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Absolute rate constant for the reaction of atomic chlorine with hydrogen peroxide vapor over the temperature range 265–400 K

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Rate constants for the reaction of atomic chlorine with hydrogen peroxide have been measured from 265–400 K using the flash photolysis–resonance fluorescence technique. Analytical techniques were developed to measure $[H_2O_2]$ under reaction conditions. Due to ambiguity in the interpretation of the analytical results, the data combine to give two equally acceptable representations of the temperature dependence: $k_1 = (3.14 \pm 0.56) \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1} independent of temperture or $k_1 = (1.24 \pm 0.74) \times 10^{-12}$ exp$(-384 \pm 168/T)$ cm^{3}molecule^{-1}s^{-1}. The results are compared to previous work at 298 K and are theoretically discussed in terms of the mechanism of the reaction. Additional experiments on the H+H_2O_2 reaction at 298 and 359 K are compared with earlier results from this laboratory and give a slightly revised bimolecular rate constant of $(4.89 \pm 0.70) \times 10^{-12}$ exp$(-2780 \pm 280/RT)$ cm^{3}molecule^{-1}s^{-1}.

INTRODUCTION

The rate constants for chlorine atom reactions with hydrogenous molecules have become increasingly important due to the current interest in the potential modification of stratospheric ozone concentration.[1] Modelers have shown that hydrogen abstraction reactions which produce HCl constitute significant sinks for chlorine atoms, and the potential depletion of ozone from the Cl—ClO chain is moderated over that which is predicted if such reactions are not operative. Due to the known abundance of CH_4 in the stratosphere, one such important reaction is Cl + $CH_4 \to$ HCl + CH_3.[2]

Watson *et al.*[3] have reviewed other important abstraction reactions including Cl + $H_2 \to$ HCl + H[4] and have explicitly discussed the stratospheric implications. One possibly important substrate is hydrogen peroxide which is presumably formed from the self-disproportionation of HO_2. These authors have additionally studied

$$Cl + H_2O_2 \to products, \qquad (1)$$

and have supplied one of the two published room temperature values to date, the other being by Leu and DeMore.[5] These two studies show adequate agreement within claimed uncertainties. On the basis of these determinations and a presumed temperature dependence, Watson *et al.*[3] have concluded that Reaction (1) is of negligible importance in the stratosphere if the currently accepted levels of $[H_2O_2]$ from modeling calculations are correct. To date there have been no stratospheric determinations of $[H_2O_2]$. Additionally, there are no measurements of k_1 at stratospheric temperatures or indeed at any temperature other than 298 K. These

factors coupled with a fundamental interest in Reaction (1) have supplied the motivation for the present study. Here we report rate constants at four temperatures ranging from 265–400 K. The low temperature limit is restricted by the vapor pressure of H_2O_2 but does slightly overlap stratospheric temperatures. The high temperature limit is restricted by thermal decomposition of H_2O_2.

EXPERIMENTAL

The technique used in the present study is flash photolysis with resonance fluorescence detection of chlorine atoms. The details of the apparatus have been given previously,[6] and the application to chlorine atom detection has also been demonstrated.[2,4] Thus, only those aspects which are specific to the present study will be emphasized here.

In all of the reported experiments, chlorine atoms were produced by the flash photolysis of phosgene.[2,4,7] A sapphire filter was used to restrict photolyzing wavelengths to $\lambda \geq 143$ nm, and the photodecomposition of H_2O_2 was therefore minimized.

As in previous studies,[2,4] chlorine atom resonance radiation was produced in a flowing microwave driven resonance lamp from premixed 0.1% Cl_2 in He mixtures at ~0.5 torr total pressure. This radiation is only partially reversed under these conditions. Resonant fluorescent photons were observed at right angles and were taken to be directly proportional to chlorine atom concentration. In this work $(1-5) \times 10^{10} \leq [Cl]_0 \leq (1-5) \times 10^{11}$ cm^{-3}. The detected photons passed through a BaF_2 window which restricts $\lambda \geq 135$ nm, and, therefore, the effective spectral response of the detector was 135 nm $\leq \lambda \leq 175$ nm, the upper limit being determined by the photomultiplier response.

For the reaction rate studies, three component mixtures of phosgene, H_2O_2, and Ar diluent were premixed, and preliminary experiments showed that pseudo-first-order decay constants from exponential decay of

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chlorine atom fluorescence were higher with static or slowly flowing mixtures than with a flow rate which was sufficient to replenish the cell between successive flashes. This behavior may be indicative of the accumulation of secondary reaction products which can contribute to chlorine atom decay. The problem was easily eliminated in practice and constancy in decay constants was obtained by using faster flow rates of the reaction mixture. Under these fast flow conditions the amount of heterogeneous loss of H_2O_2 in the cell was routinely measured as will be described below.

The observed pseudo-first-order rate constants are composite since chlorine atom loss from the reaction and diffusional loss from the reaction viewing zone both contribute. As in earlier studies,[2,4,6] separate experiments at exactly the same pressure and temperature were performed without reactant H_2O_2 in order to obtain the diffusional rate constant k_d. Again, as in earlier studies,[2,4] these constants with an initially cleaned apparatus were found to be highly dependent on flash intensity. However, after prolonged use, the values became truly constant and showed no appreciable variation from 11 to 163 J flash energy. It was only under these conditions that both reactant and diffusional experiments were performed. In all of the experiments reported here the diffusional contribution was typically 10—20% of the observed pseudo-first-order decay constant in the presence of H_2O_2 at the two lower temperatures and 20—30% at the two higher temperatures.

The previously mentioned heterogeneous decomposition of H_2O_2 necessitated the development of analytical techniques for $[H_2O_2]$ under reaction conditions. In preliminary calibration experiments with aqueous solutions, $[H_2O_2]$ was determined by I_2 liberation from 1 M H_2SO_4 solution by KI, and the liberated I_2 was titrated with standard thiosulfate solution. Thiosulfate was previously standardized with KIO_3 solution.[8] Since the secondary standard thiosulfate solution tended to decompose slowly, we elected to measure the liberated I_2 by standard spectrophotometry at 420 nm with a Model 14 Cary spectrophotometer. Blanks were routinely performed for each analysis to correct for air oxidation. Under our analysis conditions, air oxidation was always found to be negligible. A Beer's law plot of OD against liberated $[I_2]$ was constructed where $[I_2]$ was determined by standard thiosulfate titration. The results were highly linear and reproducible over $0 < OD < 2$, and aqueous $[H_2O_2]$ could be routinely determined with an accuracy of ±5%.

Once the method was established it was used for analysis of the gaseous mixtures. It was initially found that the H_2O_2 in the ternary H_2O_2—$COCl_2$—Ar mixtures decomposed at unacceptable rates in the glass reservoirs on the vacuum line. However, with prolonged exposure to H_2O_2, the mixtures showed only slight decomposition over a period of hours. This decomposition necessitated making new mixtures daily, however. The lines leading to and from the reaction cell are of stainless steel and the cell assembly itself is of brass. Since the heterogeneous decomposition is expected to be more severe on metals than on glass, it

became clear that samples for chemical analysis of the reaction mixture should be collected as close as possible to the cell. Thus, provision was made for attaching cleaned and evacuated 5 l glass bulbs to the system through high vacuum "T" connectors directly before and after the cell assembly. Thorough cleaning of the bulbs was found to be absolutely necessary for reproducibility. For a given set of experiments, samples of the mixture were admitted to the bulbs at a rate which did not appreciably perturb the flow at the ambient pressure of the experiment. Within five minutes after collection, a known volume of 1 M H_2SO_4 was introduced into the sample bulbs, and the bulbs were thoroughly shaken in order to extract the gaseous H_2O_2 into the aqueous phase. Aliquots of the solution were then treated with KI in order to liberate I_2 and the liberated $[I_2]$ was determined spectrophotometrically. Blank experiments with only $COCl_2$—Ar mixtures showed no I_2 liberation.

Ternary mixtures were then prepared using pressure measurements. Based on these measurements, chemical analyses at room temperature showed 70—80% recovery of H_2O_2 both before and after the reaction cell. Repeat experiments over a period of minutes showed reproducibility of ±10%. This uncertainty coupled with the uncertainty of the analysis method (±5%) have led us to conclude that $[H_2O_2]$ reported for any one determination is only accurate to ±15%.

Argon (Matheson, 99.9995%) and helium (Airco, 99.9999%) were used without further purification. Chlorine (Matheson, 99.5%) was purified by fractional distillation at 195 K, and phosgene (Matheson, 99%) was similarly purified at 163 K. Hydrogen peroxide (90% from FMC Corporation) was thoroughly outgassed and was pumped at 273 K for at least 30 min to remove H_2O. The sample was then further pumped for 5—10 min at 298 K before making mixtures.

RESULTS

In all experiments $[H_2O_2] \gg [Cl]$ so that pseudo-first-order kinetics are applicable, and the decay of chlorine atoms is given by

$$\ln[Cl] = -k_{obs} t + \ln[Cl]_0. \qquad (2)$$

The observed pseudo-first-order rate constant under these conditions is

$$k_{obs} = k_{bi} [H_2O_2] + k_d. \qquad (3)$$

Plots of $\ln[Cl]$ against time were strictly linear over at least two decay lifetimes, and k_{obs} was obtained from a linear least squares analysis. As in previous studies from this laboratory, k_{obs} was studied over moderate changes in total pressure and appreciable changes in flash intensity, i.e., $[Cl]$, in order to ascertain whether secondary reactions resulting in additional Cl atom loss could be of importance. With freshly cleaned apparatus an intensity dependence was noted; however, with prolonged use and exposure of the system to the reaction mixture, k_{obs} became constant and no variations with flash intensity or total pressure were documented. Variations in k_{obs} were totally determined by $[H_2O_2]$ and k_d as indicated in Eq. (3). Since k_d is de-

TABLE I. Rate constants for the reaction $Cl + H_2O_2$.

T (K)	P_{COCl_2} (mTorr)	P_{Ar} (Torr)	Flash energy (J)	No. of expt.	$[H_2O_2]$ (10^{15} molecule cm^{-3}) B.C.[a]	A.C.[b]	k_{bi}[c,e] (10^{-13} cm^3 molec.$^{-1}$ s^{-1})	k_{bi}[d,e] (10^{-13} cm^3 molec.$^{-1}$ s^{-1})
265	150	40	20–127	11	3.13	2.68	2.54 ± 0.72	2.76 ± 0.78
	120	30	20–68	10	4.30	3.20	2.48 ± 0.34	2.91 ± 0.40
				21			2.51 ± 0.56	2.83 ± 0.60
299	120	30	18–110	12	3.34	3.45	3.22 ± 0.28	3.17 ± 0.28
	230	30	11–110	8	4.52	3.45	3.64 ± 0.78	3.90 ± 0.84
	230	60	14–144	11	5.19	4.03	3.46 ± 0.48	3.96 ± 0.54
				31			3.41 ± 0.48	3.64 ± 0.52
359	160	40	32–144	12	3.46	3.36	3.46 ± 0.70	3.51 ± 0.72
	300	80	46–144	11	3.84	3.51	4.11 ± 0.68	4.30 ± 0.72
				23			3.77 ± 0.70	3.89 ± 0.72
400	130	80	14–144	8	4.98	1.80	2.60 ± 0.68	4.90 ± 1.28
	260	80	31–163	10	5.65	2.01	2.61 ± 0.56	4.97 ± 0.92
				18			2.61 ± 0.56	4.94 ± 1.08
						Grand average	3.14 ± 0.56	$A = (1.24 \pm 0.74) \times 10^{-12}$ $E = 764 \pm 334$ cal/mol

[a]Before cell concentration;
[b]After cell concentration.
[c]Using arithmetic mean concentration.
[d]Using after cell concentration.
[e]Uncertainties are two standard deviations.

termined under identical conditions, the decay due to the reaction alone, $k_{bi}[H_2O_2]$, can be readily obtained.

The concentration of H_2O_2 in the reaction cell cannot be so easily determined for several reasons. In addition to the inherent uncertainty in the analytical determination discussed in the previous section, there is also some ambiguity concerning the interpretation of the H_2O_2 analysis. With the described apparatus, the mixture inlet and exit ports to the cell assembly are not symmetric. The gas mixture channels into the cell through a 1/16" hole drilled through the cell block and enters the reaction cell at the bottom of the assembly. Thus, samples are always preheated or cooled before entering the cell. Exit from the cell is directly from the top. Thus, there is ambiguity as to whether the $[H_2O_2]$ measurement should be the arithmetic mean of the "before the cell" and "after the cell" measurements or whether the "after the cell" measurement is more appropriate. For every set of experiments we give both concentrations in Table I. Values of k_{bi} are extracted from (a) the assumption that the arithmetic mean is valid and (b) the assumption that the "after the cell" measurement is appropriate. The results in Table I indicate that, while values of k_{bi} derived on the basis of assumption (b) are uniformly higher, the differences are not significant for the three lowest temperatures in that they are within one standard deviation of the corresponding values based on assumption (a). At 400 K, however, the difference is nearly a factor of 2 as a result of substantial loss of H_2O_2 in passing through the cell. In either case the errors for each set in Table I are two standard deviations and arise from random errors in k_{obs} alone. The close agreement between values from independent determinations at any given temperature gives further credence to the method of H_2O_2 analysis but gives no information as to whether

(a) or (b) is correct. If (a) is valid, k_{bi} shows no temperature dependence. Due to the inherent error in H_2O_2 analysis ($\pm 15\%$) we recommend a temperature independent value of $k_{bi} = (3.14 \pm 0.56) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} where the error is increased to 2σ to account for the uncertainty. If (b) is valid, a slight temperature dependence is noted. Linear least squares analysis leads to $k_{bi} = (1.24 + 0.74) \times 10^{-12} \exp(-384 \pm 168/T)$ cm^3 molecule^{-1} s^{-1} where the errors are 2σ as determined from the least squares analysis.

DISCUSSION

From the present experience it is clear that the accuracy with which rate constants can be measured for reactions of atoms or radicals with H_2O_2 is largely determined by the accuracy of the $[H_2O_2]$. Real time measurements of OH,[9] O,[10] H,[11] and Cl[3] with H_2O_2 have been reported and in no case has sufficient care been taken to measure $[H_2O_2]$ under reaction conditions. In one case[3] H_2O_2 was monitored by absorption photometry before making mixtures. The absorption coefficient was taken from Calvert and Pitts[12] who reprinted Volman's compilation[13] from some 1948[14] and 1929[15] work. It should be noted that inspection of the experimental results reveals only a 10–20% confidence in concentration measurements by the original authors.[15] Even if mixtures of H_2O_2 in diluents are indefinitely stable, which was not the experience here, concentration measurements by absorption photometry based on this cited work cannot be more accurate than 10–20%. These factors led us to the described analytical methods. Previous studies from this laboratory[11] employed a comparable method but analysis was limited to samples withdrawn from the storage bulb containing the reaction mixture.

Because of the above mentioned uncertainties in

H_2O_2 analysis, we have measured the rate constants for $H + H_2O_2$ at two temperatures in order to compare with earlier results from this laboratory.[11] Values of $(4.50 \pm 0.20) \times 10^{-14}$ and $(9.90 \pm 0.47) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} were obtained at 298 and 359 K, respectively, using assumption (a) for $[H_2O_2]$. These values are consistent with the same activation energy ($E = 2780 \pm 280$ cal/mol) as reported previously, within combined errors. Also the A factor is within the given range of $(5.2 \pm 2.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; however, the present values, with $[H_2O_2]$ analyzed under reaction conditions, give more confidence to the newly recommended value of $A = (4.89 \pm 0.70) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

The present results for $Cl + H_2O_2$ can be compared to the two previous room temperature studies.[3,5] Watson *et al.* report $k_1 = 5.8 \times 10^{-13}$ ($\pm$ factor of 2) cm^3 molecule^{-1} s^{-1}. We note, however, that if the results of Table III of Ref. 3 are analyzed by standard linear least squares methods, the above quoted value is not obtainable. A recent communication with one of the authors[16] has uncovered errors which result in a recalculated value of 5.2×10^{-13} ($\pm$ factor of 2) cm^3 molecule^{-1} s^{-1}. Thus, the agreement is satisfactory in view of the low confidence on the above result. The present value is substantially lower than that of Leu and DeMore[5] who give $k_1 = (6.2 \pm 1.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 295 K. The method in this work is discharge flow-mass spectrometry with [Cl] in excess. The rate constant is based on $[H_2O_2]$ depletion under pseudo-first-order conditions. Only relative $[H_2O_2]$ is measured and the previously mentioned ambiguities with regard to analysis do not contribute. Thus, the reason for this disagreement is not clear.

The present results combine to give two equally acceptable representations of the temperature dependence: (a) $k_1 = (3.14 \pm 0.56) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, or (b) $k_1 = (1.24 \pm 0.74) \times 10^{-12}$ exp $(-384 \pm 168/T)$ cm^3 molecule^{-1} s^{-1}, both for $265 \leq T \leq 400$ K. These results apply to the overall reaction, and the experiments give no direct information about the mechanism of reaction. By analogy with the H atom reaction,[11,17] Watson *et al.*[3] have suggested three exothermic processes:

$$Cl + H_2O_2 \rightarrow HCl + HO_2 , \qquad (4)$$

$$\rightarrow ClO + H_2O , \qquad (5)$$

$$\rightarrow HOCl + OH . \qquad (6)$$

Reaction (4) may be compatible with a simple abstraction model with a path degeneracy of two whereas Reactions (5) and (6) require a chlorine atom approach near the center of the molecule. From the viewpoint of activated complex theory, the major effect on the pre-exponential factor arises from the complex to reactant molecule moment of inertia ratio. If Reaction (4) proceeds through a collinear (Cl–H–O) complex, we calculate an A factor of $\sim 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (excluding vibrational contributions). In view of recent related results,[2,4] this value is quite reasonable. By

contrast, calculations based on Cl–O activated complex models show substantial decreases in the moment of inertia ratio and yields an A factor of $\sim 1.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. We note that the experimental results, either (a) or (b), are more compatible with the latter approach and may suggest important contributions from Reactions (5) and/or (6).

There are apparently no measurements of $[H_2O_2]$ in the stratosphere. If current estimates of stratospheric $[H_2O_2]$ are correct,[18] the present results indicate that odd chlorine loss due to Reaction (1) would be negligible. Finally, if more than one reaction channel is operative in Reaction (1), in particular if Reaction (5) is important, there may be further implications for stratospheric chlorine atom depletion. HCl produced in Reaction (4) would constitute a known sink for the odd chlorine chain cycle with ozone,[1] but if Reaction (5) is of substantial importance, the presence of H_2O_2 in the stratosphere would simply serve to exchange chlorine atoms with the other principle chain center, ClO. Thus, no odd chlorine would be lost to the HCl sink.

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