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ABSOLUTE RATE OF THE REACTION OF Cl(^{2}P) WITH MOLECULAR HYDROGEN FROM 200-500 K

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Short Title: $Cl + H_2$

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ABSTRACT

Rate constants for the reaction of atomic chlorine with hydrogen have been measured from 200 - 500 K using the flash photolysis-resonance fluorescence technique. The rate constants obey the Arrhenius equation $k = (2.66 \pm 0.42) \times 10^{-11} \exp(-2230 \pm 60/T)$ cm^3 molecule^{-1} s^{-1}. The results are compared with previous work and are discussed with particular reference to the equilibrium constant for the reaction and to relative rate data for chlorine atom reactions. Theoretical calculations, using the BEBO method with tunneling, give excellent agreement with experiment.

INTRODUCTION

Rates of the reactions of chlorine atoms with hydrogenous species are currently of interest due to their possible role in determining the rate of ozone depletion in the earth's stratosphere.[1] For example, the occurrence of the reaction

$$Cl + H_2 \rightarrow HCl + H \tag{1}$$

would result in the temporary destruction of Cl atoms and interruption of the Cl - ClO chain destruction of ozone. Thus accurate k_1 values at stratospheric temperatures are important for modeling the chemistry of the stratosphere. Reaction (1) is also part of the detailed model which has been proposed to explain the stability of CO_2 in the atmosphere of Venus.[2]

Furthermore, reaction (1) is of great importance as the primary standard for numerous relative rate measurements of reactions of Cl with hydrocarbons.[3,4] Absolute rate constants for the latter reactions can only be obtained if accurate k_1 values are available. However, there is a great deal of uncertainty in the recommended kinetic parameters for reactions (1).[4] Thus, the early review by Fettis and Knox[3] of the direct determination of k_1 by Rodebush and Klingelhoefer,[5] and the indirect determinations of Ashmore and Chanmugam[6] and Steiner and Rideal[7], resulted in a recommended $k_1 = (1.38\pm0.1) \times 10^{-10} \exp(-2760\pm70/T)$ cm^3 molecule^{-1} s^{-1} for the temperature range 273-1071. More recently, Benson, Cruickshank and Shaw[8] measured k_1 indirectly from 479-610 K and obtained $k_1 = (8.0\pm2.0) \times 10^{-11} \exp(-2655\pm200/T)$ cm^3 molecule^{-1} s^{-1}.

These authors reviewed, and recalculated where necessary, all of the
earlier data, including the direct determination of k_1 by Westenberg
and deHaas[9] using e.p.r. detection of Cl, and concluded that their
own equation for k_1 from 479 - 610 K was a good representation of the
data of references (5) - (9). This evaluation has been criticized
recently by Clyne and Walker[4] who recommended an evaluated $k_1 = (3.7\pm0.6)$
x 10^{-11} exp($-2146\pm51/T$) cm^3 molecule^{-1} s^{-1} from 195 - 610 K. In parti-
cular they argued that the direct determinations of k_1 in reference (5)
and (9) should be given low or zero weighting. Subsequent to the study
reported here, the very recent review of reaction (1) by Watson[10] was
brought to our attention. This evaluation recommended $k_1 = 4.7 \times 10^{-11}$
exp($-2340\pm30/T$) cm^3 molecule^{-1} s^{-1} based on the data of references (7),
(8) and (11). Reference (11) refers to an as yet unpublished direct
study of reaction (1) using flash photolysis and resonance fluorescence
(FP-RF) from 213-350 K, which yielded $k_1 = (5.5\pm0.5)$ x 10^{-11} exp($2391\pm$
$50/T$) cm^3 molecule^{-1} s^{-1}.

What is evident from the literature is the paucity of direct
measurements of k_1. Of the three direct studies, the early measurements
in reference (5) are felt to be unreliable[4] while the measurements of
k_1 reported in reference (9) have been questioned.[4] There remains only
the FP-RF measurement of Davis, Braun and Bass[12] at 298 K and the un-
published FP-RF study by Watson, Davis, Machado, Conaway and Oh.[11] The
present study has been made with the FP-RF technique over the range
200 - 500 K.

EXPERIMENTAL

The FP-RF apparatus and techniques used here have been described in detail previously.[13] Chlorine atoms were produced by the flash photolysis of phosgene[14] at $\lambda \geq 143$ nm (the sapphire cut-off). Chlorine atom resonance radiation was produced in the microwave discharge resonance lamp using a flow of 0.1% Cl_2 in He at a pressure of ~ 0.5 Torr,[13b] and resonantly scattered photons were viewed without wavelength resolution through a BaF_2 window at right angles to the resonance lamp. The signal detected was assumed to be linearly proportional to the atom concentration.[15]

Preliminary experiments showed that the pseudo first-order rate constants arising from exponential decay of the resonance fluorescence were slightly higher under either static or very slow flow conditions. This was the case for both diffusion and reaction mixtures and indicates that secondary complications contribute at insufficiently fast flow rates. Consequently the 2-component phosgene/argon diffusion mixtures and the 3-component phosgene/argon/hydrogen reaction mixtures were pumped through the cell at a rate sufficient to replenish the mixture at least once between successive flashes of photolyzing light. Care was taken to ensure that the particular flow rate used for any series of experiments was sufficiently fast such that the observed decays were well within the flow-independent region.

The diffusion correction term, k_d, which must be applied to the pseudo first-order reaction decay constants to allow for diffusion of Cl atoms out of the reaction viewing zone, was determined independently in the normal way.[13] Once again[13b] it was observed that k_d for the

earlier series of experiments, performed with a freshly cleaned optical train from flash lamp to reaction cell, depended on the intensity of the photolyzing flash, indicating secondary reactions in addition to pure diffusion out of the viewing zone. This effect was only significant for the early experiments, at room temperature, and was easily allowed for in practice.

One further unsatisfactory feature of the "diffusion" correction was that the measured k_d values were in general higher than those measured under apparently similar conditions in a previous study.[13b] Although the origin of this effect could not be identified with certainly, the history of the reaction vessel seemed to be a prime candidate. Thus, prolonged heating of the reaction vessel at 500 K, followed by measurement of k_d at room temperature, resulted in higher k_d values than measured prior to heating. Remeasurement of k_d following ultrasonic cleaning of the reaction vessel resulted in lower k_d values. This behaviour was not associated with any possible complexity in the photochemistry of $OCCl_2$, since identical behaviour was observed in check experiments with CCl_4 photolysis as the source of Cl atoms. The k_d corrections were measured immediately before and after each series of reaction experiments and were essentially constant with time. They amounted to $\sim$ 0-12% of the observed reaction rate decays for experiments from 260-406 K, and $\sim$ 20% at 500 K. Because of the high H_2 pressures required at the two lowest temperatures, the reactions being performed in undiluted H_2 and high mole fractions of H_2 at 200 K and 227 K respectively, k_d was measured in He diluent at these two temperatures, with the approximation

that rates of diffusion of Cl through He and H_2 are the same. The diffusion corrections at 227 K were ~ 20% of the reaction decay rates, while those at 200 K were ~ 25%.

Argon (Matheson, 99.9995%) and helium (Airco, 99.9999%) were used without further purification. Chlorine (Matheson, 99.5%) was further purified by fractionation at 195 K and phosgene (Matheson, 99%) was purified by fractionation at 163 K. The purity of the hydrogen re-actant (Matheson, 99.9995%) is critical for the low temperature experiments performed here, because of the low k_1 at these temperatures. For example, at 200 K the presence of as little as 7 ppm of an impurity as reactive as $C_2H_6^{16}$ would provide a contribution to Cl decay equal to that of H_2. However, the research purity hydrogen used was rated at < 0.5 ppm hydrocarbons as CH_4, the only major impurity being N_2 at < 5 ppm. Thus reactant impurities are not a problem here.

RESULTS

The decay of Cl atoms for the pseudo first-order conditions used here of $[H_2] \gg Cl$ may be represented by

$$\ln[Cl] = - k_{observed} \, t + \ln[Cl]_o, \tag{2}$$

where

$$k_{observed} = k_1 [H_2] + k_d. \tag{3}$$

Plots of $\ln[Cl]$ vs t were linear and values of $k_{observed}$ were obtained using a linear least squares analysis. The resulting k_1 values, presented in Table 1, were independent of both P_{total} and $[H_2]$ as expected. Table 1 also indicates that k_1 was independent of a wide range of flash energy, and hence a wide range of $[Cl]$, for each set of experimental conditions, confirming that secondary reactions involving Cl were negligible.

The lower set of points in Fig. 1 is an Arrhenius plot of the mean k_1 obtained at each of the 7 temperatures investigated. A linear least squares analysis provides the equation $k_1 = (2.66 \pm 0.14) \times 10^{-11}$ exp $(-2230 \pm 20/T)$ cm^3 molecule^{-1} s^{-1} from 200-500 K where the quoted error limits represent one standard deviation. The rather small error limits in the Arrhenius parameters obtained here may be fortuitously low, given the relative uncertainty in the applied diffusion corrections, as discussed in the previous section. More realistic error limits might be 3 standard deviations, which results in $A_1 = (2.66 \pm 0.42) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $E_1/R = (2230 \pm 60)$.

DISCUSSION

The results obtained here are compared with those from all other direct studies of reaction (1) in Fig. 1. The present FP-RF results from 200-500 K are seen to be in excellent agreement with the e.p.r. results of Westenberg and de Haas[9] from 251-456 K, as indicated by the similarity in the Arrhenius parameters (Table 2). The present results also are in excellent agreement with the data of Watson et al.[11] from 213-350 K, with the exception of their measurement at 350 K which appears to be $\sim 50\%$ higher than expected on the basis of the data of ref. (9) and the present work. This discrepancy contributes substantially to the difference between the Arrhenius parameters from the 3 temperature-dependent studies detailed in Table 2.

A recommended k_1 at 298 K of $(1.49\pm0.23) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, where the error limit is the standard deviation, is obtained as the mean from the 3 temperature-dependent studies plus the room temperature value of Davis et al.[12] A recommended Arrhenius expression for the 200-500 K range may also be obtained from the combined data of all 4 direct studies of k_1. A linear least squares treatment gives $k_1 = (2.40\pm0.32) \times 10^{-11} \exp(-2200\pm40/T)$ cm^3 molecule^{-1} s^{-1}. If only the data from room temperature and below are considered, which is the temperature range of interest for stratospheric modeling, the Arrhenius parameters for k_1 are essentially unchanged and are detailed in Table 2.

Non-linear Arrhenius behaviour has been observed[13b,17] in the $Cl + CH_4$ system from 200-500 K and has been predicted for the present

system from one study of the reverse reaction, H + HCl, between 195 and 373 K.[18] Neither the present results, nor the other direct studies of reaction (1),[9,11] provide any evidence for a curved Arrhenius plot in the 200-500 K range. However, also included in Fig. 1 are data from 3 indirect determinations of k_1.[6-8] While other indirect data for k_1 can be calculated, in particular from rate data for the reverse reaction[18-20] and the equilibrium constant, only those indirect data which extend the temperature range of the direct determinations are included in Fig. 1. Inclusion of these data introduces a suggestion of slight curvature between 200 and 1071 K, but the relatively large uncertainty in the indirectly determined k_1 values emphasises the necessity for a more detailed and direct study of k_1 above 500 K.

The present results shed light on the controversy[21] surrounding the ratio k_1/k_{-1}. This controversy arose from the rate constant measurements of k_1 and k_{-1} by Westenberg and de Haas,[9] who found that the measured k_1/k_{-1} from 251-456 K was lower than the equilibrium constant calculated from thermodynamic data by a factor of 2-3. Recent studies[19,20] of reaction (-1) concluded independently that Westenberg and deHaas' measurements of k_{-1} were in error, but that their k_1 measurements were probably correct, and that therefore there was agreement between k_1/k_{-1} and K. The results presented here support the k_1 data of Westenberg and de Haas and therefore indirectly support the recent k_{-1} data[19,20] at room temperature. Furthermore, the study[20] of k_{-1} from 298-521 K, together with the recommended k_1 for 200-500 K from all direct studies of reaction (1) (Table 2), yield the equation

$k_1/k_{-1} = (3.0\pm1.2) \exp(-610\pm80/T)$. This equation is in good agreement with the expression $K = 2.0 \exp(-525/T)$ which can be calculated from thermodynamic data[22] for 298 K and which is a good representation of K throughout the range of temperature studied here.

The results of competitive chlorinations are also clarified using the present recommended k_1 value. Thus, Fettis and Knox[3] recommended a rate constant expression for k_4

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad (4)$$

of $(4.0\pm2.0) \times 10^{-11} \exp(-1930\pm130/T)$ cm^3 molecule^{-1} s^{-1} from 193-593 K. This recommendation was based on the primary standard equation of $k_1 = 1.3 \times 10^{-10} \exp(-2760/T)$ cm^3 molecule^{-1} s^{-1}. Using the combined k_1 equation from all direct studies of reaction (1) (Table 2), the competitive chlorination data reviewed by Fettis and Knox would yield $k_4 = (7.4\pm3.7) \times 10^{-12} \exp(-1370/T)$ cm^3 molecule^{-1} s^{-1} from 193-593 K which is in good agreement with the linear least squares equation very recently obtained[13b] by FP-RF from 200-500 K: $k_4 = (11.0\pm1.2) \times 10^{-12} \exp(-1350\pm30/T)$ cm^3 molecule^{-1} s^{-1}.

A theoretical description of reaction (1) has been performed previously[23] in an attempt to explain measured isotope effects. These authors considered several models for the intermediate configurations, based on semi-empirical potential energy calculations. The most extensive calculation (LEPS), which was adjusted to an activation energy of 23.0 kJ mole^{-1}, failed to predict the experimental isotope effects, particularly when tunneling was included. Klein and co-workers[24,25]

have extended both experimental isotope effect measurements and LEPS and empirical models for the reaction with additional success in explaining the measured isotope effects. We have calculated k_1 at 400 and 300K based on **one LEPS model**[23], with tunneling corrections, but the calculated k_1 values are a factor of 3 and 4 higher than experiment, respectively.

Reaction (1) has previously been examined[24-26] using the BEBO method[26]. Our own BEBO calculation, without adjustable parameters, using separate values for the bond indices and including unsymmetrical Eckart tunneling factors[26] almost exactly reproduces the intermediate configuration and force constants of the general LEPS model of Persky and Klein[24] (that labelled Sato II in reference 24). The predicted activation energy is 25.1 kJ mole^{-1}. The computed tunneling factors contribute at the lower temperatures of the present study. In agreement with earlier work[25] the resulting overall rate constants, even when tunneling is applied, show very little curvature on an Arrhenius plot, being well represented by the equation $k = (3.04 \pm 0.70) \times 10^{-11} \exp(-2250 \pm 60/T)$ cm^3 molecule^{-1} s^{-1} from 200-500 K.

The close agreement between theory and experiment may be fortuitous given the approximate nature of both the BEBO method[26] and the methods of applying tunneling corrections[27]. In the present case we have used the "conservation of vibrational energy" criterion of Truhlar and Kuppermann[28]. As pointed out previously[25] the experimental isotope effects can be explained without the necessity

of tunneling. The absolute rate for $Cl + H_2$ has also been explained without tunneling[9]; however the LEPS potential energy barrier height was adjusted to be equal to the experimental activation energy by parametric variation of the Sato k value. Thus, it appears in the present case that the experimental values of thermal rate constants can give no information as to the correctness of the

activated complex theoretical approaches either with or without

tunneling. By contrast the theoretical classical dynamical approach of Porter, et al[29] gives $k_1 = 7.08 \times 10^{-11} \exp(-1610/T)$ cm^3 molecule^{-1} s^{-1}. Thus, this detailed theory, which involves a more fundamental approach to potential energy derivation and detailed trajectory calculations for various initial energy states of reactants, also fails in the present instance.

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TABLE 1. Rate Data for the Reaction $Cl + H_2 \rightarrow HCl + H$

$\dfrac{T}{K}$	$\dfrac{P_{OCCl_2}}{mTorr}$	$\dfrac{P_{H_2}}{Torr}$	$\dfrac{P_{total}}{Torr}$	Flash energy J	No. of experiments	$\dfrac{k_1 \,[a]}{10^{-15} cm^3 molecule^{-1} s^{-1}}$
200	100	20.0	20	20-182	13	0.375 ± 0.029
	150	30.0	30	56-182	11	0.394 ± 0.057
	100	40.0	40	56-182	8	0.370 ± 0.043
					32	0.380 ± 0.044 [b]
227	150	16.0	20^c	56-182	8	1.48 ± 0.12
	100	8.00	40^c	20-182	16	1.35 ± 0.07
					24	1.39 ± 0.11 [b]
260	200	2.00	100	20-182	8	4.99 ± 0.27
	200	4.00	100	36-182	7	5.21 ± 0.20
	400	4.00	200	36-182	8	5.23 ± 0.36
	400	8.00	200	20-155	9	4.93 ± 0.27
					32	5.08 ± 0.30 [b]
302	80	1.60	40	36-182	7	17.7 ± 1.3
	150	1.50	75	9-182	8	18.0 ± 0.6
	150	3.00	75	36-182	8	17.9 ± 0.7
	300	3.00	150	9-182	16	17.0 ± 1.4
					39	17.0 ± 1.3 [b]

345	100	1.00	20	20-182	11	37.6 ± 1.9
	100	0.500	20	25-182	8	40.0 ± 2.7
	200	1.00	40	56-182	8	45.1 ± 3.0
	200	2.00	40	56-182	8	40.1 ± 2.5
					35	40.4 ± 3.7[b]
406	100	0.250	40	20-182	16	109 ± 6
	100	0.500	40	20-182	16	105 ± 11
	150	0.375	60	56-182	16	122 ± 7
	150	0.750	60	56-182	16	102 ± 5
					64	110 ± 11[b]
500	100	0.150	50	56-182	11	311 ± 27
	150	0.180	50	56-182	14	292 ± 16
					25	300 ± 23[b]

[a] error limit is the standard deviation

[b] mean k_1 at that temperature

[c] diluent was helium; argon in all other experiments

TABLE 2. Comparison of Arrhenius Parameters for k_1

$\dfrac{T}{K}$	A_1 10^{-11} cm^3 molecule^{-1} s^{-1}	E_1 k J mol^{-1}	k_1 at 298 K 10^{-14} cm^3 molecule^{-1} s^{-1}	Reference
298			1.25 ± 0.1	12
251–456	2.0 ± 0.5	18.0 ± 0.8	1.4	9
213–350	5.5 ± 0.5	19.75 ± 0.84	1.80 ± 0.20	11
200–500	2.66 ± 0.42^a	18.5 ± 0.5^a	$1.50\pm0.30^{a,c}$	d
200–500	2.40 ± 0.32^b	18.4 ± 0.3^b	1.49 ± 0.23^b	9,11,12,d
200–302	2.65 ± 0.55^b	18.5 ± 0.4^b	---	9,11,12,d

[a] error limit is 3 standard deviations.

[b] error limit is one standard deviation

[c] error limit is based on the standard deviation at 302 K (Table 1).

[d] this work.

CAPTION TO FIGURE

Fig. 1.   Comparison of directly measured k_1 values: □, ref. 12;

O, ref. 9;   △, ref. 11; ●, this work.   Also included are

indirect determinations: X, ref. 7; ▽, ref. 8;   ◊ , ref. 6.