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Kinetic study of the reaction of atomic chlorine with hydrogen bromide

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The reaction $Cl + HBr \rightarrow HCl + Br$ was studied by a competitive method using the reaction $Cl + C_2H_6 \rightarrow HCl + C_2H_5$ as a reference reaction. Experiments to determine ratios of rate constants $k_{Cl+HBr}/k_{Cl+C_2H_6}$ in the temperature range 222–504 K were carried out in a fast flow system with mass spectrometric analysis of the reaction mixture. The results fit the Arrhenius expression: $k_{Cl+HBr}/k_{Cl+C_2H_6} = (0.53 \pm 0.03) \exp[-(321 \pm 16)/T]$.
A comparison is made with values calculated from reported results for the individual rate constants k_{Cl+HBr} and $k_{Cl+C_2H_6}$.

I. INTRODUCTION

The exothermic reactions

$$Cl + HBr \rightarrow HCl + Br \quad (\Delta H_0^0 = -15.7 \text{ kcal/mol})$$

and

$$Cl + HI \rightarrow HCl + I \quad (\Delta H_0^0 = -31.7 \text{ kcal/mol})$$

have been the subject of extensive experimental and theoretical studies in recent years. This is mainly due to their practical importance as reactions for which chemical laser emission has been observed,[1–4] and to their basic theoretical importance, as relatively "simple" triatomic elementary reactions. Detailed studies of such systems are expected to contribute significantly to the development of basic theories in chemical dynamics.

Most of the dynamical studies of the $Cl + HBr$ and $Cl + HI$ reactions have been devoted to the energy partitioning among the reaction products, including experimental measurements by the method of infrared chemiluminescence[5–7] and theoretical studies by methods of classical trajectories[8–12] and surprisal analysis.[13–15] Fewer studies have been devoted to the kinetics of these reactions. Mei and Moore determined the rate constants for these reactions[16] and for the isotopic reaction $Cl + DI \rightarrow DCl + I$,[17] over wide temperature ranges by a method involving laser photolysis of Cl_2 molecules and measurements of the fluorescence of the excited HCl (or DCl) molecules produced in the reactions. Their experimental results showed non-Arrhenius temperature dependences. For the $Cl + HBr$ reaction the Arrhenius plot is nonlinear with the rate constants increasing much less at high temperatures than at low temperatures. For the $Cl + HI$ reaction the deviation from linearity is even more pronounced, with the rate constant passing through a maximum around 320 K and then decreasing as the temperature is increased further. This behavior was explained in terms of a reaction model in which the chlorine atom is first attracted to the halogen end of the hydrogen halide molecule and then the H atom rotates around and reacts with the chlorine atom to produce HCl. A non-Arrhenius behavior was also observed for the $Cl + DI$ reaction.[17]

In the present study rate constants for the $Cl + HBr$ reaction were carefully measured over a wide temperature range, by a competitive method, employing the experimental technique of discharge-flow-mass spectrometry, which is entirely different than the technique used by Mei and Moore.[16] The results are presented and compared to those of Ref. 16.

II. EXPERIMENTAL METHOD

A competitive method was employed, using the reaction between chlorine atoms and C_2H_6 molecules as a reference reaction. The two competing reactions in the system are

$$Cl + HBr \xrightarrow{k_{Cl+HBr}} HCl + Br \,, \tag{1}$$

$$Cl + C_2H_6 \xrightarrow{k_{Cl+C_2H_6}} HCl + C_2H_5 \,. \tag{2}$$

Studies of the temperature dependence of $k_{Cl+C_2H_6}$ have been reported by two research groups. Manning and Kurylo[18] studied this reaction over the temperature range 222–322 K, by the method of flash photolysis resonance fluorescence. Their results fit the Arrhenius equation

$$k_{Cl+C_2H_6}(\text{Ref. } 18, 222\text{–}322 \text{ K}) = (7.29 \pm 1.23) \times 10^{-11} \times \exp[-(61 \pm 44)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \,. \tag{I}$$

Lewis *et al.*[19] studied this reaction over a wider temperature range 220–604 K by the method of discharge-flow-resonance fluorescence. Their results fit the Arrhenius equation

$$k_{Cl+C_2H_6}(\text{Ref. } 19, 220\text{–}604 \text{ K}) = (9.01 \pm 0.48) \times 10^{-11} \times \exp[-(133 \pm 15)/T] \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \,. \tag{II}$$

Values of $k_{Cl+C_2H_6}$ calculated from Eqs. (I) and (II) are in good agreement in the temperature range of the experiments of Ref. 18 (differences of about 3% to 12%). The linearity of the Arrhenius plot for $k_{Cl+C_2H_6}$ and the slight temperature dependence make the $Cl + C_2H_6$ reaction an appropriate reference reaction for the present study.

Experiments were carried out in a fast flow system with mass spectrometric analysis of the reaction mixture. The flow system and the experimental procedure were similar to those used in previous kinetic studies of the reactions of chlorine atoms[20] and of fluorine

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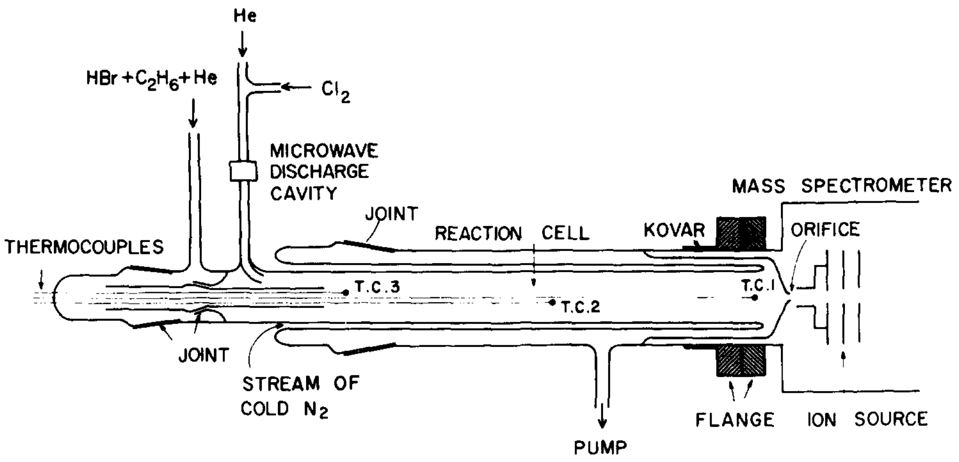

FIG. 1. Schematic diagram of the fast flow reaction system.

atoms.[21–24] A schematic diagram of the reaction system is shown in Fig. 1. The system consists of a quartz reaction cell (internal diameter 1.6 cm, length 20 cm) which can be cooled by a stream of cold nitrogen gas or heated by an electric heating coil (not shown in the diagram). The cell is wrapped with copper foil in order to achieve a uniform temperature. The temperature in the reaction cell is measured by copper–Constantan thermocouples which are placed inside thin-wall quartz tubes at three locations along the axis of the reaction cell (T.C.1, T.C.2, and T.C.3). The temperature in the reaction cell was uniform to about ± 1 °C at all temperatures of our experiments.

Chlorine atoms were produced by a microwave discharge in a dilute mixture of Cl_2 in He. The chlorine atoms reacted with a mixture of HBr and C_2H_6, diluted by He, which flowed into the reaction cell through a second inlet. The reaction mixture was continuously sampled through a small orifice (approximately 0.2 mm diam) and analyzed by a quadrupole mass spectrometer. In order to minimize the heterogeneous recombination of chlorine atoms, the walls of the reaction cell, the discharge tube, and all the other surfaces which came in contact with the atoms, were coated with a dilute solution of phosphoric acid (10%) and dried by heating under vacuum.

The flow rates of the gases He, Cl_2, HBr, and C_2H_6, into the reaction cell were controlled by calibrated capillaries. Five-liter flasks were used for storing the gases Cl_2, HBr, and C_2H_6. The inside diameters of the capillaries for these gases were such that during an experimental run only a small decrease in pressures in the flasks took place and as a result the flow rates did not vary significantly. The helium flowed into the reaction cell, through a capillary, directly from the metal cylinder, and its pressure before the capillary was constantly kept about 20 Torr above atmospheric pressure. The pressures of the Cl_2 and HBr before the respective capillaries were measured by pressure transducers. The pressure of the C_2H_6 was measured by a mercury manometer. Typical flow rates for the He, Cl_2, HBr, and C_2H_6 were about 40, 0.15, 0.15, and 0.07 $\mu mol\ s^{-1}$, respectively. The total pressure in the reaction cell was 0.4 to 0.5 Torr.

All the reagents used in this study were obtained from Matheson. The helium was of the grade "ultra high purity" with a stated purity of 99.999% and was used without any further treatment. The Cl_2, HBr, and C_2H_6 had the stated purities of 99.9%, 99.8%, and 99.96%, respectively. They were further purified by distillation from the condensed phase, collecting only the middle fraction.

As will be discussed below, under the conditions of our experiments the only reactions responsible for the consumption of the HBr and C_2H_6 are the reactions of these reagents with chlorine atoms [reactions (1) and (2)] and there are no secondary reactions which reproduce them to any significant extent. The differential equations for the consumption of HBr and C_2H_6 are therefore:

$$-d[\mathrm{HBr}]/dt = k_{\mathrm{Cl+HBr}}[\mathrm{Cl}][\mathrm{HBr}] \tag{III}$$

and

$$-d[\mathrm{C_2H_6}]/dt = k_{\mathrm{Cl+C_2H_6}}[\mathrm{Cl}][\mathrm{C_2H_6}] \ . \tag{IV}$$

From Eqs. (III) to (IV) we obtain, after division and integration, the following expression for the ratio of rate constants $k_{\mathrm{Cl+HBr}}/k_{\mathrm{Cl+C_2H_6}}$:

$$k_{\mathrm{Cl+HBr}}/k_{\mathrm{Cl+C_2H_6}} = \ln([\mathrm{HBr}]_0/[\mathrm{HBr}])/(\ln[\mathrm{C_2H_6}]_0/[\mathrm{C_2H_6}]) \ . \tag{V}$$

[HBr] and $[C_2H_6]$ are the concentrations of the molecular reagents at the end of the reaction cell when a reaction takes place (microwave discharge turned on), and $[HBr]_0$ and $[C_2H_6]_0$ are their initial concentrations, as determined from the mass spectrometric measurements when no chlorine atoms are present (microwave discharge turned off). Relative concentrations of HBr and C_2H_6 are determined from the mass spectrometric signals due to the ions HBr^+ ($m/e = 80$) and $C_2H_6^+$ ($m/e = 30$).

Table I represents a typical set of measurements for one experimental run determining $k_{\mathrm{Cl+HBr}}/k_{\mathrm{Cl+C_2H_6}}$ at 298 K. These measurements consisted of recording the signals due to the ions with $m/e = 80$ and 30 for the following experimental steps:

(a) Only He and Cl_2 flow into the reaction cell without applying the microwave discharge (background without

TABLE I. A typical set of measurements for an experimental run to determine $k_{\mathrm{Cl+HBr}}/k_{\mathrm{Cl+C_2H_6}}$ at 298 K.

m/e	a[a]	b	c	d	e	f	g	$[A]_0/[A]$	$\ln([A]_0/[A])$	$\frac{k_{\mathrm{Cl+HBr}}}{k_{\mathrm{Cl+C_2H_6}}}$
80	4.5	4.5	47.2	37.5	46.6	4.5	4.5	1.285	0.251	0.19_0
30	1.0	1.5	23.5	7.5	23.2	1.0	1.5	3.73	1.32	

[a] a to g are given in arbitrary units.

discharge). (b) The microwave discharge is turned on. A very slight increase in signals is sometimes observed (background with discharge). (c) The microwave discharge is turned off and the molecular reagents HBr and C_2H_6 flow into the reaction cell. (d) The microwave discharge is turned on. At this stage the chlorine atoms react with the HBr and C_2H_6. (e) Stage (c) is repeated as the discharge is turned off. The signals at this stage are usually slightly lower than in stage (c), because of small decreases in flow rates caused by small decreases in pressure in the reservoirs of the reagents. (f) The flows of HBr and C_2H_6 are stopped [background without discharge—same as (a)]. (g) The microwave discharge is turned on [background with discharge—same as (b)].

The ratio of concentrations of each of the molecular reagents before and after reaction, was calculated from the measurements in steps (a) to (g) by the equation

$$[A]_0/[A] = [(c+e)/2 - (a+f)/2]/[d - (b+g)/2] , \qquad \text{(VI)}$$

where $[A]$ represents the concentration of either HBr or C_2H_6.

The ratio of rate constants $k_{\mathrm{Cl+HBr}}/k_{\mathrm{Cl+C_2H_6}}$ was then calculated from the ratios of $[\mathrm{HBr}]_0/[\mathrm{HBr}]$ and $[C_2H_6]_0/[C_2H_6]$ using Eq. (V).

In the derivation of Eq. (V) only reactions (1) and (2) were taken into account. Other reactions that may consume or produce HBr or C_2H_6 have to be considered. In the gas phase such reactions are

$$\mathrm{Br} + C_2H_6 \rightarrow \mathrm{HBr} + C_2H_5 , \qquad (3)$$

$$C_2H_5 + \mathrm{HBr} \rightarrow C_2H_6 + \mathrm{Br} , \qquad (4)$$

$$C_2H_5 + C_2H_5 \rightarrow C_2H_6 + C_2H_4 . \qquad (5)$$

In addition, in our discussion of the contributions of reactions (3) to (5) we have to take into account the following reactions of C_2H_5 radicals:

$$C_2H_5 + Cl_2 \rightarrow C_2H_5Cl + Cl , \qquad (6)$$

$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10} . \qquad (7)$$

Reaction (3) is a very slow reaction having an activation energy of about 13 kcal/mol[25] and it may therefore be neglected under the conditions of our experiments. Reactions (4) to (7) are competing reactions, all involving C_2H_5 radicals. Out of these four reactions the fastest, under the conditions of our experiments, is reaction (6) for which the reported Arrhenius parameters are[26] $E_a = 1.0$ kcal/mol and $A = 2.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. For reaction (4) no absolute values of rate constants or Arrhenius parameters are reported in the literature. However, from indirect determinations of several rate constants and ratios of rate constants[27,28] an approximate value of $E_a = 2.5$ kcal/mol is obtained for this reaction. Assuming that the preexponential factor for this reaction is approximately the same as for the similar reaction of C_2H_5 radicals with HI, $A = 1.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1},[28] and considering the low concentration of the C_2H_5 radicals and the kinetic data for reaction (6), we may conclude that reaction (4) is also negligible. Reaction (5) is negligible as well in our experiments since it involves two C_2H_5 radicals of very low concentration which, in any case, prefer to react by reaction (7). At room temperature $k_5/k_7 = 0.14$.[29,30] This ratio is only slightly temperature dependent and it decreases with the increase in temperature.[29]

Recombination of chlorine atoms on the walls of the reaction cell which may occur to some extent in spite of the preventative treatment, should not affect the results. This is true because of the nature of the competitive reaction technique used in this study, as described above. Furthermore, as will be shown below, we can conclude from the experimental results that other surface reactions, if they occur at all, do not significantly affect the concentrations of HBr and C_2H_6.

Experiments were carried out at six temperatures in the temperature range 222–504 K. At each temperature 14 to 20 experiments were performed, except for room temperature at which the number of experiments was much larger 69. Experiments at room temperature were repeated frequently, usually before and after sets of experiments at other temperatures, in order to check the reproducibility of the results. Experiments at each temperature were usually repeated after an interval of several weeks, and interspersed with experiments at other temperatures. The reproducibility of the results was very satisfactory.

For a series of experiments at each temperature the flow rates of the reagents were varied over wide ranges in order to ensure that the results are independent of the relative concentrations. In general the flow rates of HBr and C_2H_6 were varied by factors of about 2 and 4, respectively (2 and 5 at room temperature), their ratio was varied by a factor of about 2 (5 at room temperature), and the flow rate of Cl_2 was varied by a factor of 2 to 3 (5 at room temperature). The variation of the flow rates was accompanied by a considerable variation in the degree of conversion for the two competing reactions. For example, at room temperature the percentage of conversion for the Cl + HBr reaction varied

TABLE II. Experimental values for the ratio $k_{\mathrm{Cl+HBr}}/k_{\mathrm{Cl+C_2H_6}}$ as a function of temperature (present results).

T(K)	No. of Experiments	$k_{\mathrm{Cl+HBr}}/k_{\mathrm{Cl+C_2H_6}}$
222	17	0.12 ± 0.01
256	14	$0.16 \pm 0.01_5$
298	69	0.18 ± 0.02
397	20	0.24 ± 0.02
460	18	0.26 ± 0.02
504	14	0.28 ± 0.02

between 14% and 27%, while the corresponding conversion for the $\mathrm{Cl + C_2H_6}$ reaction varied between 55% and 85%. The results, within experimental error, were not affected by all of these changes in the experimental conditions.

Most of the experiments were carried out with the walls of the reaction cell coated with phosphoric acid to minimize recombination, as described above. However, experiments at room temperature over wide ranges of flow rates were also performed after applying a different surface treatment. The procedure in this case involved treating the walls with a 10% solution of HF, washing them with distilled water and drying under vacuum. This procedure was found to be less effective than the former, and larger flow rates of $\mathrm{Cl_2}$ (two to three times larger) were needed in order to get the same amount of reaction. Nevertheless, the results obtained for $k_{\mathrm{Cl+HBr}}/k_{\mathrm{Cl+C_2H_6}}$ were found to be the same, within experimental error.

The very good reproducibility of the results for a wide range of experimental conditions (different surface treatments, wide variations in the flow rates, and degree of conversion and large number of experiments conducted over an extended period of time) indicates that surface reactions do not interfere with the measurements to any significant extent. Such a reproducibility would be very improbable for a system in which surface reactions either consume or produce significant amounts of reagents (HBr or $\mathrm{C_2H_6}$).

III. RESULTS AND DISCUSSION

The experimental results for $k_{\mathrm{Cl+HBr}}/k_{\mathrm{Cl+C_2H_6}}$ are summarized in Table II and plotted as a function of $10^3/T$ in Fig. 2. The straight line in Fig. 2 was calculated by the method of least squares and corresponds to the Arrhenius equation

$$k_{\mathrm{Cl+HBr}}/k_{\mathrm{Cl+C_2H_6}} = (0.53 \pm 0.03)\exp[-(321 \pm 16)/T] \;. \quad \text{(VII)}$$

The determination of $k_{\mathrm{Cl+HBr}}/k_{\mathrm{Cl+C_2H_6}}$ in every experimental run in the present study is based on measurements of relative mass spectrometric signals from which relative concentrations are obtained ($[\mathrm{HBr}]_0/[\mathrm{HBr}]$ and $[\mathrm{C_2H_6}]_0/[\mathrm{C_2H_6}]$). No absolute determinations of concentrations of reagents are involved and no calibration of the sensitivity of the mass spectrometer for different species is needed. We therefore estimate the accuracy of our results at each temperature to be about the same as the standard deviation indicated in Table II and Fig. 2 (7% to 10%). Values of $k_{\mathrm{Cl+HBr}}/k_{\mathrm{Cl+C_2H_6}}$ calculated from Eq. (VII) should be somewhat more accurate.

Figure 2 also contains values (without indicating error limits) of $k_{\mathrm{Cl+HBr}}/k_{\mathrm{Cl+C_2H_6}}$ calculated from results of Ref. 16 for $k_{\mathrm{Cl+HBr}}$ and those of either Refs. 18 or 19 for $k_{\mathrm{Cl+C_2H_6}}$. From Fig. 2 it can be seen that while the results calculated from Refs. 16 and 19 show a non-Arrhenius temperature dependence over the temperature range 218–402 K, the present results fit a straight line, well within experimental error, over a wider temperature range (222–504 K) and no sign of any curvature is observed. Since the reported results of Ref. 19 for $k_{\mathrm{Cl+C_2H_6}}$ exhibit Arrhenius behavior without any significant curvature over the temperature range 220–604 K, we may conclude that the rate constants for the Cl + HBr reaction also exhibit Arrhenius

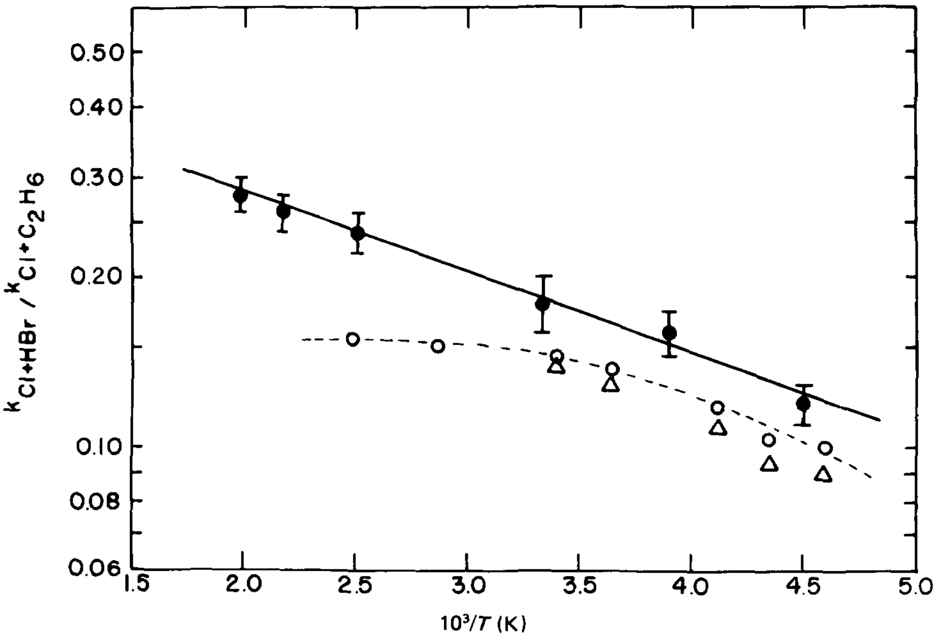

FIG. 2. Semilog plots of the ratios of rate constants $k_{\mathrm{Cl+HBr}}/k_{\mathrm{Cl+C_2H_6}}$ as a function of $10^3/T$. Present results (●), values calculated from the results of Refs. 16 and 19 (○), values calculated from Refs. 16 and 18 (△).

behavior in the temperature range of the present study. In this case, the mechanism of this reaction might be a direct one, as opposed to the nondirect mechanism which was suggested by Mei and Moore.[16,17]

The present results are thus in disagreement with the results of Mei and Moore[16] who found a non-Arrhenius temperature dependence for the Cl + HBr reaction. However, a further examination of Fig. 2 shows that in the low temperature range, around room temperature and below, the present results and those calculated from Refs. 16 and 19 agree reasonably well, taking into account the random and systematic errors in the different experimental techniques used in these three studies. The results in this temperature range differ by about 20% (the differences are larger for the values calculated from Refs. 16 and 18, 25% to 40%). The authors of Ref. 19 estimate the uncertainties in their measured values of $k_{Cl+C_2H_6}$ to be around 15% (much larger than the standard deviations), while the authors of Ref. 16 estimate the accuracy of their results to be of the same order as the standard deviations 6% to 8%. It seems therefore that the present results and those calculated from Refs. 16 and 19 agree within experimental error, for room temperature and below. For higher temperatures the differences between the results seem to be outside the experimental error limits of the three studies (38% difference at 350 K and 53% at 400 K).

Values of k_{Cl+HBr} can be calculated from the present results for $k_{Cl+HBr}/k_{Cl+C_2H_6}$ and the reported results for $k_{Cl+C_2H_6}$.[18,19] The calculations based on the results of Ref. 19 [Eq. (II)] which cover the whole temperature range of our measurements give the Arrhenius equation

$$k_{Cl+HBr} = 4.8\times10^{-11}\exp(-454/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ . \tag{VIII}$$

No error limits are indicated in this equation. However, based on the accuracy as estimated by the authors of Ref. 19, and the estimated errors in the present measurements the accuracy of rate constants calculated from Eq. (VIII) should be around 20%. Values calculated from Eq. (VIII) are in reasonable agreement, within experimental error, with the results of Ref. 16 at room temperature and below. Above room temperature the differences increase with temperature and are outside the estimated error limits. While the values of k_{Cl+HBr} calculated from our results continue to increase with temperature according to the Arrhenius Eq. (VIII), the experimental values of Ref. 16 increase with temperature much less than at the low temperature range.

In two quasiclassical trajectory studies[11,12] rate constants were calculated for the Cl + HBr reaction. Brown, Bass, and Thompson,[11] using a potential energy surface based on valence-bond formalism, calculated for 300 K, a value of $k_{Cl+HBr} = 5.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. This value is about five times larger than the value obtained in the present study. Smith[12] used a LEPS potential energy surface and obtained a value of 4.7×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K which is about 50% lower than the present results.

Experiments similar to those reported here are planned for the reaction $Cl + HI \rightarrow HCl + I$.

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