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Rate Coefficients for the OH + CF_3I Reaction between 271 and 370 K

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The rate coefficient, k_1, for the reaction OH + CF_3I → products was measured under pseudo-first-order conditions in hydroxyl radical, OH. OH temporal profiles were monitored by laser-induced fluorescence (LIF), and CF_3I concentrations were determined by UV/Visible absorption. We determined k_1 (T) to be $(2.10 \pm 0.80) \times 10^{-11} \exp[-(2000 \pm 140)/T]$ cm^3 molecule^{-1} s^{-1}, over the temperature range 271 to 370 K. The quoted uncertainties are 2σ (95% confidence limits, $\sigma_A = A\sigma_{\ln A}$). Previous measurements of k_1(T) are compared with our values, and possible reasons for the discrepancies are discussed. The heat of formation of HOI is deduced to be less than -16 kcal mole^{-1}, if the products of reaction 1 are mostly HOI and CF_3. These measurements support the earlier conclusion that the reaction of OH with CF_3I plays a negligibly small role in the atmospheric removal of CF_3I.

Introduction

Since CF_3I was first proposed for use as a fire suppressant, its atmospheric chemistry has received increased attention. Laboratory studies of photolysis rates and reactions with tropospheric reactive species have been used to determine its atmospheric lifetime, ozone depletion potential, and global warming potential.[1−3] Since OH is a major oxidant in the troposphere, the rate coefficient for the reaction of OH with CF_3I

$$OH + CF_3I \rightarrow \text{products};\ k_1 \qquad (1)$$

is of interest.

The measured values for the rate coefficient, k_1, are highly disparate. Garraway and Donovan,[4] Brown et al.,[5] and Berry et al.[6] reported, respectively, k_1 (295 K) = $(1.2 \pm 0.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, k_1 (300 K) = $(3.1 \pm 0.5) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, and k_1 (292 K) = $(5.9 \pm 1.4) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. Garraway and Donovan[4] employed flash photolysis of a mixture of O_3, H_2O, and CF_3I and monitored the OH reactant concentration by time-resolved absorption at 308.15 nm. They measured k_1 under pseudo-first-order conditions in [OH], i.e., an excess of CF_3I, and reported that k_1 was not a function of photolysis lamp intensity. Berry et al.[6] employed flash photolysis ($\lambda > 120$ nm) of a mixture of H_2O vapor and CF_3I and monitored OH concentration via resonance fluorescence detection. In these experiments, the value of k_1 measured was a function of photolysis energy. Therefore, they measured k_1 at several flash lamp energies and obtained their value of k_1 from the intercept of a plot of measured k_1 vs photolysis energy. This type of linear extrapolation is based on the assumption that secondary chemistry of OH with CF_3I photolysis products is responsible for the increase in k_1 with increasing flash energy. Given the CF_3I concentrations used in the studies of Berry et al.[6] and Garraway and Donovan[4] and that CF_3I absorbs strongly at wavelengths <175 nm as well as between 240 and 320 nm ($\sigma > 10^{-19}$ cm^2 molecule^{-1}), substantial photolysis of CF_3I must have occurred in both experiments.

Brown et al.[5] produced OH from the reaction of NO_2 with H atoms from a microwave discharge and monitored OH radical concentrations using resonance fluorescence. Hence, they did not photolyze CF_3I. Their reported k_1 is a factor of 2 smaller than that of Berry et al.[6] and nearly a factor of 4 smaller than that of Garraway and Donovan.[4] However, Brown et al.[5] observed nonexponential OH loss profiles and speculated that a chain reaction was responsible for the increase in OH loss rate at longer reaction times in their experiments. Only Berry et al.[6] have reported the temperature dependence of k_1. Thus, it appears that k_1 (298 K) has not been measured in the absence of secondary reactions and only a single study has explored the temperature dependence of k_1. Therefore, we have measured k_1 using a different OH precursor and briefly investigated the effect of secondary chemistry in previous measurements of k_1.

Experimental Section

In our experiments, OH was produced by pulsed photolysis in the presence of excess CF_3I. OH temporal profiles were monitored by laser-induced fluorescence. The pseudo-first-order rate coefficients for the loss of OH, k_1', were measured as a function of CF_3I concentration, and k_1 was derived from a weighted linear least-squares fit of k_1' vs [CF_3I]. The concentration of CF_3I was determined via UV absorption. By photolyzing HONO at 351 nm, we minimize CF_3I photolysis to obtain a more accurate value for k_1 between 271 and 370 K. Further, we report that the value for k_1 measured using 248 nm laser photolysis depends on photolysis laser fluence because CF_3I absorbs significantly at this wavelength. The OH detection[7] and UV absorption apparatuses are described in previous publications.[8] Details specific to the present study are presented here.

Determination of CF_3I Concentration. The concentration of CF_3I was determined by UV/Visible absorption using Beer's

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law over the wavelength range (225−450 nm) using a deuterium lamp and a diode array spectrometer. The entire length of the absorption cell was maintained at a constant temperature by using recessed windows that constrained the absorption volume to a uniform temperature region. The absorption cross section of CF_3I ($\sigma_{266.6\ nm}$ (298 K) = 6.44 × 10^{-19} cm^2 molecule^{-1}) shows a small temperature dependence; therefore, the temperature-dependent absorption cross sections of Solomon et al.[1] were used to determine CF_3I concentrations.

OH Production. The primary OH source for these experiments was HONO photolysis at 351 nm. Since CF_3I photolyzes readily in the UV, 351 nm was preferred over 248 nm ($\sigma_{248\ nm}/\sigma_{351\ nm} \sim 1500$)[1] for photolysis. One test for secondary chemistry is to employ multiple radical sources. This proved difficult in the present study since the low value of k_1 required the use of relatively high concentrations of CF_3I. Photolysis of an O_3/H_2O mixture at 248 nm and H_2O_2 photolysis at 248 nm were used as alternative OH sources. These are discussed in more detail in the following sections.

351 nm Photolysis of HONO. In the majority of experiments, OH was produced by pulsed laser photolysis of HONO at 351 nm (XeF excimer laser).

$$\mathrm{HONO} + h\nu \rightarrow \mathrm{OH} + \mathrm{NO} \tag{2}$$

In the concentration range used, (4.8−8.5) × 10^{13} molecule cm^{-3}, with a typical path length of 15.1 cm, absorption due to HONO would be <0.0002, and hence, it could not be directly measured via UV/Visible absorption. Therefore, the concentration of HONO was estimated from the known rate coefficient (k_3 (298 K) = 4.5 × 10^{-12} cm^3 molecule^{-1} s^{-1})[9] for the reaction

$$\mathrm{OH} + \mathrm{HONO} \rightarrow \mathrm{products} \tag{3}$$

and the measured OH loss rate coefficient in the absence of CF_3I. Assuming that reaction with HONO was the only loss process for OH (i.e., neglecting loss of OH due to reactions with impurities in the bath gas or in the HONO gas mixture and the loss due to flow out of the detection region and diffusion) an upper limit for [HONO] was calculated. This estimate was sufficient to calculate a limit for the initial OH concentration ($[OH]_0$, < 2 × 10^{11} molecule cm^{-3}) from the measured photolysis laser fluence, the known absorption cross section of HONO ($\sigma_{351\ nm}$ = 21.2 × 10^{-20} cm^2 molecule^{-1}), and the assumed unit quantum yield for OH production. The calculated $[OH]_0$ ensured that our experiments were carried out under pseudo-first-order conditions.[9]

248 nm Photolysis of an O_3/H_2O Mixture. One alternative OH source was ozone photolysis at 248 nm

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \tag{4}$$

followed by the reaction

$$O(^1D) + H_2O \rightarrow 2\ OH \tag{5}$$

In these experiments, $[O_3]$ was ~1.5 × 10^{14} molecule cm^{-3}, photolysis fluences were <0.4 mJ pulse^{-1} cm^{-2}, and $[H_2O]$ was ~3.4 × 10^{15} molecule cm^{-3}, resulting in $[OH]_0$ of (2.6−4.9) × 10^{11} molecule cm^{-3}. The first-order loss of OH in the absence of CF_3I was due to its reactions with O_3 (k (298 K) = 6.8 × 10^{-14} cm^3 molecule^{-1} s^{-1})[9] and impurities and due to flow and diffusion out of the detection region. For these experiments, CF_3I was measured using a separate 50-cm-long absorption cell prior to entering the reaction cell because any slight fluctuations in $[O_3]$ would interfere with the determination of $[CF_3I]$ ($\sigma_{O_3}/\sigma_{CF_3I}$) = ~100 at this wavelength).[9] The CF_3I concentration in the reaction cell was corrected for the pressure difference (usually 25−35%) between the absorption cell and the reactor. At the beginning of the experiment, the ozone concentration was determined from its absorption at 253.7 nm in the 50 cm cell. During subsequent experiments, the ozone was flowed directly into the reaction cell. $[H_2O]$ was calculated from its vapor pressure, the measured flow rates of He through the H_2O bubbler, and of other gases, and the reaction cell pressure was measured by a capacitance manometer.

248 nm Photolysis of H_2O_2. A single experiment using H_2O_2 photolysis at 248 nm was attempted, but due to the low absorption cross section of H_2O_2, a large (~8 mJ pulse^{-1} cm^{-2}) photolysis fluence was needed. This resulted in concentrations of CF_3I photolysis products that were much larger than $[OH]_0$, for example, $[CF_3]/[OH]_0$ > 15. It was immediately apparent that the measured rate coefficient was much larger (greater than a factor of 5) than those done with ozone or HONO photolysis; H_2O_2 photolysis was not used further as an OH source.

Materials. He (99.997%) and O_2 (99.99%) buffer gases were used as supplied. CF_3I (99%) was kept in an ice water bath to suppress any possible I_2 contamination. HONO was produced by the dropwise addition of $NaNO_2$ (0.1 M) to H_2SO_4 (40 wt %, 20 wt %, and 10 wt % solutions were used). A small He flow, (1−6) sccm^{-1}, over this solution was further diluted with He, (80−140) sccm^{-1}, and CF_3I prior to entering the reaction cell. $NaNO_2$ (assay 97%) and H_2SO_4 (assay 70.7%) were used as supplied by the vendors and mixed with distilled water to make the solutions for the HONO production. (We should note that on one occasion we reused the H_2SO_4 solution from a previous day for HONO generation: OH regeneration at longer times was observed. In all subsequent experiments, fresh reagents were used for HONO production, and they were changed every few hours. In all of the data reported here there was no indication of OH regeneration.) Ozone was prepared by passing ultrahigh purity O_2 through a commercial ozonizer and stored on a silica gel trap kept in a dry ice/ethanol bath. Several Torr of ozone was added to a preconditioned blackened 12-L Pyrex bulb and diluted with He. Deionized H_2O was kept in a bubbler held at room temperature through which He was flowed.

Results

The temporal profile of OH in the presence of CF_3I is governed by the equation:

$$\ln S_t = -k_1' t + \mathrm{constant} \tag{I}$$

where S_t is the OH fluorescence signal at time t and $k_1' = k_1 + k_{loss}$. k_{loss} is the first-order rate coefficient for the loss of OH due to its reaction with the OH precursor (HONO or O_3) and impurities in the bath gas as well as flow out of the detection region. The detection region is defined as the volume produced by the intersection of the photolysis and probe laser beams. The temporal profiles of OH were recorded and fit to eq I using a weighted linear least-squares method to obtain k_1'. k_1' values were measured as a function of CF_3I concentration and a weighted linear least-squares fit of k_1' vs $[CF_3I]$ data yielded k_1 as the slope and k_{loss} as the intercept.

351 nm Photolysis of HONO. As seen in Figure 1, the temporal profiles of OH obtained using HONO photolysis, both in the absence and in the presence of CF_3I, were exponential. The ratio of $[CF_3I]/[OH]_0$ was generally >5000 in these experiments with the estimated $[OH]_0$ between (0.6−1.3) × 10^{11} molecule cm^{-3} and $[CF_3I]$ from (1.0−11) × 10^{16} molecule

TABLE 1: Summary of k_1 Measurements at 296 K Using HONO Photolysis at 351 nm to produce OH[a]

pressure	v	probe fluence	photolysis fluence	[HONO]	$[OH]_0$	*l*	$[CF_3I]$	no of measurements	$k_1 \pm 2\sigma^c$
24.3	20	0.6	5.5	4.8−5.8	1.1	13.2	1.07−9.24	12	2.21 ± 0.44
25.5	20	0.6	3.3	6.7−8.5	1.0	13.2	1.91−11.4	15	2.09 ± 0.16
29.5	22	0.6	5.5	5.2	1.0	13.2	1.0−10	12	2.11 ± 0.22
23.9	18	0.6	3.3	5.4	0.6	13.2	2.2−11	7	2.11 ± 0.34
24.3	20	0.6	4.4	5.0	0.9	13.2	1.35−10.8	8	1.87 ± 0.32
24.3	19	0.8	4.7	5.0	0.9	25.8	1.86−8.02	6	2.39 ± 0.18
24.3	19	1.2	4.7	5.3	0.9	25.8	1.86−8.02	6	2.31 ± 0.37
17.5	12	0.9	1.3−7.0	6.0	1.2	25.8	7.2	5	*b*
20.3	12	0.8	5.5	5.6	1.1	25.8	1.97−7.28	8	2.61 ± 0.42
25.2	10	0.5	5.3	6.6	1.3	25.8	2.19−8.53	6	2.46 ± 0.25
25.3	20	2.3	5.9	7.0	1.5	25.8	1.45−6.00	5	2.78 ± 0.82
25.0	21	0.3	4.2	4.9	0.8	15.1	1.04−6.92	15	2.62 ± 0.13
average									2.35 ± 0.54

[a] Units are pressure: Torr; linear velocity, v: cm s^{-1}; fluence: mJ $pulse^{-1}$ cm^{-2}; [HONO]: 10^{13} molecule cm^{-3}; $[OH]_0$: 10^{11} molecule cm^{-3}; *l*, absorption pathlength: cm; $[CF_3I]$: 10^{16} molecule cm^{-3}; k_1: 10^{-14} cm^3 $molecule^{-1}$ s^{-1}. [b] In this experiment, the photolysis laser fluence was varied at a fixed CF_3I concentration. There was no significant change in the observed OH first-order loss rate coefficient. [c] σ is precision from the fit.

TABLE 2: Measured Value of k_1 as a Function of Temperature and Experimental Conditions Used[a]

T (K)	Pressure	probe fluence	photolysis fluence	[HONO]	$[OH]_0$	$[CF_3I]$	no of measurements	$k_1 \pm 2\sigma^c$
271	25	0.23	3.9	5.5	8.0	2.49−8.37	12	1.19 ± 0.19
296							105	2.35 ± 0.54[b]
315	25	0.25	2.8	6.4	6.4	1.56−10.3	11	3.40 ± 0.27
337	25	0.23	3.0	6.0	6.6	0.55−6.59	12	5.67 ± 0.31
354	26	0.30	4.6	5.5	9.2	1.25−4.41	15	7.21 ± 0.48
370	26	0.38	5.5	4.9	9.7	0.26−3.12	13	9.12 ± 0.22

[a] Units are pressure: Torr; fluence: mJ $pulse^{-1}$ cm^{-2}; [HONO]: 10^{13} molecule cm^{-3}; $[OH]_0$: 10^{10} molecule cm^{-3}; $[CF_3I]$: 10^{16} molecule cm^{-3}; k_1: 10^{-14} cm^3 $molecule^{-1}$ s^{-1}. [b] This is the average value for all 296 K experiments. [c] σ is precision from the fit.

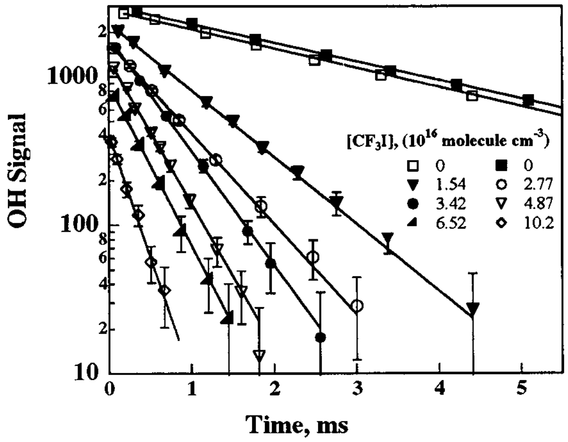

Figure 1. Examples of the decay of OH signal in the presence of CF_3I. The two decays with $[CF_3I] = 0$ were measured at the beginning and in the middle of the experiments.

cm^{-3}. The measured values of k_1 (296 K) along with a summary of the experimental conditions are presented in Table 1.

Since previous measurements of k_1 have reported either nonexponential loss of OH, or a dependence of measured k_1 on fluence, we were particularly concerned about secondary chemistry that could influence the determination of k_1. Therefore, we carried out numerous tests using the HONO source for OH production. To ensure the accuracy of the determination of the CF_3I concentration at 296 K, several different absorption path lengths (13.2, 15.1, and 25.8 cm) were used. To verify whether photolysis of CF_3I affected the observed OH loss rate coefficient, both the probe laser fluence, 0.24−2.3 mJ $pulse^{-1}$ cm^{-2}, and the photolysis laser fluence, 2.8−5.9 mJ $pulse^{-1}$ cm^{-2}, were varied. In another experiment, $[CF_3I]$ was fixed and the photolysis laser fluence was varied from 1.3−7 mJ $pulse^{-1}$ cm^{-2}: no change in the OH loss rate coefficient was observed. Hence, we believe that photolysis of NO_2 present in the HONO sample did not influence the measured OH loss rate coefficients. The probe laser fluence was varied since previous attempts to measure k_1 in this laboratory using HNO_3 photolysis at 193 nm to produce OH has shown a dependence on this parameter. In addition, the linear gas flow velocity was changed by a factor of 2, 10−22 cm s^{-1}. With these linear flow velocities at pressures of 17.5 to 29.5 Torr, the gas mixture within the detection volume was replenished several times between laser pulses (10 Hz). None of these variations affected the measured value of k_1. Typical first-order OH loss rate coefficients in the absence of CF_3I were 230−340 s^{-1}. In many experiments, these loss rate coefficients were measured both before and after determining a first-order rate coefficient in the presence of a known $[CF_3I]$. This was done because variations in [HONO] would affect the value measured for k_1' at a given $[CF_3I]$. These loss rate coefficients were dependent upon He flow through the solution used to generate HONO (increasing or decreasing [HONO]), pressure, total flow rate, and temperature. First-order OH loss rate coefficients measured in the presence of CF_3I ranged from ∼500−1800 s^{-1} at 271 K and from ∼500−3500 s^{-1} at 370 K. Generally, the first-order rate coefficient for OH loss due to diffusion and reaction with HONO was <20% of the measured value of k_1' at average CF_3I concentrations. The variety of tests performed in the 351 nm experiments, none of which produced a change in the measured value of k_1, gave us confidence in our reported value of k_1 (296 K) of (2.35 ± 0.54) × 10^{-14} cm^3 $molecule^{-1}$ s^{-1}.

The values of k_1 measured between 271 and 370 K are presented in Table 2. These were fit to an Arrhenius expression using a least-squares analysis of ln k_1 (T) versus 1/*T* data to obtain $k_1(T) = (2.10 \pm 0.80) \times 10^{-11} \exp[-(2000 \pm 140)/T]$ cm^3 $molecule^{-1}$ s^{-1}. Here, the uncertainty in E/R is twice the standard deviation of the slope and the uncertainty in *A* is $2\sigma_A = 2A\sigma_{\ln A}$. Figure 2 displays the Arrhenius plot for these experiments along with previous determinations of k_1. The uncertainty in k_1 due to any fluctuations in [HONO] at average CF_3I concentrations was <5% at every temperature except 271

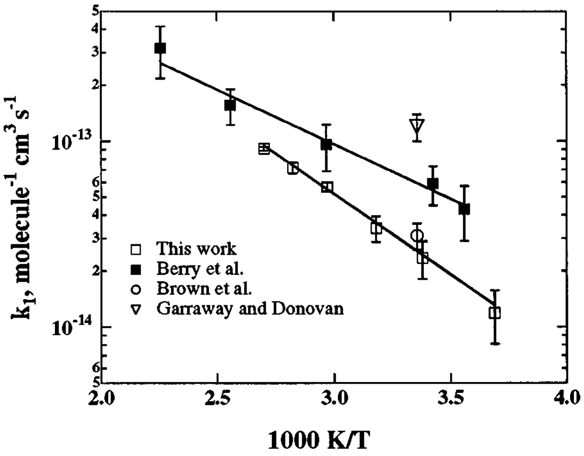

Figure 2. Plots of k_1(T) vs 1000/T from this study, and those of Berry et al.[6] Brown et al.,[5] and Garraway and Donovan.[4] The temperature dependence for this work from the least-squares fit of ln k_1 versus 1/T is given by $k_1(\mathrm{T}) = (2.10 \pm 0.80) \times 10^{-11} \exp[-(2000 \pm 140)/\mathrm{T}]$ cm^3 molecule^{-1} s^{-1}, (2σ measurement precision).

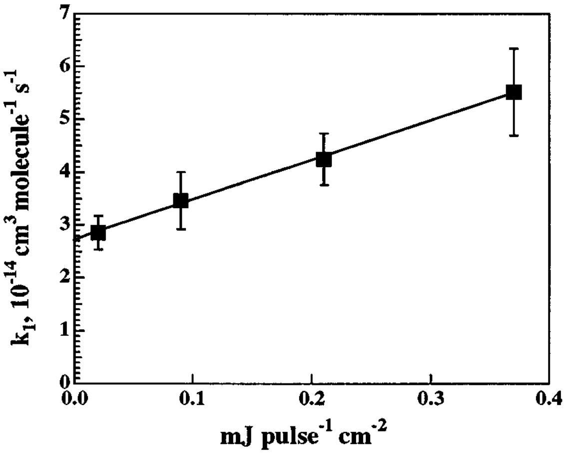

Figure 3. A plot of k_1 versus photolysis laser fluence when O_3 was photolyzed at 248 nm, followed by reaction with H_2O for OH production. The intercept yields a value for k_1 of (2.67 ± 0.15) × 10^{-14} cm^3 molecule^{-1} s^{-1}.

K, where it was <8%. The largest uncertainty in the CF_3I concentration is from the uncertainty in its absorption cross section at 266.6 nm, which is estimated to be <5%. (Uncertainty due to its UV/VIS absorbance is estimated to be less than 3%.) Adding these uncertainties and combining them in quadrature with 2σ precision of the fit gives an uncertainty of k_1 of ~20% at 271 and 296 K and ~10% at higher temperatures, all at the 95% confidence level.

248 nm Photolysis of an O_3/H_2O Mixture. At a fixed ozone concentration, increasing the photolysis laser fluence from 0.02 to 0.2 mJ pulse^{-1} cm^{-2} increased the measured value of k_1 by nearly a factor of 2. Typical first-order OH loss rate coefficients measured in the absence of CF_3I were ~135 s^{-1} (those in the presence of CF_3I were from 180 to 450 s^{-1}). A plot of k_1 vs 248 nm photolysis laser fluence is shown in Figure 3 and experimental conditions are given in Table 3. The linear extrapolation of the rate coefficient to a photolysis laser fluence of zero yielded a value of $k_1 = \sim 2.7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} as the intercept. We should note that altering the photolysis laser fluence varies not only the fraction of CF_3I dissociated but also $[OH]_0$ in these experiments. Although less precise than the value obtained using HONO photolysis, this intercept is consistent with that value of k_1.

TABLE 3: Measured Values of k_1 (296 K) Using Photolysis of O_3/H_2O Mixture at 248 nm to Produce OH[a]

fluence	k_1	no. of measurements	$[CF_3I]$	$[OH]_0$	$[O_3]$	$[H_2O]$
0.02	2.85 ± 0.32	5	1.17−9.57	0.7	3.15	3.4
0.09	3.46 ± 0.54	6	1.39−6.14	2.6	1.65	3.4
0.21	4.25 ± 0.49	5	1.16−7.59	4.9	1.48	3.4
0.37	5.52 ± 0.82	5	1.02−7.63	3.5	1.36	3.4
intercept	2.67 ± 0.15					

[a] Units are fluence: mJ pulse^{-1} cm^{-2}; k_1: 10^{-14} cm^3 molecule^{-1} s^{-1}; $[CF_3I]$: 10^{15} molecule cm^{-3}; $[OH]_0$: 10^{10} molecule cm^{-3}; $[O_3]$: 10^{14} molecule cm^{-3}; $[H_2O]$: 10^{15} molecule cm^{-3}. Uncertainties are 2σ precision of the slope in plots of k'_1 vs $[CF_3I]$.

Discussion

Three previously reported values for k_1, and the results from this study, are summarized in Table 4. Measuring k_1 is particularly difficult because it is relatively small and CF_3I is thermally and photolytically unstable. Because k_1 is small, higher concentrations of CF_3I are required to measure a significant increase in the OH loss rate coefficient. The larger $[CF_3I]$ coupled with its susceptibility to photolysis leads to high radical concentrations when OH is generated by photolysis, particularly at wavelengths <300 nm. Thus, one would conclude that the pulsed photolysis method might not be ideal for this measurement. However, the earlier flowtube experiments also observed nonexponential decays at longer times. In the following sections, we discuss possible secondary chemistry in experiments where OH was produced photolytically. We also discuss the effect of small I_2 impurities in these experiments.

Possible products from CF_3I photolysis are CF_3, and I or I*, I ($^2P_{1/2}$). CF_3I photolysis resulting in an excited state iodine atom occurs primarily at $\lambda < 300$ nm.[10,11] However, the obvious reactions,

$$\mathrm{I\ (or\ I^*) + OH \rightarrow IO + H} \tag{6a}$$

$$\mathrm{\rightarrow HI + O} \tag{6b}$$

are endothermic given the currently accepted values for the enthalpies of formation for IO and HI.[9] Addition of O_2 would deactivate I* produced by CF_3I photolysis through the near resonant electronic−electronic energy transfer process

$$\mathrm{I\ (^2P_{1/2}) + O_2\ (^3\Sigma) \rightarrow I\ (^2P_{3/2}) + O_2\ (^1\Delta)} \tag{7}$$

where $k_7 = 4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.[12] O_2 also reacts with CF_3

$$\mathrm{CF_3 + O_2 + M \rightarrow CF_3O_2 + M} \tag{8}$$

(k_8 296 K, 25 Torr) = ~3 × 10^{-12} cm^3 molecule^{-1} s^{-1}.[13] By sequestering CF_3 radicals, we should minimize the possible reaction of

$$\mathrm{CF_3 + OH + M \rightarrow CF_3OH + M} \tag{9}$$

To the best of our knowledge the rate coefficient for reaction 9 has not been published. Nevertheless, we expect the rate coefficient for OH reaction with CF_3O_2 to be smaller (or at least different) than that with CF_3. In the 351 nm experiments we added 5 Torr of O_2, and the measured value of k_1 was not significantly different than those measured in the absence of O_2. Hence, we believe these reactions did not influence our 351 nm experiments. In addition, varying the radical concentration in the 351 nm experiments by a factor of 2 (by varying the photolysis laser fluence) did not affect the measured value for

TABLE 4: Comparison of Measured k_1 with the Previously Reported Values[a]

k_1	T (K)	Pressure	temp range (K)	A	Ea	method	ref
12 ± 2	295					dis flow, res fluor (OH)	4
3.1 ± 0.5	300	1.8−5.0				dis flow, res fluor (OH)	5
5.9 ± 1.4	292	0.045−0.069	281−443	$(5.8 \pm 2.3) \times 10^{-12}$	2.7 ± 0.3	flash photolysis (H_2O) res fluor (OH)	6
2.35 ± 0.54	296	17.5−29.5	271−350	$(2.10 \pm 0.80) \times 10^{-11}$	4.0 ± 0.3	laser photolysis (HONO), laser induced fluorescence (OH)	this work

[a] Units are k_1: 10^{-14} m^3 molecule^{-1} s^{-1}; A: cm^3 molecule^{-1} s^{-1}; Ea: kcal mole^{-1}. Uncertainties are 2σ precision only for the work of Brown et al.[5] and this work, 1σ precision for Berry et al.[6] and unspecified for Garraway and Donovan.[4]

k_1. It is important to note that typical CF_3 concentrations, calculated from [CF_3I], photolysis laser fluences, and its known absorption cross section, were in the range $(0.6-3) \times 10^{11}$ molecule cm^{-3} for the 351 nm experiments.

In our 248 nm experiments (O_3/H_2O), significantly larger fractions of CF_3I were photolyzed, i.e., $[CF_3]_0$ ranged from $(0.3-7.0) \times 10^{12}$ molecule cm^{-3} even though lower photolysis laser fluences were used. Unfortunately, O_2 could not be added to these experiments since it quenches[9] $O(^1D)$ to $O(^3P)$ and prevents OH formation. Another reason to use low ozone concentrations and photolysis laser fluences in these experiments was to minimize the reaction

$$I + O_3 \rightarrow IO + O_2 \tag{10}$$

[k_{10} (298 K) = 1.2×10^{-12} cm^3 molecule^{-1} s^{-1}].[9] Although there are no reported values for the rate coefficient for the reaction,

$$OH + IO \rightarrow \text{products} \tag{11}$$

the IO product from reaction 10 could react rapidly with OH and influence the measured value for OH loss rate coefficient. The ClO + OH and BrO + OH reactions have rate coefficients on the order of 10^{-11} cm^3 molecule^{-1} s^{-1}.[9,14−16] One test for the influence of reactions 10 and 11 was to vary [O_3] from $(1.5-4.2) \times 10^{14}$ molecule cm^{-3} at a fixed [CF_3I] such that the IO production rate is altered. The photolysis laser fluence was varied to maintain a constant $[OH]_0$. The measured OH loss rate coefficient was not affected by varying the ozone concentration over this range.

Because photolysis of O_3 at 248 nm also produces $O(^3P)$ with a quantum yield of 0.1, the reaction

$$O(^3P) + CF_3I \rightarrow CF_3 + IO \tag{12}$$

[k_{12} (298 K) = 4.3×10^{-12} cm^3 molecule^{-1} s^{-1}],[17] followed by reaction 11 could also influence the OH loss rate. In an experiment where $O(^3P)$ was produced in the presence of CF_3I, Watson et al.[18] observed IF and postulated it to be formed via the reactions

$$O(^3P) + CF_3 \rightarrow F_2CO + F \tag{13}$$

$$F + CF_3I \rightarrow IF + CF_3 \tag{14}$$

Reaction 14 is thought to be rapid,[19] $k_{14} \sim 10^{-10}$ cm^3 molecule^{-1} s^{-1}, and k_{13} (294 K) = 3.1×10^{-11} cm^3 molecule^{-1} s^{-1}.[20] If the IF molecule were formed in our experiment it would probably react with OH, since both channels

$$IF + OH \rightarrow HOF + I \tag{15a}$$

$$\rightarrow HOI + F \tag{15b}$$

are likely to be exothermic. However, given the value of k_{12} and CF_3I concentrations used, reaction 12 should have consumed all $O(^3P)$ before a significant fraction of CF_3 (produced by reaction 12 or photolysis) could react with $O(^3P)$. Since we observed k_1 to vary with photolysis fluence when photolyzing both H_2O_2 and O_3/H_2O sources at 248 nm, we believe that reaction 9 contributed at least partially to the measured value of k_1, but we cannot rule out some influence from reaction 11 in the O_3/H_2O experiments.

Berry et al.[6] used flash photolysis ($\lambda > 120$ nm) of water vapor to produce OH in the presence of excess CF_3I in Ar buffer gas. They observed the measured k_1 to increase with flash lamp energy and extrapolated the measured value to zero energy to obtain the true value of k_1. Water absorbs strongly at $\lambda < 190$ nm, and the flashlamp radiation extends to longer wavelengths where $\sigma(CF_3I) \gg \sigma(H_2O)$. It is probable that significantly more CF_3I was photolyzed than water because the [H_2O]/[CF_3I] ratio in their experiments on the average was only ~3.5. If $[CF_3]_0$ is about equal to $[OH]_0$, reaction[9] could contribute to an increase in the OH loss rate coefficient, if the rate coefficient for the association reaction of CF_3 radicals with OH is $\sim 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 25 Torr. If $[CF_3]_0$ is greater than $[OH]_0$, a smaller rate coefficient for the reaction of CF_3 radicals with OH could influence the value measured by them.

Thus, there are many reactions that could have contributed to the measured dependence of k_1 on laser or flash lamp fluence. In our 248 nm experiments, we observe a dependence upon laser fluence; however, since we are unable to completely isolate specific reactions, we cannot identify which reactions are responsible for the fluence dependence.

Another possible reason for the measured k_1 to increase with photolysis laser fluence is the production of H atoms from photolysis of water

$$H_2O + h\nu \rightarrow OH + H \tag{16}$$

which reacts quickly [k (298 K) ~ 1.35×10^{-11} cm^3 molecule^{-1} s^{-1}][6,19] with CF_3I

$$H + CF_3I \rightarrow HI + CF_3 \tag{17}$$

Given an average concentration of CF_3I of $\sim 1.6 \times 10^{15}$ molecule cm^{-3}, <140 μs are necessary for complete removal of H atoms (i.e., 3 1/e lifetimes for reaction 17). The rate coefficient for the reaction,

$$HI + OH \rightarrow H_2O + I \tag{18}$$

($k_{18} = 3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1})[9] is over a thousand times larger than the value for k_1 reported in this paper and more than 500 times larger than the value of k_1 reported by Berry et al.[6] This implies that $[CF_3I]/[OH]_0$ must be >2500 for reactions 17 and 18 to have less than a 20% influence on their measured value of k_1. If only reaction 18 contributed the increase in measured k_1, the slope of their measured value of k_1 with photolysis energy should be larger than what we observe, but the intercept should be the same as our measured value, as long as the concentration of radicals that react with OH increased linearly with photolysis energy. However, Berry et al.[6] obtained a value of (5.9×10^{-14} cm^3 molecule^{-1} s^{-1}; 292 K) cm^3 molecule^{-1} s^{-1}, which is higher than the intercept we obtained in our ozone photolysis experiments ($\sim 2.7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}; 296 K) or the value we measured using HONO photolysis. The difference could be due to nonlinear dependence of measured k_1 on photolysis energy and/or additional OH loss processes. In any case, due to the absence of secondary chemistry, we believe that the 351 nm photolysis of HONO for OH production is a more reliable method of determining k_1. It should be noted that Garraway and Donovan[4] should have seen a dependence on photolysis energy based on our above analysis; they did not report such dependence.

Contamination of the CF_3I Sample. Another potential problem in determining k_1 is the possibility of I_2 contamination. Because of the large rate coefficient for the reaction of I_2 with OH, 2.1×10^{-10} cm^3 molecule^{-1} s^{-1},[21] a 0.01% contamination of I_2 in CF_3I will lead to an OH loss rate coefficient due to reaction with I_2 that is approximately the same as that due to reaction with CF_3I. In our experiments, CF_3I (99%) was kept in an ice water bath to suppress any possible I_2 contamination. To test for the presence of I_2, a 100-cm cell was filled with the CF_3I sample and its absorption at 508 nm (Cd lamp) was monitored. There was no change in absorbance at this wavelength upon addition of 300 Torr of the CF_3I sample. Given an absorption cross section of 2.5×10^{-18} cm^2 molecule^{-1} for I_2 at 508 nm and assuming we should have been able to observe an absorbance of at least 3%, we place a limit of $<0.002\%$ for the contamination from I_2 in CF_3I. In addition, the regulator on the CF_3I cylinder was flushed out at the beginning and end of each set of experiments and the main He flow was added directly after the CF_3I regulator to continually flush out this line. This was done because a slight trace of pink was observed in the Teflon line upon prolonged use in preliminary experiments where the He main flow was not added directly after the CF_3I gas regulator. Also, slightly larger values for k_1 were measured, presumably due to I_2 formation. However, we should note that an I_2 contamination of 0.02% of the CF_3I concentration would be sufficient to account for the difference in the value of k_1 measured by Berry et al.[6] and that reported here. Also, the presence of such an impurity would account for differences in the activation energies measured by Berry et al.[6] and us.

Reaction 1 could have several product channels, e.g.,

$$OH + CF_3I \rightarrow CF_3 + HOI \qquad (1a)$$

$$\rightarrow CF_3H + IO \qquad (1b)$$

However, only the HOI product has been observed.[22] The enthalpy of formation for HOI has been estimated from experimental and theoretical studies. Berry et al.[6] reported an activation energy of 2.7 kcal mol^{-1}, while we report a slightly larger value: 4.0 kcal mol^{-1}. Using $\Delta_f H°$ (298 K) (OH) = 9.3 kcal mole^{-1}, $\Delta_f H°$ (298 K) (CF_3I) = -140.9 kcal mole^{-1}, and $\Delta_f H°$ (298 K) (CF_3) = -112 kcal mole^{-1}, we arrive at $\Delta_{rxn}H° = \Delta_f H°$ (298 K) (HOI) + 19.6 kcal mole^{-1}. Combined with $\Delta_{rxn}H° = E\text{a} - RT = 3.4$ kcal mole^{-1}, for a bimolecular reaction, yields $\Delta_f H°$ (298 K) (HOI) = -16.2 kcal mole^{-1}. This is true if the products of reaction 1 are solely, or mostly, HOI and CF_3. It is important to ensure that the main products of reaction 1 are HOI and CF_3. The enthalpy of formation of -16.2 kcal mole^{-1} for HOI is significantly larger than the value of -8 to -9 kcal mole^{-1} recommended by Ruscic and Berkowitz,[23] and of -11.7 kcal mole^{-1}, given by Glukhovtsev et al.[24] However, it is in reasonable agreement with the -14.3 ± 1.6 recommended by Hassanzadeh[25] and excellent agreement with the value of -16.6 ± 1.3 of Berry et al.[6]

The atmospheric lifetime of iodine containing species has been discussed in detail in other publications.[1-3] In general, the photolysis rates of iodine compounds are rapid, resulting in atmospheric lifetimes on the order of days. CF_3I is expected to have a tropospheric lifetime of less than 2 days.[1] Previous calculations[1] assumed a rate constant of 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} for reaction 1 and showed that reaction with OH could lower the calculated atmospheric lifetime of CF_3I by $< 25\%$. The much lower value of k_1 reported here will further lower the significance of CF_3I loss due to reaction with OH, as compared to its photolytic loss.

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