Kinetic studies of the reaction of atomic hydrogen with trifluoroiodomethane.

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Abstract

Rate constants for the reaction of H atoms with CF₃I have been measured using the flash-photolysis/resonance fluorescence technique over 295 -730 K. The results are $k = (6.7 \pm 0.3) \times 10^{-11} \exp[(-3.8 \pm 0.2) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, where the uncertainties represent $\pm 1\sigma$ in the Arrhenius parameters. Error limits for k are $\pm 10\%$. The reaction is shown to be the dominant pathway for consumption of CF₃I in a stoichiometric methane/air flame.

1. INTRODUCTION

Production of halon fire extinguishing agents such as CF_3Br and CF_2ClBr is banned under the Montreal Protocols on Substances that Deplete the Ozone Layer, and CF_3I is a potential candidate for service in some applications as a new fire suppressant [1], but there is a lack of kinetic information on its reactions at elevated temperatures. Here we present the first measurements of the rate constant k_1 for the reaction

above room temperature. The results are used to assess likely destruction pathways for CF_3I in a stoichiometric methane/air flame.

2. EXPERIMENTAL METHOD

The experimental apparatus and modifications for H-atom kinetics have been described elsewhere [2][3][4]. In brief, atomic H was generated by pulsed flash lamp photolysis of NH_3 , through MgF_2 optics, in the presence of a large excess of CF_3I . The nominal discharge time was 7 μs . All experiments were carried in Ar bath gas at a total pressure P , and the reagent concentrations were derived from P and the mole fractions of reagents in mixtures made in darkened glass bulbs. The gas mixtures flowed slowly through the reactor, on a time scale long compared with that for loss of H atoms, so that the kinetic conditions were effectively static. The relative concentration of H was monitored using time-resolved resonance fluorescence at a wavelength of 121.6 nm. Fluorescence was detected with a solar-blind photomultiplier tube (PMT) employed with pulse counting and signal averaging. A filter of dry air was employed in front of the PMT to help separate the Lyman- α radiation from other scattered vacuum UV

radiation from the microwave-powered resonance lamp. Under pseudo-first-order conditions and constant $[\text{NH}_3]$,

$$d[\text{H}]/dt = -(k_1[\text{CF}_3\text{I}] + k_{\text{diff}})[\text{H}] = -k_{\text{ps1}}[\text{H}] \quad (2)$$

where k_{diff} accounts for loss of H atoms out of the reaction zone other than by reaction with CF_3I , primarily via diffusion to walls of the reaction cell. Depending on the conditions, k_{diff} varied between 50 - 300 s^{-1} . k_{ps1} was obtained by fitting the observed fluorescence intensity I_f versus time profiles to an exponential decay (an example is shown as the inset on Fig. 1) over typically about four to eight lifetimes:

$$I_f = A \exp(-k_{\text{ps1}} t) + B \quad (3)$$

The second-order rate constant k_1 was obtained as the slope of a linear plot of k_{ps1} versus typically five values of $[\text{CF}_3\text{I}]$, from 0 to $[\text{CF}_3\text{I}]_{\text{max}}$ (see Fig. 1 for an example). An important verification that pseudo-first-order conditions were achieved is that the measured k_1 should be independent of the initial concentration of H atoms. $[\text{H}]_0$ was altered by changing the concentration of NH_3 (by up to about a factor of 3) and/or the energy discharged through the flash lamp, F , which was varied by a factor of 2. The temperature T in the reaction zone was monitored with a thermocouple, corrected for errors which arise from radiative heat transfer between the thermocouple and the heated reactor walls of up to 10 K, before and after each set of k_{ps1} measurements, and is expected to be accurate to within $\pm 2\%$ [5]. The average residence time of gas mixtures in the heated reactor before photolysis, τ_{res} , was varied by up to a factor of 4 to check for possible pyrolysis of CF_3I .

The Ar (Air Products, 99.997%) was used directly from the cylinder, and NH_3 (MG Industries, 99.99%) and CF_3I (Alfa Aesar, certified analysis 99.95%, air 0.05%, HI not detectable)

were purified by freeze-pump-thaw cycles at 77 K.

4. RESULTS

The experimental conditions and results for k_1 are summarized in Table 1. The independence of k_1 from F and $[NH_3]$ shows that secondary chemistry involving photolysis or reaction products was negligible and that pseudo-first-order conditions were attained, and the lack of dependence of k_1 on τ_{res} shows that pyrolysis of CF_3I was unimportant. Table 1 also lists the weighted mean values [6] of k_1 at each temperature.

The Arrhenius plot for reaction 1 is shown in Fig. 2, and a weighted linear fit [7] to the set of 24 measurements yields

$$k_1 = (6.7 \pm 0.3) \times 10^{-11} \exp((-3.8 \pm 0.2) \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (4)$$

The quoted errors in the Arrhenius parameters are 1σ and are statistical only. Consideration of the covariance leads to a 2σ precision for the fitted k_1 of 3-5 %, and allowance for possible systematic errors (up to 2% each in the flow rates, T and P) leads to 95% confidence intervals of about $\pm 10\%$.

5. DISCUSSION

Our k_1 values are compared with previous measurements by Morris et al. [8] over 196-293 K in Fig. 2. It may be seen that there is excellent accord at room temperature where the two temperature ranges meet. Given that the earlier work used a different technique, ESR detection of H atoms in a discharge/fast-flow apparatus, there seems to be little evidence of systematic error in either data set. Apparently k_1 exhibits a linear Arrhenius dependence over a wide range of

temperature, so that eq. 4 is also a reasonable representation of the combined data set, over 200-730 K. For comparison, an unweighted fit to the points on Fig. 2 yields

$$k_1 = (6.4 \pm 0.3) \times 10^{-11} \exp((-3.7 \pm 0.1) \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (5)$$

and the parameters are not significantly different from those in eq. 4.

Reaction 1 has similar rate constants to its methyl analog

The Arrhenius parameters for k_5 are $A = (6.3 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $E_a = (-5.0 \pm 0.3) \text{ kJ mol}^{-1}$ [9], which are very close to those for k_1 summarized in eq. 4. We have shown that reaction 5 proceeds via I-atom abstraction rather than substitution of I by H or H-atom abstraction [9], and *ab initio* calculations have indicated very large barriers to F-atom abstraction in reactions of H with hydrofluoromethanes [10], so the product assignment in reaction 1 seems reasonable. The C-I bond dissociation enthalpy in CH_3I at 298 K is $237.2 \pm 1.3 \text{ kJ mol}^{-1}$ [11], somewhat greater than $227.2 \pm 1.3 \text{ kJ mol}^{-1}$ in CF_3I [12], so that reaction 1 is more exothermic than reaction 5. Possibly this contributes to the marginally smaller E_a for reaction 1, although the two reactions have very similar kinetics.

Reaction 1 is fairly fast even at room temperature. We now consider the likely fate of CF_3I in combustion systems. We have calculated effective loss rates for CF_3I via attack by the flame radicals H, OH [13], O [14] and CH_3 [15], and by unimolecular decomposition [16], using concentration and temperature profiles calculated using the Chemkin package [17] and the GRI mechanism [18] for an atmospheric pressure, stoichiometric methane/air flame. The results apply to traces of added CF_3I , where the C/H/O chemistry is unperturbed. As may be seen from Fig. 3, at all points in the flame, reaction 1 is the most important pathway for destruction of CF_3I . This

reflects both the large value of k_1 and the high relative abundance of H atoms in flames, where they are important chain carriers. The reactivity of CF_3I makes it an efficient scavenger of H atoms at low and moderate temperatures, so this agent might be a useful inhibitor of ignition and other lower temperature combustion processes.

6. CONCLUSIONS

The rate constant for reactions of H atoms with CF_3I has been measured at temperatures up to about 730 K. The results agree well with earlier work at room temperature and below, and are similar to those for the analogous reaction $\text{H} + \text{CH}_3\text{I}$. Modeling of a stoichiometric methane/air flame indicates that the $\text{H} + \text{CF}_3\text{I}$ reaction is the fastest destruction pathway for CF_3I in all parts of the flame.

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Table 1

Rate constant measurements of the reaction $\text{H} + \text{CF}_3\text{I}$

T, K	P, mbar	τ_{res} , s	F, J	$[\text{NH}_3]$	$[\text{CF}_3\text{I}]_{\text{max}}^{\text{a}}$	$k_1 \pm \sigma_{k1}$
				$10^{15} \text{ molecule cm}^{-3}$	$10^{12} \text{ molecule cm}^{-3}$	$10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
295	64.5	1.3	4.05	3.32	3.79	1.39 ± 0.04
295	66.0	1.4	5.00	2.63	3.16	1.35 ± 0.01
295	66.0	1.4	2.50	2.63	3.16	1.39 ± 0.04
295	73.7	3.1	4.05	4.24	5.25	1.37 ± 0.06
295						$1.35 \pm 0.02^{\text{b}}$
354	92.6	2.4	6.05	2.12	2.20	1.69 ± 0.06
354	92.6	2.4	1.80	2.12	2.20	1.66 ± 0.05
354	64.7	0.8	4.05	0.75	1.15	1.74 ± 0.07
354	74.1	1.3	4.05	1.47	1.47	1.91 ± 0.06
354						$1.74 \pm 0.06^{\text{b}}$
415	102.6	2.2	4.05	2.00	1.56	2.44 ± 0.10
415	69.4	1.0	4.05	1.35	0.96	2.50 ± 0.09
415	105.0	1.2	4.05	1.38	1.33	2.30 ± 0.05
415	59.7	0.7	4.05	0.96	0.93	2.15 ± 0.04
415						$2.26 \pm 0.06^{\text{b}}$
502	59.3	0.7	4.05	1.98	0.83	2.73 ± 0.17
502	58.5	0.7	5.00	1.96	0.83	2.78 ± 0.09
502	58.5	0.7	2.50	1.96	0.83	2.40 ± 0.15
502	76.5	1.6	4.05	2.24	1.39	2.76 ± 0.14
502						$2.70 \pm 0.12^{\text{b}}$

622	87.8	0.9	4.05	1.51	0.98	3.36 ± 0.11
622	87.4	1.7	4.05	1.53	1.08	2.77 ± 0.12
622	51.1	1.0	4.05	1.72	1.07	3.07 ± 0.25
622	122.8	1.2	4.05	1.37	1.02	3.19 ± 0.08
622						3.14 ± 0.12^b
731	111.7	1.8	4.05	1.64	2.07	3.22 ± 0.15
731	66.9	0.5	4.05	0.74	0.71	3.85 ± 0.20
731	113.8	1.1	4.05	1.08	1.20	3.41 ± 0.22
731	151.0	1.9	4.05	2.71	2.13	3.46 ± 0.07
731						3.45 ± 0.12^b

^a Smallest non-zero $[\text{CF}_3\text{I}]$ employed was typically about $0.25 [\text{CF}_3\text{I}]_{\text{max}}$.

^b Weighted mean value $\pm 2\sigma$ statistical precision.

Figure captions

Fig. 1 Plot of pseudo-first-order rate constant k_{ps1} vs $[\text{CF}_3\text{I}]$ at $P = 69$ mbar and $T = 415$ K. The inset shows the decay of time-resolved fluorescence intensity I_f for the filled point. The error bars represent $\pm 2\sigma$ statistical precision in k_{ps1} .

Fig. 2 Arrhenius plot of rate constants for $\text{H} + \text{CF}_3\text{I}$ ($\bullet$, this work; $\square$, ref. 8). Error bars represent $\pm 2\sigma$ statistical uncertainty at each temperature.

Fig. 3 Pseudo-first-order consumption rates of CF_3I by various pathways in a stoichiometric atmospheric pressure methane/air flame (solid lines, left-hand axis), and temperature profile (dashed line, right-hand axis).