Wide Temperature Range Kinetics of the O + CHF_3 Reaction

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Rate coefficients for the depletion of ground-state oxygen atoms by CHF_3 have been measured using a high-temperature photochemistry (HTP) reactor. The O atoms were generated by the vacuum ultraviolet (VUV) flash photolysis of either SO_2, O_2, or CO_2, and their relative concentrations were monitored by resonance fluorescence. The data are best fitted by the expression $k(630-940\ K) = 2.5 \times 10^{-11} \exp(-7236\ K/T)$ cm^3 molecule^{-1} s^{-1}. The data are contiguous with those from an earlier laser-photolysis shock-tube study for temperatures ranging from 960 to 1330 K. A fit to the combined data yields the recommendation $k(630-1330\ K) = 5.1 \times 10^{-10} \exp(-9536\ K/T)$ cm^3 molecule^{-1} s^{-1}, with 2σ precision levels varying from ±8 and ±22% and corresponding suggested accuracy levels of ±22 to ±29%. Transition-state theory predictions, made using input data from a literature ab initio study, are in excellent agreement with this recommendation over the entire temperature domain.

Introduction

A ban has been established on the use of halons, which are effective fire suppressants.[1] Suitable halon replacements are needed. Rumminger and Linteris have shown that FeO inhibits flames due in part to catalytic O- and H-atom scavenging cycles that are limited by saturation effects due to equilibrium constraints.[2] They suggested that an effective fire suppressant might include a blend of catalytic agents with those that reduce the equilibrium chain-carrying radical mole fractions. Hydrofluorocarbons could be used for the latter type, and trifluoromethane (HFC-23) is being considered as a suitable constituent.[3,4] Kinetic data for its reactions with such radicals are needed to model its effectiveness. A number of studies of CHF_3 destruction by O atoms in the ground-state reaction

$$O + CHF_3 \rightarrow OH + CF_3 \qquad \Delta H^{\circ}_{298} = 17 \pm 6\ \text{kJ/mol} \qquad (1)$$

have been reported;[5,6] however, the rate coefficients are in considerable disagreement.[7−11] The present work comprises an effort to clarify the situation. Experiments and transition-state theory calculations are reported and compared.

Experimental Section

The older-style HTP reactor[12] was used. Briefly, it consists of an alumina reaction tube (5.1 cm i.d.) that is surrounded by helical SiC heating elements and insulation and is enclosed in a water-cooled, steel vacuum chamber. To achieve the desired temperatures without decomposition of the reactant gases, a movable, air-cooled inlet is used. After emerging, the gases are mixed with the heated Ar bath gas. The residence time needed for the mixture to reach the reaction zone is adjusted so that the reactant gases are ≥95% mixed with the Ar.[13] The temperature of the reaction zone was measured before and after each experiment by a Pt−Pt/13% Rh thermocouple, which was doubly shielded to minimize radiation effects. A Fluid Precision, Inc., pressure transducer was used. The gas flow rates were controlled by Teledyne-Hastings flow controllers.

Ground-state $O(^3P)$ atoms were generated by the flash photolysis of SO_2, O_2, or CO_2 through a MgF_2 window ($\lambda >$ 110 nm). The decrease in the relative concentration of $O(^3P)$ atoms was monitored by fluorescence on the 130.2−130.6 nm resonance triplet. The fluorescence was induced by a constant wave (CW) microwave discharge lamp through which flowed 99.999% He, which contains O_2 and H_2 impurities. A CaF_2 (λ > 125 nm) window was used to transmit O-atom radiation and filter out Lyman α-radiation. The O-atom fluorescence was detected by an EMI 9403B solar-blind photomultiplier tube (PMT) and fed to a multichannel scaler signal averager.

The gases used were CHF_3 (99.8% from the Army Research Laboratory (ARL) and >98% from Aldrich), 99.993% O_2 ("UHP") from Praxair, 99.98% SO_2 ("anhydrous") and 99.8% CO_2 ("bone dry") from Matheson, and Ar (99.998%) obtained from the liquid form (Praxair).

The experiments were carried out under pseudo-first-order conditions, where $[O] \ll [CHF_3] \ll [Ar]$. Under these conditions, the fluorescence intensity I, which is proportional to [O], is expressed by

$$I = I_0 \exp(-k_{ps1}t) + B \qquad (2)$$

where k_{ps1} is the pseudo-first-order rate coefficient, $I_0 + B$ is the intensity at time $t = 0$, and B is the background, due mainly to scattered light. The values of k_{ps1} were obtained by a weighted fit of the observed I vs t profiles to eq 2.[14] Typically, five k_{ps1} measurements at varying $[CHF_3]$, with the minimum $[CHF_3]$ set at a factor of ca. 5−10 times lower than the maximum values listed in Table 1, were used to obtain the bimolecular rate coefficients at the temperature and pressure of the experiment (see also Figure 1).

The exponentiality of the I vs t plots was first tested by a two-stage residual analysis.[15] The analysis consists of a visual

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TABLE 1: Summary of Rate Coefficient Measurements of the O + CHF_3 → OH + CF_3 Reaction

T^a (K)	P (mbar)	[M] (10^{18}/ cm^3)	[photolyte] (10^{15}/cm^3)	F^b (J)	$[CHF_3]_{max}$ (10^{15}/cm^3)	z^c (cm)	$\bar{v}^d$ (cm/s)	$k_i \pm \sigma_{ki}$ (10^{-15} cm^3 molecule^{-1} s^{-1})
633	409	4.68	4.34^e	38	139	10.0	2.1	0.175 ± 0.025
650	273	3.05	~0.106^f	66	80.4	15.0	4.4	0.297 ± 0.067
661	137	1.51	5.27^e	59	44.5	10.0	6.5	0.451 ± 0.066
685	268	2.83	2.83^e	38	38.4	10.0	6.6	0.771 ± 0.10
697	211	2.19	4.10^e	59	36.3	10.0	9.8	1.20 ± 0.087
707	145	1.49	4.08^e	59	46.0	4.5	6.9	0.537 ± 0.10
710	140	1.41	1.34^g	72	54.7	10.0	6.4	1.23 ± 0.11
732	149	1.48	3.98^e	59	26.9	4.5	11.0	1.30 ± 0.24
775	298	2.78	3.73^h	54	59.0	15.0	4.8	1.74 ± 0.12
777	411	3.84	5.18^h	46	37.5	15.0	3.5	1.80 ± 0.25
794	268	2.44	2.39^e	59	34.4	10.0	7.7	3.11 ± 0.16
795	311	2.81	2.20^g	66	15.0	10.0	4.8	3.60 ± 0.45
817	112	1.32	8.61^e	50	14.1^i	6.0	7.3	3.85 ± 0.29
819	112	1.32	8.58^e	50	14.0	6.0	7.4	3.62 ± 0.29
833	416	3.65	1.63^h	50	19.4	15.0	5.5	7.04 ± 0.82
834	185	2.14	12.1^e	50	20.7^i	6.0	4.6	4.20 ± 0.14
857	137	1.16	2.75^e	59	14.6	4.5	13.5	6.00 ± 0.75
870	124	1.03	0.757^g	50	25.2	3.5	9.9	5.48 ± 0.78
889	203	1.65	5.42^e	38	26.6	4.5	9.5	5.57 ± 0.59
890	136	1.11	3.64^e	38	12.1	4.5	14.1	7.16 ± 0.59
896	137	1.11	3.61^e	59	3.65	4.5	8.8	13.3 ± 1.4
927	181	1.89	7.62^e	50	13.2	6.0	5.2	7.64 ± 0.41
931	408	3.20	1.78^g	59	0.961	12.0	4.2	8.52 ± 1.78
936	123	1.27	6.54^e	50	11.8^i	6.0	7.7	11.8 ± 0.47

[a] $\sigma_T/T = \pm 2\%$. [b] Flash energy. [c] Distance from the cooled inlet to the reaction zone. [d] Velocity. [e] O_2 photolyte. [f] No added photolyte was used; 10−60 ppm O_2 was present in the Ar bath. [g] SO_2 photolyte. [h] CO_2 photolyte. [i] CHF_3 (98%) in Ar from Aldrich was used. In all other experiments, the 99.8% CHF_3 from ARL was used.

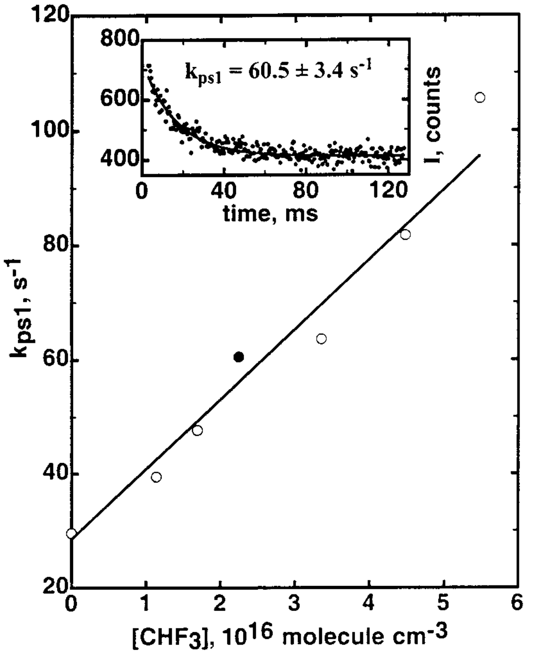

Figure 1. Plot of the pseudo-first-order decay rate coefficients of relative [O] versus [CHF_3] obtained at 710 K. The inset corresponds to the darkened circle and shows the decrease in fluorescence intensity with respect to time.

inspection of the residual plot followed by the runs test. However, the runs-test method has been suggested to be statistically unsound since it measures the randomness of the order of the signs of the residuals, not the goodness of fit.[16] Therefore, a new and statistically correct validation method, based on the combination of the χ^2 goodness of fit and the Monte Carlo technique has been developed[16] and has been used additionally. This led to the rejection of 8% of the data passed by the runs test without significantly affecting the ultimate $k(T)$ fit expression given below.

Results and Discussion

The rate coefficients are summarized in Table 1. At $T < 630$ K, the reaction became too slow to observe. Attempts at measuring rate coefficients >940 K yielded a large scatter. This can be attributed to the onset of the thermal decomposition of CHF_3, as estimated by extrapolation from the unimolecular decomposition rate coefficient data of Wagner and co-workers.[17] Calculations yield an estimate of ca. 1% decomposition at 940 K for the present conditions. The following experimental parameters were varied over wide ranges: P, total pressure; [M], the total gas concentration; z, the distance from the top of the cooled inlet to the center of the observed reaction zone; $\bar{v}$, the average linear gas velocity; [photolyte]; and F, the energy of the flash lamp. To demonstrate that the rate coefficients do not depend on any of these parameters, plots of $[k(T) - k_i]/k(T)$ vs these parameters were made, where $k(T)$ represents the rate coefficients obtained from the fit expression given below and k_i values are the individual rate coefficients measured. These residual plots are independent of these parameters. No dependence on the nature of the O-atom precursors was found.

Figure 2 shows the present data fitted by the Marquardt algorithm[18] to the form $A\exp(-E_a/RT)$, where σ_{ki} and $\sigma_T/T = \pm 2\%$ contribute to the weighting of each point. The fitted expression is

$$k_1(630\text{−}940\ \text{K}) = 2.5 \times 10^{-11} \exp(-7236\ \text{K}/T)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \quad (3)$$

The variances and covariances are $\sigma_A^2 = 1.4 \times 10^{-1}\ A^2$, $\sigma_E^2 = 9.1 \times 10^4$, and $\sigma_{AE} = 1.1 \times 10^2\ A$. The resulting 2$\sigma$ precision levels of the fit lie between ±9 and ±22%, depending on the temperature. Allowing deviations of ±20% for systematic errors, we found that the accuracy of the measurements varies from ±22 to ±30% at the 2σ statistical confidence limit. Attempts at fitting the present data to the expression $AT^n\exp(-E/RT)$ did not yield a better fit.

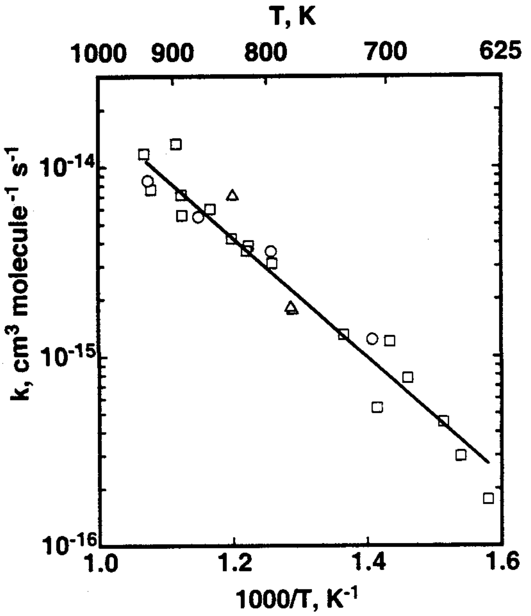

Figure 2. Arrhenius plot of the present rate coefficients of the O + $CHF_3 \rightarrow OH + CF_3$ reaction (□, measurement using O_2; ○, measurement using SO_2; △, measurement using CO_2; —, best fit to the measurements, eq 3).

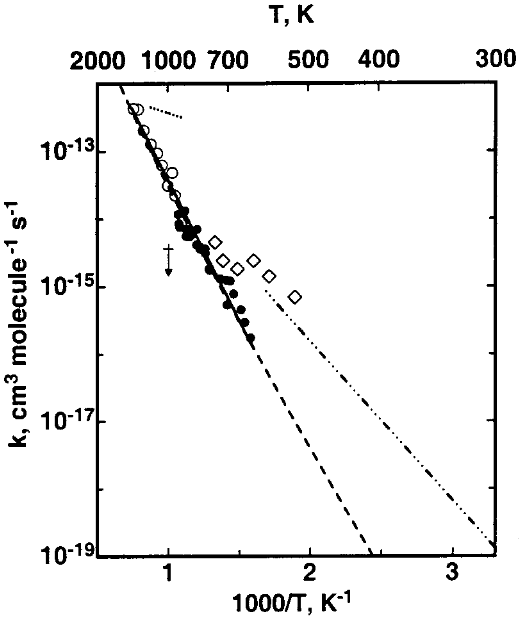

Figure 3. Comparison of the present rate coefficient measurements on the O + $CHF_3 \rightarrow OH + CF_3$ reaction with those of other data (◇, Medhurst et al.[7] 529−753 K; —•••—, Jourdain et al.[8] at ≈300−600 K; +, Wilson and O'Donovan[9] at 1000 K; •••, Richter et al.[10] at 920−1150 K; ○, Miyoshi et al.[11] at 956−1328 K; ●, present work at 633−936 K; —, present recommendation: a combined fit to data from both Miyoshi et al. and the present study, eq 4; — —, TST calculation).

Figure 3 compares the present results with literature values. The 530−750 K data recently reported by Medhurst et al. were obtained in an apparatus similar to that used here.[7] However, they followed the reaction using OH-product fluorescence and, consequently, had to account for the separately measured rate coefficients for OH consumption by CHF_3. The results confirm reaction 1 as the dominant reaction path, and their rate coefficients approach those of the present measurements at their higher temperatures. However, the slope of a line through their data does not agree with those of other studies. Impurities could be responsible for the difference between their results and those of the present work at lower temperatures.[7] No checks for exponentiality have been reported in that work. Jourdain et al. worked with a microwave discharge fast-flow reactor at low pressure, 0.4−4 mbar.[8] They give a $k(T)$ expression, but no individual data. Also, their actual temperature range has to be surmised. They used conditions such that $[O] \gg [CHF_3]$. As their measurements are higher than the present ones, an impurity may have been present in their work, or secondary CHF_3 reactions may have interfered. Wilson and O'Donovan's experiments, carried out at temperatures ranging from 300 to 1000 K, were made relative to O + CH_4 in a reactor similar to Jourdain's except that $[O] \ll [CHF_3]$.[9] In contrast to all other studies, no reaction could be observed, even at 1000 K, for which temperature they give the upper limit shown in Figure 3. The Richter et al. experiments[10] were carried out in a flame, i.e., a multireaction system, which is frequently rather unreliable for kinetic measurements. Certainly their activation energy is at odds with those in the other studies.

Miyoshi et al. worked with temperatures ranging from 956 to 1328 K with a flash-photolysis shock tube.[11] Burgess et al.[19] have suggested that Miyoshi's data, measured at these higher temperatures, could have been subject to CHF_3 dissociation. However, the use of data from Wagner and co-workers[17] to estimate the amount of decomposition under Miyoshi et al.'s conditions varied from $5 \times 10^{-5}\%$ to 0.05% over their temperature range; this implies that their system was not significantly affected by thermal decomposition. Their data, fitted by the expression $k(960-1330\text{ K}) = 7.6 \times 10^{-10} \exp(-9826\text{ K}/T)$, are somewhat larger and show a slightly higher activation energy than an extrapolation of our results would suggest. Possible reasons for this discrepancy are discussed below. As they give their individual data and associated uncertainties, the two data sets can be combined and treated as done above for the present measurements. This yields the recommendation

$$k_1(630-1330\text{ K}) = 5.1 \times 10^{-10} \exp(-9536\text{ K}/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1} \quad (4)$$

The variances and covariances are $\sigma_A^2 = 5.1 \times 10^{-2} A^2$, $\sigma_E^2 = 4.2 \times 10^4$, and $\sigma_{AE} = 4.6 \times 10^1 A$. The resulting 2σ precision levels of the fit lie between ±8 and ±22%, depending on temperature. The corresponding accuracy of the measurements varies from ±22 to ±29%. This recommendation is shown in Figure 3. As in the previous case, we did not obtain a better fit by fitting the data to a non-Arrhenius expression.

These results may be compared to information obtained from theory. To do this, we use the transition-state theory (TST) expression

$$k_{TST}(T) = \frac{k_B T}{h} \frac{Q^{\neq}_{OCHF_3}}{Q_O Q_{CHF_3}} \exp(-E_0^{\neq}/RT) \quad (5)$$

and assume that the vibrational and rotational motions of the transition state are separable. Here, k_B is the Boltzmann constant, h is the Planck constant, the values of Q are the total partition functions, and $E_0^{\ddagger}$, the classical activation barrier, represents the energy change, including zero-point energy produced going from reactants to the transition state for the reaction at 0 K.[20] The partition functions are calculated in the usual way using the ab initio results of Kreye.[21] Kreye investigated the reaction using the slightly modified G2 method at the UMP2/6-311g** level and reported the geometry, vibrational frequencies, and activation barrier values of 63.30 and 63.31 kJ/mol for two nearly identical transition states, $^3A'$ and $^3A''$, respectively. Since these two transition states are equivalent, eq 5 is multiplied by 2.[21] We assume that the O−H−C angle in both complexes is 180°, i.e., of C_{3v} symmetry. This is reasonable since Kreye reported angles of 177.26° and 181.6°. This assumption is implicit in the expression for the rotational partition function of the transition complex, which contains a symmetry factor of 3 in the denominator for the total number of rotations that yield indistinguishable representations. The evaluation of eq 5 with these values at 50 K intervals from 300 to 1500 K yields

$$k_{\mathrm{TST}}(300-1500\ \mathrm{K}) = 3.69 \times 10^{-18}\, T^{2.36} \exp(-7294\ \mathrm{K}/T)\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1} \quad (6)$$

This expression is plotted as the dashed curve in Figure 3. The TST results are nearly indistinguishable from the best fit from eq 4 over the common temperatures. Thus, the present recommendation, based on the results from both Miyoshi et al. and the present study, is further justified. The curvature indicated by eq 6 implies that the slope increases by 9% from the temperature range covered by the present data (630−930 K) to that of Miyoshi et al. (950−1330 K). By contrast, the experimental data show an increase of 36%. This difference can be attributed to the uncertainties of both experiments and the TST input data.

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