p</i>)	$UMP4SDQ^{\bullet}$ /6-311 + + G(d,p)	$PMP4SDQ^{a}$ $/6-311 + + G(d,p)$
Н	${}^{2}S_{1/2}$	- 4.498 23	- 0.498 23	- 0.499 81	- 0.499 82	- 0.499 82
F	${}^{2}P_{3/2}$	- 99.364 96	99.489 04	- 99.572 62	- 99.569 12	- 99.569 83
HF	Σ_{g}	100.002 91	- 100.184 16	- 100.286 08	100.281 24	100.281 24
HCO	${}^{2}A'$	- 113.247 66	- 113.540 33	113.630 60	- 113.609 19	- 113.610 59
FCO	² A'	- 212.112 06	- 212.574 53	- 212.734 28	- 212.692 55	- 212.695 37
F,CO	¹ A ₁	- 311.615 31	- 312.265 16	- 312.503 94	- 312.442 82	- 312.442 82
HFCO	¹ A ₁	- 212.747 84	- 213.229 26	- 213.397 53	- 213.358 80	- 213.358 80
HF ₂ CO	$^{2}A^{'}$	- 312.145 38	312.755 24	- 313.000 77	- 312.959 97	- 312.961 43
Transition structure						
[F + HFCO→						
$HF + FCO]^{\ddagger}$ $[F + HFCO \rightarrow$	² A'	312.066 01	- 312.702 10	- 312.956 14	- 312.914 60	- 312.917 09
HF ₂ CO] [‡]	² A	- 312.081 23	- 312.693 77	- 312.931 89	- 312.903 45	- 312.918 26
[HF ₂ CO→	a					
$H + F_2CO]^{\ddagger}$ $[H + F_2CO \rightarrow$	'A'	- 312.081 94	- 312.720 04	- 312.967 50	- 312.919 13	- 312.927 42
$HF + FCO]^{\ddagger}$	² <i>A</i> ′	- 312.008 75	- 312.672 59	- 312.919 75	- 312.870 13	- 312.872 81
[H + HFCO→						
HF + HCO] [‡]	² A'	- 213.145 79	- 213.639 32	- 213.818 77	- 213.791 86	- 213.799 52

TABLE III. Total energies (hartrees) for geometry-optimized species.

* UMP4SDQ and PMP4SDQ energies (frozen core) are calculated using geometries optimized at the UMP2/6-311G(d,p) level of theory.

The reaction path for the abstraction of hydrogen from formyl fluoride (reaction I), shown in Fig. 8(a), involves the approach of the incoming fluorine atom along the CH axis of formyl fluoride. The three atoms involved in the bond breaking and bond forming process are not colinear along the CH axis. The fluorine makes an angle of $\sim 162^{\circ}$ with the CH bond. The CH bond is increased by ~ 0.08 Å in the transition state, while the forming HF bond is ~ 1.315 Å, whereas the equilibrium HF bond in its ground state is 0.917 Å. Inclusion of electron correlation is found to significantly decrease the CH bond distance and increase the HF bond distance; this shifts the transition state closer to the reactant side and concomitantly, as shown below, it lowers the barrier to activation.

A competitive pathway with the hydrogen abstraction route is fluorine addition to formyl fluoride (reaction II) to yield difluoromethoxy radicals. The reverse of reaction II is fluorine elimination from difluoromethoxy radicals and shows much similarity to the $F + F_2CO$ reaction.² Fluorine atom addition does not occur in the symmetry plane of the molecule which results in a transition state of C_1 symmetry [Fig. 8(b)]. The fact that addition does not occur with symmetry constraints does not significantly alter geometric parameters for the forming CF' bond. The CF' bond in the F + HFCO reaction transition state is quite similar to that in the $F + F_2CO$, i.e., 1.795 and 1.762 Å, respectively, at the UHF/6-31G(d) levels of theory. As expected, the CH and CF bonds in the transition state are quite similar to the reactant HFCO; however, the CO bond lengthens in the transition state. The extension of the CO bond is also accompanied by a redistribution of unpaired electron density from the approaching fluorine atom toward the oxygen.

A direct route to the formation of HF from difluoromethoxy radicals is unimolecular dissocation via 1,1 elimination of HF. Investigation of the minimum-energy pathway failed to locate any new transition state structure on the UHF/6-31G(d) surface. All attempts to optimize a structure led only to dissociation along the fluorine elimination (II) or hydrogen elimination (IV) route. Reaction of HF_2CO is a process that involves only extrusion of fluorine as well as hydrogen and does not involve molecular elimination of HF.

Hydrogen elimination from difluoromethoxy radical (reaction IV) to form carbonyl difluoride (CF₂O) is a second yet higher energy pathway. It may be compared to CH₃O dissociation into CH₂O and H atoms.²⁵⁻²⁷ As in CH₃O, the transition state occurs at a CH distance of ~1.8 Å [see Fig. 8(a)].

Provided hydrogen atoms are released from dissociation of difluoromethoxy radical (reaction IV), there are two possible pathways for the formation of HF. The first is by fluorine abstraction from carbonyl difluoride (reaction V); the second, by fluorine abstraction from formyl fluoride (reaction VI). Considering the transition state for reaction V, hydrogen prefers to approach the CF' bond linearly along the $[\mathbf{C}\cdots\mathbf{F}'\cdots\mathbf{H}]^{\ddagger}$ axis, quite different from the approach of F along the $[C \cdots H \cdots F]^{\ddagger}$ axis [Fig. 8(d)]. The most significant changes in the optimized transition structures occur in the HF bond. At the Hartree–Fock level using polarized basis, the HF bond is 1.267 Å. Inclusion of electron correlation shortens this bond to 1.197 Å. At the MP2/6-311G(d,p) level, this bond shortens further. Concomitantly, the breaking CF' bond also shortens with addition of electron correlations and basis set enlargement. The shifts in the transition structure are closer to the product side, indicative of a late transition state. Like reaction V, the route to the formation of HF by fluorine abstraction from formyl fluoride (reaction VI) occurs linearly along the $[C \cdots F \cdots H]^{\ddagger}$ axis [Fig. 8(e)]. However, the structural trends at the MP2/6-311G(d,p) level suggest that the transition struc-



FIG. 8. Structures of the F + HFCO reaction transition state: UMP2/6-31G(d) optimized (no superscript), UMP2/6-311G(d,p) optimized (asterisk) in Å.

ture occurs later along the reaction path than the $H + CF_2O$.

The vibrational frequencies for the transition states above discussed along with those for reactants and products are collected in Table IV. Vibrational frequencies for all the transition states show one imaginary eigenvalue, which attest to the fact that the transition structures are first order saddle points.

2. Energetics—Heats of reaction and barrier heights

Reliable heats of reaction are available for most reactant and products involved in the F + HFCO system. The ΔH_f^0 (298 K) for H, F, HF, HCO, FCO, HFCO, and F₂CO are 51.6, 19.0, 0.9, -42, 89.9, and 152.7 kcal mol⁻¹, respectively.^{28,29} However, the heat of formation for HF₂CO radical is not available. Nevertheless, heats of reaction for pathways calculated with experimental enthalpies can be used to assess reliabilities of predictions involving HF₂CO. Listed in Table V are such data for the F + HFCO system. For the reaction of F + HFCO \rightarrow HF + FCO, the agreement between our highest level of theory and experimental heat reaction is quite good. Including reactions V and VI along with I, an estimate of differences between theoretical and experimental reaction enthalpies is 5.8 kcal mol⁻¹ (rms).

Thermodynamically, all the reactions outlined in scheme I are favored since all are predicted to be exotherimic. Consequently, the kinetics, as governed in part by the activation energy, determine the relative importance and rate ordering for pathways which result in the formation of HF. There are no previous measurements of experimental activation energies for reactions in scheme I. However, the present exprimental work determines an activation energy for F + HFCO \rightarrow HF + FCO of 1.8 + 0.4 kcal mol⁻¹. The calculated barrier for reaction I following optimizations at the UMP2/6-311G(d,p), enlarging the basis set, including higher order correlation, and annihilation of the highest spin contaminant using spin projection gives a barrier of 2.9 kcal mol^{-1} , which is in reasonable agreement with the experimental results that there is a low barrier for the F + HFCO reaction (see Table VI).

Initially, we thought that fluorine addition to HFCO(II) may be the preferred route, if not a competitive one. Certainly, at the lower levels of theory this is the picture; however, at the PMP4//6-311 + + G(d,p) level, the abstraction pathway I is favored, but these calculations suggest that the addition could be competitive. From the fluorine atom addition route probable reaction steps which yield HF results from the reaction of hydrogen atoms with $CF_2O(V)$ or with HFCO, the dominant reactant VI. Barriers for these processes are quite high. Calculated barriers heights are 43.3 kcal mol⁻¹ for $H + CF_2O \rightarrow HF + F$ -CO(V) and 35.3 kcal mol⁻¹ for $H + HFCO \rightarrow HF + H$ -CO(VI). Consequently, these reactions would not contribute to the production of HF except at high temperatures, and at such temperatures, the Arrhenius plot should show curvature. From the summary of the potential energy surface given in Fig. 9, the present calculation thus predicts that hydrogen abstraction by fluorine atoms (I) is the dominant reaction pathway; this suggests that the observed HF results from this reaction. Conclusions from previous dynamical studies on the F + HFCO reaction are consistent with these findings.¹³ Moreover, the addition route should be competitive, but should not contribute to the observed HF signal because of large barriers to fluorine abstraction by hydrogen from carbonyl difluoride (V). Experimental evidence from

Molecules	Vibrational frequencies	Zero point energy (ZPE)	Thermal energy
	4356(4139) ^b	6.2	7.7
нсо	2925(2488),2143(1861),1250(1081)°	9.0	10.8
FCO	2141(1862),1210(1026),708(626) ^d	5.8	7.7
F ₂ CO	2187(1928),1462(1249),1093(95) ^c 873 (774),683(627),631(584)	9.9	11.9
HFCO	3360(2981),2103(1837),1539(1342) ^f 1248(1064),1176(1030),738(663)	14.5	16.4
HF ₂ CO	3308,1532,1492,1250,1212, 1096,608,389,87	15.8	18.4
Transition structure			
$[F + HFCO \rightarrow HF + FCO]^{\ddagger}$	2161,1294,1206,967,774 430.167.113.3562 <i>i</i>	10.2	13.1
[F + HFCO→ HF-CO] [‡]	3413,1596,1470,1267,957, 702,368,293,1052 <i>i</i>	14.4	16.8
$[HF_2CO \rightarrow H + F CO]^{\ddagger}$	1814,1425,1082,857,789, 736 591 588 1638 <i>i</i>	11.3	13.4
$[H + F_2CO \rightarrow HE + FCO]^{\frac{1}{2}}$	2180,1252,829,641,583 569,266,257,2342;	9.4	12.1
$[H + HFCO] \rightarrow HF + HCO]^{\ddagger}$	3165,2128,1300,772,761, 581,340,326,2393 <i>i</i>	13.4	15.9

TABLE IV. Vibrational frequencies (cm⁻¹), zero point energies (kcal mol⁻¹), and thermal energies (kcal mol⁻¹) calculated at the UHF/6-31G(d) level of theory.

* Experimental values in parentheses.

^bB. Rosen, Spectroscopic Data Relative to Diatomic Molecules (Pergamon, New York, 1970).

^c D. E. Milligan and M. E. Jacox, J. Chem. Phys. 41, 3032 (1964).

^d K. Nagai, C. Yamada, Y. Endo, and E. Hirota, J. Mol. Spectrosc. **90**, 249 (1981); M. E. Jacox, *ibid.* **80**, 257 (1980).

A. H. Nielsen, T. G. Burke, P. J. H. Woltz, and E. A. Jones, J. Chem. Phys. 20, 596 (1952).

^fR. F. Stratton and A. H. Nielsen, J. Mol. Spectrosc. 4, 373 (1960).

the present work which supports this conclusion is the observation of CF_2O in the reaction mixture. However, note that CF_2O can also result from the recombination of fluorine atoms with FCO radicals produced by reaction I. Francisco and Li^8 have found that the reaction of F + FCO has no barrier to the formation of CF_2O . Consequently, its rate coefficient should be close to that of the collision rate.

C. Comparison of experimental and theoretical reaction rates

The rate coefficient for the hydrogen abstraction reaction from formyl fluoride by fluorine atoms can be computed by using the transition-state theory³⁰

$$k(T) = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_F Q_{HFCO}} e^{E_0 / k_B T},$$
(7)

where Q_F , Q_{HFCO} , and Q^{\ddagger} are total partition functions for reactants (F and HFCO) and transition state. These quantities can be evaluated using statistical mechanical methods from the structures, the total energies, and the vibrational frequencies for the reactant and transition state. In our evaluation of the rate coefficient, we used UMP2/6-311G(d,p) results for the structure, vibrational frequencies given in Table IV, and total energies calculated at the PMP4/6-311 + + G(d,p)//UMP2/6-311G(d,p) level. Results of these calculations are shown graphically in Fig. 10, where

TABLE V. Heats of reaction	(kcal mol ⁻¹) for F +	 HFCO reaction 	pathways
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Level of theory	F + HFCO→ HF + FCO	F + HFCO→ HF₂CO	$\begin{array}{c} HF_2CO \rightarrow \\ H+F_2CO \end{array}$	HF₂CO→ HF + FCO	$H + F_2 CO \rightarrow HF + FCO$	H + HFCO→ HF + HCO
UHF/6-31G(d)	- 1.4	20.4	20.0	19.1	- 0.9	2.8
UMP2/6-31G(d)	25.4	- 23.2	- 5.1	2.2	3.0	1.9
UMP2/6-311G(<i>d</i> , <i>p</i>)	- 31.5	- 19.2	1.9	- 12.3	- 10.4	- 12.1
UMP4SDQ/6-311 + + G(d,p)// UMP2/6-311G(d,p)	-27.8	20.1	10.9	-8.7	- 19.6	- 20.0
PMP4SDQ /6-311 + + $G(d,p)//$						
UMP2/6-311G(<i>d</i> , <i>p</i>)	- 30.1	- 20.6	11.8	- 9.5	- 21.3	- 20.8
ΔZPE ^a	- 2.5	1.3	- 5.9	- 3.8	2.1	0.7
Thermal correction ^a	- 1.0	2.0	- 6.5	- 3.1	3.5	2.1
$\Delta H^{0}(0 \mathrm{K})$	- 32.6	- 19.3	5.9	- 13.3	- 19.2	- 20.1
$\Delta H^{0}(298 \text{ K})$	- 31.1	- 18.6	5.3	- 12.6	- 17.8	- 18.7
Expt. $\Delta H^0(298 \text{ K})$	- 36.1				6.5	- 16.8

^aCalculated at the UHF/6-31(d) level of theory.

	F + HFCO→	F + HFCO→	HF₂CO→	$H + F_2CO \rightarrow$	H + HFCO→
Level of theory	HF + FCO	HF ₂ CO	$H + F_2CO$	HF + FCO	HF + HCO
UHF/6-31G(d)	29.4	19.8	39.8	65.8	62.9
UMP2/6-31G(d)	10.2	15.4	22.1	57.0	55.3
UMP2/6-311G(d,p)	8.8	24.0	20.9	52.7	49.3
UMP4SDQ/6-					
311 + + G(d,p)					
//UMP2/6-311G(d,p)	8.4	15.4	25.6	45.5	41.3
PMP4SDQ/6-31 + + G(d, p)))				
//UMP2/6-311G(d,p)	7.3	6.5	21.4	43.8	36.5
$\Delta ZPE[UHF/6-31G(d)]$	- 4.4	- 0.1	4.6	- 0.5	- 1.2
PMP4SDQ/6-					
$311 + + \hat{G}(d,p)$					
$+ \Delta ZPE$	2.9	6.4	16.8	43.3	35.3
Experimental	1.8 ± 0.4				

TABLE VI. Barrier heights (kcal mol^{-1}) for F + HFCO reaction pathways.

 $\ln k(T)$ has been plotted against 1/T, with the rate constant expressed in units of cm^3 molecule⁻¹ s⁻¹ and the temperature T in Kelvin. As can be seen in Fig. 10, the calculated rates are systematically lower than the experimental ones. Rates calculated from the classical transition state theory expression using Eq. (7) predicts a rate which is too slow. Incorporating tunneling correction using Wigner³¹ ane Eckart³² potential procedures both improve the agreement with the experimental data. However, calculated rates using the Eckart potential show better consistency with the experimental data in that it can reproduce the shape of the Arrhenius plot within the experimental uncertainty. The differences between calculated and experimental rates could be attributed to an overestimation of the reaction barrier and a lack of cancellation of anharmonicity corrections between transition state and reactants. Nevertheless, these calculations show that tunneling plays a role in the F + HFCO reaction rate. Moreover, it is very encouraging that the theoretical rate coefficient for the F + HFCO reaction differs from the experimental value by only a factor of 4. In recent work by Gonzales et al.33 they applied a similar theoretical approach to describe the $CH_4 + OH$ reaction and they obtained reasonable agreement. Therefore, this approach should be very useful for estimating rate coefficients for those reactions involving species for which experimental data is not known and for those for which experimental rates cannot be measured.



FIG. 9. A summary of the F + HFCO potential energy surface. Energies are in kcal mol⁻¹.

D. Comparison with other systems—an overview of hydrogen abstraction reactions by fluorine atoms

A common feature of reactions involving hydrogen abstraction from fluorine atoms is the very low energy barrier associated with the reaction. Trends in the magnitude of the rate coefficients are consequently manifested largely in the A factor or the Arrhenius term for the rate coefficient. An examination of differences in experimental and theoretical reaction rates for the F + HFCO reaction supports this view. From Table VII, one can see that the hydrogen abstraction rate coefficients for successive fluorine substitution show a consistent trend of a slower rate when compared with the unsubstituted methane. This leads to the suggestion that the transition state becomes more rigid as one goes from $[\mathbf{F}\cdots\mathbf{H}'\cdots\mathbf{C}\mathbf{H}_3]^{\ddagger}$. One would expect similar behavior in the rate coefficient for $F + H_2CO$ and F + HFCO and indeed there is such a trend in the H₂CO and HFCO system. A comparison of the rates show that F + HFCO is nearly 27 times slower than the rate for abstraction of hydrogen from H_2CO . However, in this case, the differences in the rates cannot be directly attributed to the rigidity or looseness of the transition states for the F + HXCO (where X = H or F)



FIG. 10. The plot of ln k as a function of inverse temperature for calculated and experimental rate constants. Curve A, calculated rate coefficient with Eckart tunneling correction; curve B, calculated rate coefficient with Wigner correction; curve C, calculated rate coefficient using only the classical transition state theory expression; \Box are experimental points from the present study.

R	k^{298} (cm ³ molecule ⁻¹ s ⁻¹)	$\log[A(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})]$	$E_{\rm act}$ (kcal mol ⁻¹)	Reference
H,	$2.7 \pm 1.3 \times 10^{-11}$	- 9.8	0.525 ± 0.25	34
CH₄	$8.0 \pm 1.5 \times 10^{-11}$	9.52	0.400 ± 0.3	34
CH	$4.6 \pm 0.2 \times 10^{-11}$			35
2	$3.8 \pm 0.2 \times 10^{-11}$			36
CH ₂ F ₂	$8.8 \pm 0.6 \times 10^{-12}$			35
* *	$\sim 2.4 + 0.6 \times 10^{-12}$			36
CHF ₃	$2.2 \pm 0.7 \times 10^{-13}$	- 10.98	2.4 ± 0.7	37
2	$1.5 \pm 0.1 \times 10^{-13}$		_	38
H,CO	$6.6 \pm 1.1 \times 10^{-11}$			39
-	$5.79 \pm 0.56 \times 10^{-11}$			40
HFCO	$2.3 + 0.2 \times 10^{-12}$	-10.4 ± 0.2	1.8 ± 0.4	This work

TABLE VII. Rate coefficients and Arrhenius parameters for some $F + R - H \rightarrow HF + R$ reactions.

system, since there are no active rotations in the $[F \cdots H' \cdots XCO]^{\ddagger}$ complex. To give a plausible explantion for the differences in the rates, preliminary *ab initio* calculations of the $F + H_2CO$ potential surface for comparison with the F + FHFCO system were performed. No evidence of any unusual structural orientation of the attacking fluorine was found to play a role in the H_2CO and HFCO system. The addition of the fluorine, however, does significantly couple more modes in the transition state in addition to increasing the number of lower frequency modes. This has the effect of significantly lowering all the transition state modes. Consequently this lowers the *A* factor and results in a slower abstraction rate.

V. SUMMARY

Examination of the kinetics of the F + HFCO reaction suggests that the reaction leads directly to a clean source of fluoroformyl radicals FCO, which are useful for kinetic studies. The reaction takes place via the abstraction route. Addition of the fluorine to HFCO followed by elimination is unlikely. This is consistent with the conclusions from analysis of HF product distributions for the reaction of $F + H_2CO^{41}$ and F + HFCO.¹³ Moreover, substitution on the H₂CO reactant does alter the reactivity of the hydrogen abstraction process. Fluorine substitution, in particular, slows the rate of hydrogen abstraction by fluorine atoms. Moreover, tunneling is found to play a role in the F + HFCO reaction rate.

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