Gas-Phase Atom–Radical Kinetics of Atomic Hydrogen, Nitrogen, and Oxygen Reactions with CHF Radicals

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The absolute rate constants for the reactions of atomic hydrogen, nitrogen, and oxygen with CHF radicals have been measured in a gas-flow system with photoionization mass spectrometry detection. CHF($\tilde{X}^{1}A'$) radicals were produced by dissociation of CH₂F₂, CH₂FCl, or CHFBr₂ in a radiofrequency discharge. CHFBr₂ proved unsatisfactory as a precursor for CHF in kinetics studies. Atomic reactants were produced by dissociation of the corresponding elemental gas in a microwave discharge. The pressure was 1.7 Torr. The rate constants for CHF decay under pseudo-first-order conditions at 293 K in units of cm³ molecule⁻¹ s⁻¹ are (4.9 ± 0.9) × 10⁻¹⁰ for CHF + H, (2.4 ± 0.4) × 10⁻¹¹ for CHF + N, and (1.4 ± 0.2) × 10⁻¹⁰ for CHF + O. These reactions appear to proceed by an association-elimination mechanism.

Introduction

As part of a larger investigation of radical-radical reactions in the gas phase, the present study of $CHF(\tilde{X}^1A')$ radicals has as one objective a comparison of reactivity in the carbene radical series, $CH_2(\tilde{X}^3B_1)$, $CHF(\tilde{X}^1A')$, and $CF_2(\tilde{X}^1A_1)$. A striking example of the differences that can exist is found in the reactions with molecular oxygen shown in reactions 1-3:¹

$CHF + O_2 \rightarrow CO_2 + HF \qquad \Delta H \ (kJ$	mol^{-1}) = -790 (1a))			
$\rightarrow CO_2 + H + F \qquad \Delta H \ (kJ$	mol^{-1}) = -220 (1b))			
\rightarrow CO + HOF ΔH (kJ	mol^{-1}) = -334 (1c)			
\rightarrow CO + OH + F ΔH (k.	$J \text{ mol}^{-1}$) = -117 (1d)			
\rightarrow FCO + OH ΔH (kJ	mol^{-1}) = -258 (1e)			
\rightarrow HCO + OF ΔH (kJ	mol^{-1}) = 27 (1f)			
$CH_2 + O_2 \rightarrow CO_2 + H_2 \qquad \Delta H \ (kJ \ m)$	nol^{-1}) = -779 (2a))			
$\rightarrow CO + H_2O \qquad \Delta H (kJ m)$	nol^{-1}) = -739 (2b))			
\rightarrow HCO + OH ΔH (kJ	mol^{-1}) = -304 (2c)			
$CF_2 + O_2 \rightarrow CO_2 + F_2 \qquad \Delta H$	$(kJ mol^{-1}) = -211$ (3a))			
$\rightarrow CO_2 + F + F \qquad \Delta H \ (kJ)$	mol^{-1}) = -52 (3b))			
$\rightarrow CO + OF_2 \qquad \Delta H \ (kJ$	mol^{-1}) = 96 (3c)			
\rightarrow FCO + OF ΔH (kJ	mol^{-1}) = 119 (3d)			
Despite the open-shell electronic structures of the reactants and the large experimities for all three reactions. CHE and CE, do					

the large exoergicities for all three reactions, CHF and CF₂ do not react with O_2 . Their rate constants are smaller than 5×10^{-16} cm³ s^{-1,2} CH₂, on the other hand, does react with O_2 , and the rate constant is 3.3×10^{-12} cm³ s^{-1,3} CH₂ is a triplet in its ground state and the other two are singlets, but since there are spin-allowed exoergic pathways for all three reactions, spin conservation rules alone cannot account for the failure of the fluorocarbon radicals to react with O_2 . Apparently, significant energy barriers exist in these reactions.

In the present article, a study of the reactions of CHF radicals with atomic H, N, and O is presented. The energetically most

favorable product channels are listed in reactions 4-6:

$CHF + H \rightarrow CH + HF$	$\Delta H (kJ mol^{-1}) = -22$	(4a)

$$\rightarrow$$
 CF + H₂ ΔH (kJ mol⁻¹) = -88 (4b)

$$\rightarrow CH_2 + F \qquad \Delta H (kJ \text{ mol}^{-1}) = 122 \qquad (4c)$$

$$CHF + N \rightarrow CN + HF \qquad \Delta H (kJ mol^{-1}) = -436$$
 (5a)

$$\rightarrow$$
 FCN + H $\Delta H (kJ mol^{-1}) = -344$ (5b)

$$\rightarrow \text{HCN} + \text{F} \qquad \Delta H (\text{kJ mol}^{-1}) = -384 \qquad (5c)$$

$$\rightarrow$$
 CF + NH $\Delta H (kJ mol^{-1}) = 34$ (5d)

$$CHF + O \rightarrow CO + HF \qquad \Delta H (kJ mol^{-1}) = -758$$
 (6a)

$$\rightarrow$$
 FCO + H $\Delta H (kJ mol^{-1}) = -328$ (6b)

$$\rightarrow$$
 HCO + F $\Delta H (kJ mol^{-1}) = -252$ (6c)

 \rightarrow CF + OH $\Delta H (kJ mol^{-1}) = -30$ (6d)

The mechanisms of these reactions involve attractive potential energy surfaces leading to the formation of stable intermediates that dissociate to form products.

The room temperature rate constants have been determined under pseudo-first-order conditions, and product analysis has been accomplished, by using a discharge-flow method with photoionization and electron impact mass spectrometry (PI/EI-MS) detection. The results are compared with published values for the N and O reactions. The rate constant for the H reaction is presented for the first time. A comparison of the CHF reactions with the analogous reactions of CH₂ and CF₂ with H, N, and O shows a different trend from that observed with molecular oxygen.

Experimental Section

The discharge-flow apparatus with photoionization and electron impact mass spectrometry (PI/EI-MS) detection has been described in detail previously, as have the experimental procedures and data analysis.⁴ A brief description of experimental details specific to the present study is included here.

The flow tube and movable reactant inlet were coated with a film of TFE Teflon for the atomic hydrogen reaction only.

CHF radicals were produced in a low power (2 W) radiofrequency discharge (13.5 MHz) of 0.01–0.05% halocarbon precursor molecules diluted in helium carrier gas as previously described. Recent experiments have shown that higher purity radical sources are attained at 2 W compared to 5 W, which was the typical power used in the earlier experiments.

⁽¹⁾ All ΔH values are based on heats of formation at T = 298 K from: JANAF Thermochemical Tables, 3rd ed. J. Phys. Chem. Ref. Data 1985, 14, Suppl. 1.

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Figure 1. Typical examples of data from CHF radical reactions with H, N, and O atoms. Each panel consists of semilog plots of fluoromethylene radical signals (total accumulated counts/100 s) versus reaction distance for three reactant atom concentrations. The radical signal versus injector position with zero atom concentration shows an increase that is due to a corresponding decrease in wall recombination as the injector is withdrawn. The first-order rate constant for wall loss, k_{w_1} is derived from the solope of this line and taken into account in the analysis (see ref 4a). The solid lines are linear least-squares fits to the measurements. Flow velocity, 2940 cm s⁻¹. Total pressure, 1.7 Torr. Radical precursor, CH₂F₂.

The precursors investigated were CH_2F_2 , CH_2FCl , and CHF-Br₂. At a power of 2 W, the minimum power required to sustain a discharge in halocarbon plus helium mixtures, the production of impurity radicals was minimized. In the case of CH_2FCl , only CHF radicals were detected. Here, presumably, dissociation occurs predominantly by elimination of HCl. The carbon-chlorine bond is relatively weak, and energetics favor the simultaneous departure of an H atom to form HCl. In the case of CH_2F_2 , both CHF and CF_2 radicals were produced. Here, where a weakly bound Cl atom is absent, energetics favor H_2 elimination which competes with elimination of HF. Free atoms are not observed as discharge products. Less selectivity is observed in the dissociation of CHFBr₂. CHFBr, CFBr, and CH were all present in the mass spectrum.

Although CH_2FCl was the cleanest source for CHF radicals, in kinetics experiments CH_2F_2 and CH_2FCl gave identical results. CHFBr₂ yielded very different results, however: The rate constants were 40–60 times smaller than for the other two sources. A possible explanation for the smaller observed CHF decay rate is secondary production of CHF by reaction between CH and CHFBr impurities to form CHBr and CHF.

Typical maximum CHF radical concentrations in the kinetics experiments were estimated to be in the range $(2-4) \times 10^{11}$ cm⁻³.

None of the precursor molecules reacted with the atomic reactants on the time scale of the present experiments. The room temperature rate constants for these reactions were estimated roughly to be less than 5×10^{-13} cm³ molecule⁻¹ s⁻¹. Likewise, CHF radicals did not react with H₂, O₂, or N₂. The slope of the



Figure 2. Pseudo-first-order rate constants in units of s^{-1} , diffusion and flow corrections applied, plotted versus reactant atom concentration in units of molecules cm⁻³ for the reactions of CHF radicals with H, N, and O atoms. The solid lines are linear least-squares fits to the data. The slope of each line is equal to the biomolecular rate constant, k_b , for the reaction.

TABLE I: Rate Constants, k_b (cm³ molecule⁻¹ s⁻¹), for Reactions of CHF Radicals with Atomic Hydrogen, Nitrogen, and Oxygen at Room Temperature

reaction	this work	ref 6
CHF + H CHF + N CHF + O	$(4.9 \pm 0.9) \times 10^{-10}$ $(2.4 \pm 0.4) \times 10^{-11}$ $(1.4 \pm 0.2) \times 10^{-10}$	$(2.5 \pm 0.5) \times 10^{-11}$ $(1.5 \pm 0.2) \times 10^{-10}$

CHF decay plot was unaffected by the addition of these molecular gases.

The chemicals used were CH_2F_2 (gas, 98.7%, PCR, Inc.), CH_2FCI (gas, 98.7%, PCR, Inc.), $CHFBr_2$ (liquid, 99.2%, PCR, Inc.), He (99.99%), and H₂ (99.999%). The gases were used without further purification. The liquid samples were subjected to several freeze-pump-thaw cycles at liquid nitrogen temperature to remove trapped noncondensible gases.

The linear flow velocity in the kinetics experiments was normally 2940 cm s⁻¹. The total pressure was 1.7 Torr, and the pressure drop over a typical reaction distance was less than 2%.

The pseudo-first-order rate constants were corrected for the effects of diffusion coupled with laminar flow as described previously. The binary diffusion coefficient, D, for CHF in He was calculated as $320 \text{ cm}^2 \text{ s}^{-1}$ for the typical operating pressure of 1.7 Torr at 293 K.⁵ The magnitudes of the diffusion and flow corrections to k_b were 24% for the H atom reaction, 12% for N, and 18% for O.

⁽⁵⁾ Kennard, E. H. Kinetic Theory of Gases; McGraw-Hill: New York, 1938.

Results and Discussion

Typical examples of the measurements are shown in Figure 1. Pseudo-first-order rate constants derived from the slopes of these and similar plots and corrected for diffusion and flow effects are plotted versus the atomic reactant concentrations in Figure 2. Bimolecular rate constants, k_b , derived from the slopes of these graphs are listed in Table I and compared to previous results obtained by a different technique, pulsed laser photolysis coupled with time-resolved laser spectroscopic detection.⁶ Although the rate constant for the H atom reaction is more than 3 times larger than for the O atom reaction, when k_b is divided by the relative velocity to give a measure of the reaction cross section, the ratio of reaction cross sections, $\sigma_{\rm H}/\sigma_{\rm O}$, is only 1.05.

As shown in the figures, scatter in the experimental data is small. The 95% confidence intervals for the slopes in Figure 2 obtained from a statistical analysis (software Statview 512+, BrainPower, Inc.) correspond to uncertainties in $k_{\rm b}$ of $\pm 4.9\%$ for H, $\pm 5.1\%$ for N, and $\pm 6.0\%$ for O. Other estimated errors in the measurements included 11% for diffusion and laminar flow corrections, 5% in absolute pressure, 5% in mass flow measurements, and 10% in atomic density. The overall percent uncertainty in $k_{\rm b}$ is about ±18% for each reaction. This value was determined by taking the square root of the sum of the squares of the individual uncertainties giving the uncertainty in pressure a weight of 2 because pressure appears as the square in the calculations.

A search for all possible reaction products listed in reactions 4-6 was made by using both PI and EI mass spectrometry. A single reaction channel corresponding to HF elimination from the intermediate complex was observed both for the N (5a) and the O (6a) atom reactions. Both CN and HF were detected in the former reaction and CO and HF in the latter.

The formation of CO product molecules via channel 6a for the O + CHF reaction was measured as a function of [O] for a fixed reaction distance (i.e., time t). For pseudo-first-order kinetics, the rate of CO primary product formation depends on the total rate of decay of CHF and not just on the decay rate for the channel that produces CO.7 The integrated rate equation expressed in terms of [CO] is given by

$$\ln \left\{ \frac{[CO]_{\infty} - [CO]_{t}}{[CO]_{\infty}} \right\} = -k_{b}[O]t - k_{w}t$$
(7)

Rearrangement of eq 7 shows that [CO], increases asymptotically with increasing [O] to a constant value, which is taken as $[CO]_{\infty}$. If CO is a primary product, then a plot of the left-hand side of eq 7 versus [O] for fixed reaction time is linear and its slope is the bimolecular rate constant for the overall reaction multiplied by the reaction time. The rate constant determined in this way was found to be identical with the CHF decay constant presented above, thus confirming that CO is a primary product of the reaction.

It is noteworthy that the highly excergic channels corresponding

TABLE II: Rate Constants, k_b (10⁻¹⁰ cm³ molecule⁻¹ s⁻¹), for **Carbene Radical-Atom Reactions at Room Temperature**

reaction	-ΔH, kJ mol ⁻¹	k _b , this work	k _b , other works
$CH_2 + H \rightarrow CH + H_2$	10	in progress	2.79
$CHF + H \rightarrow CF + H_2$	88	4.9	
\rightarrow CH + HF	22		
$CF_2 + H \rightarrow CF + HF$	53	0.39 ¹⁰	
$CH_2 + N \rightarrow CN + H_2$	424	0.1611	
$CHF + N \rightarrow CN + HF$	435	0.24	0.2512
$CF_2 + N \rightarrow FCN + F$	175	0.07213	
$CH_{2} + O \rightarrow CO + H_{2}$	746	in progress	1.314
$CHF + O \rightarrow CO + HF$	758	1.4	1.515
$CF_2 + O \rightarrow FCO + F$	159	0.2016	0.1817
\rightarrow CO + 2F	20		

to the displacement of a single H or F atom were not observed. It appears that the light and highly mobile hydrogen atom encounters the fluorine atom to which it is strongly attracted early in the breakup of the complex, such that energy transfer is able to stabilize the nascent HF bond. In the analogous reactions of CF_2 with O and N, F_2 elimination is an accessible channel but was not observed. Displacement of one or both of the F atoms dominated in that case.8

In the case of the H atom reaction, both accessible product channels corresponding to HF or H_2 elimination from the complex were observed. Here, CH, HF, and CF were detected. The background of undissociated H₂ from the H atom source interfered with the detection of the H_2 product. It was not possible to determine an accurate branching ratio, but the ratio of the CH and CF signals (uncorrected for relative detection efficiency or loss of signal due to secondary reaction) was about 10 to 7.

Table II summarizes the available results for the nine reactions involving CH₂, CHF, and CF₂ radicals and H, N, and O atoms. A consistent trend is observed in the three sets of reactions. In each case CHF is the most reactive radical. Replacement of the fluorine atom by hydrogen slows down the reaction, but only slightly. Replacement of the hydrogen atom by fluorine also lowers the reactivity, but by a much larger factor of between 3 and 10. Comparing cross sections rather than rate constants gives the same qualitative results. These observations run counter to the trend for molecular oxygen mentioned in the Introduction, where CHF was unreactive and replacement of the fluorine atom on CHF by hydrogen enhanced the reactivity by 4 orders of magnitude.

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