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Thermal rate constants, energy dependence and isotope effect
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for halogen-hydrogenhalide reactions  
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(Received)

Thermal rate constants have been determined for the reaction $\text{Cl} + \text{DI}$ and $\text{Br} + \text{HI}$ in the temperature range 220 - 400 K. For $\text{Cl} + \text{DI}$ the effective reaction cross section reaches a maximum of $18.8 \text{ \AA}^2$ near 345 K. The isotope effect increases in favor of HI from 1.5 to 2.7 as the temperature decreases from 400 to 223 K. For $\text{Br} + \text{HI}$ the effective reaction cross section decreases slightly with increasing temperature. The cross section at enhanced collisional energy, with various rotational energies, is determined for the reaction $\text{Cl} + \text{HI}$ (DI). It is found that, a factor of 3.9 increase in translational velocity over room temperature actually decreases the cross section for $\text{Cl} + \text{HI}$ and DI by factors of 9 and 6.6, respectively. At 11.4 kcal/mole relative translational energy, the cross section for the reaction $\text{Cl} + \text{HI}$ increases by 1.2 as the rotational temperature increases from 223 to 295 K. The results are discussed in

terms of a reaction model in which the attacking halogen atom is attracted to the halogen end of the hydrogen halide and then rotation of the hydrogen completes the reaction. A semi-quantitative analysis shows that tunneling makes an important contribution to the isotope effect.

I. INTRODUCTION

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Over the past few years, a wide variety of chemical reactions involving halogens and hydrogenhalides have been extensively studied.^{1 - 11} These reactions are of particular importance both for a practical understanding of chemical laser processes⁴ and for a theoretical elucidation^{9 - 11} of elementary three-center exchange reactions. Due to computational limitations,¹² detailed information on the potential surface and dynamics for this many-particle system cannot now be provided by fundamental quantum mechanics. However, it is possible to attempt to understand chemical dynamics from the classical motions^{12, 13} of the atoms and molecules on semi-empirical potential energy surfaces. Thus, it is essential to draw sufficiently detailed macroscopic and microscopic information¹⁴ from experimental data in order to construct an accurate potential energy surface.

The exothermic halogen-hydrogenhalide reactions have been studied in molecular beams^{7, 8} and by infrared chemiluminescence.¹ These studies have given the angular distribution of products and the energy distribution of the products, quantities which are sensitive to the potential surface for the products as they separate.¹⁵ Valuable information about the shape of the potential surface for the approaching reagents can be obtained by investigating the temperature variation of the total reaction rate, the specific

energy dependence of the reaction and the relative rates for isotopically substituted reagents.³ In a previous article,¹⁶ the thermal rate constants for $\text{Cl} + \text{HI}$ and $\text{Cl} + \text{HBr}$ and the collisional energy dependence of the reaction $\text{Cl} + \text{HI}$ were reported and a qualitative model for the reaction dynamics was proposed.

In the present work, measurements of rate constants as a function of temperature are reported for

The energy dependence of the cross section at enhanced collisional energy, with various rotational energies, is also reported for the reaction $\text{Cl} + \text{HI}$ (DI). These results are compared to those for

and discussed in terms of a quantitative model for the reaction dynamics.

II. EXPERIMENTAL

Measurements were made according to Ref. 16. In order to have good transmission for the DCI fluorescence, a new cell was built in which fluorescence was viewed through

a sapphire window and a KCl top window. For experiments involving Cl atom reactions, a Molectron N₂-laser (5mJ/pulse, 0.2 cm², 10 nsec, 25 pulses/sec, λ = 337 nm) was used. For Br₂, the 5900 Å output (10 mJ/pulse, 0.5 cm², 1 μsec, 30 pulses/sec) from a Chromatix CMX-4 dye laser was selected to excite the bound levels of the ³Π_{0+u} state.¹⁷ Br(²P_{3/2}) is then produced by predissociation or collision-induced dissociation.¹⁸ The estimated maximum dissociation is about 0.15%.

The gases and their purities were described previously.^{3b, 3c} Before using the DI gas, the entire vacuum system and flow system were deuterated by repeated filling with 10 - 30 Torr of DI for 40 - 60 min. and pumping down to at least 10⁻³ Torr before each refill. The isotopic purity of DI is checked by ir absorption spectroscopy. The contamination was less than 4%.

Broad band interference filters with transmission ranges 3 - 5 μ were used for the HCl, HBr fluorescence and 4.8 - 8 μ for the DCl fluorescence. Any HCl fluorescence was completely blocked by the 4.8 - 8 μ filter.

III. RESULTS

A. Thermal rate constant

Cl + DI. The experimental conditions and measured rate constants as a function of temperature are summarized in Table I. Three independent sets of experiments were carried out for each temperature. Each set contained 6 - 8 runs

corresponding to different combinations of $[Cl_2]$ and $[DI]$ pressures. The lower limit of $[Cl_2]$ pressure for the DI reaction is twice that for the HI reaction¹⁶ due to the poorer S/N ratio.³ No prereaction¹⁶ is observed. The uncertainties in Table I and in all the rate constant tables thereafter are the standard deviations of a single value from the mean of the complete sets of data. The comments for HI about the systematic errors¹⁶ are also valid for DI. A graph of $\log k_1^D$ and $\log \sigma_1^D$ vs T^{-1} is shown in Fig. 1. The room temperature result $(8.6 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ agrees with Bergmann's result^{3b} of k_1^D (295°K) $= (8.89 \pm 1.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

Br + HI. The fluorescence signal consists of one single exponential rise and one single exponential decay. No fluorescence signal is observed for the transition of $Br(^2P_{1/2}) \rightarrow Br(^2P_{3/2})$ at 3685 cm^{-1} . The production of Br atoms in the upper spin-orbit state is negligible¹⁹ and the exponential rise of the signal results from the reaction of ground state Br atoms. The amplitude of the signal indicates that the quantum yield of the ground state atom is fairly large, hence, the dissociation from the bound levels of $Br_2(^3\Pi_{0+u})$ ^{18, 20} is quite efficient.

The experimental conditions and measured rate constants as a function of temperature are summarized in Table II and the results shown in Fig. 2. Two independent sets of

experiments were carried out for each temperature. Each set contained 5 - 10 runs corresponding to different combinations of $[\text{Br}_2]$ and $[\text{HI}]$ pressures. Prereaction is negligible.

Bergmann and Leone^{3c} have measured the reaction rate of $\text{Br} + \text{HI}$ at 295 K by laser dissociation of Br_2 in the 4700 Å region. Both ground state and electronically excited Br atoms were produced with a 1 : 1 ratio via absorption to the $\text{Br}_2(^3\Pi_{0+u})$ state.²¹ A double exponential rise of the fluorescence signal was observed. The corresponding rate constants are $k_{\text{fast}} = (1.0 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and $k_{\text{slow}} = (0.25 \pm 0.10) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. From the measurement of the decay rate for the excited $\text{Br}(^2P_{1/2})$,^{3c} k_{slow} was assigned as an upper limit for the reaction rate constant of $\text{Br}(^2P_{1/2}) + \text{HI}$. In this work, the reaction rate constant for the reaction of ground state $\text{Br}(^2P_{1/2})$ with HI has been precisely determined to be $(1.09 \pm 0.07) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. The agreement of $k_3(295 \text{ K})$ with k_{fast} confirms the argument made by Bergmann and Leone that the reaction $\text{Br}(^2P_{1/2}) + \text{HI} \rightarrow \text{HBr} + \text{I}(^2P_{3/2})$ is at least 4 times slower than that of ground state. Houston²² has discussed the possibility that the reaction $\text{Br}(^2P_{1/2}) + \text{HI} \rightarrow \text{HBr} + \text{I}(^2P_{1/2})$ which may occur on a single surface^{3c, 23} is faster.

B. Energy dependence

The determination of the hot atom reaction rate constant for $\text{Cl} + \text{HI}$ has been described in detail.^{3b} Here, rate

constants for $\text{Cl} + \text{HI}$ (DI) were measured at 13.8 kcal/mole translational energy (~ 11.4 kcal/mole relative collisional energy). The Boltzmann rotational energy was varied by changing the bath temperature T . The slopes at the beginning of the intensity vs $P_{\text{HI}} \cdot t$ curves were measured for $P_{\text{HI}} \cdot t \leq 0.2 \mu\text{sec Torr}$. Within experimental error, the ratio of rate constants for thermal and hot atom reactions can be determined as the $[\text{Cl}_2]/[\text{HI}]$ ($[\text{Cl}_2]/[\text{DI}]$) ratio approaches zero,^{3b} Table III. The partial pressures of the reagents are less than 0.4 Torr. The uncertainties for the reaction rates and cross sections at enhanced collisional energy include the standard deviation of the thermal rate constant and that of the rate constant ratio. A systematic error might result from the change in product vibrational distribution with velocity. As $P_{\text{HI}} \cdot t$ increases from 0 to 0.2 $\mu\text{sec Torr}$, the initial relative velocity decreases by $\sim 20\%$.^{3b} The product vibrational distribution is narrowed and peaked at lower v as velocity decreases.^{1d} From the rate constant for the production of a specific vibrational state of the product and the vibrational distribution,^{1d} it can be shown that the mean vibrational quantum number of the product decreases by $\sim 11\%$ as the relative collisional energy decreases from 12 kcal/mole to 6 kcal/mole. Thus, an over-estimate of the slope at the beginning of the intensity vs $P_{\text{HI}} \cdot t$ curve by $\leq 11\%$ is possible.

C. Isotope effect

A semi-log plot of the ratio of the rate constants for the reactions $\text{Cl} + \text{HI}$ and DI vs T^{-1} is shown in Fig. 3. The uncertainty for the isotope effect has been calculated from the standard deviation of each rate constant, not including the possible systematic errors which will cancel out in the ratio.

IV. DISCUSSION

In Ref. 16, a reaction model was proposed for the thermal reaction $\text{Cl} + \text{HI}$ and $\text{Cl} + \text{HBr}$ in which the attacking halogen atom is attracted to the halogen end of the hydrogen-halide and then rotation of the hydrogen completes the reaction. It was suggested that the increase in reaction rate at lower temperature might result from a barrier to reaction in the rotational coordinate. Such a "rotational-barrier" effect has been discussed before in the work of Stolte et al.²⁴ for the reaction cross section of $\text{CsF} + \text{K} \rightarrow [\text{CsFK}] \rightarrow \text{Cs} + \text{KF}$.

The temperature dependence of the reaction cross section for $\text{Cl} + \text{HI}$ might be described by

$$\sigma_1^H(T) = \sigma_h^H + A \cdot 1/T^n \cdot e^{-V_1/RT} \quad (1)$$

where σ_h^H is the head-on collision cross section;

$\sigma_h^H \leq \sigma_{\text{hot}}^H (= 3.4 \text{ \AA}^2)$, V_1 is the rotational barrier, and $1/T^n$ accounts for the decreasing of the reaction cross section with increasing translational energy. The experimental result for the $\text{Cl} + \text{HI}$ reaction can be reproduced within 4%

error with $n = 4.8$, $V_1 = 2.9$ kcal/mole and $A = 2.7 \times 10^{15} \text{ }^\circ\text{K}^2$. The n factor obtained is unreasonably high as compared to that in the cross section function from a long range attraction,²⁵ $\sigma_R \propto 1/T^{2/s}$ ($s > 2$). Furthermore, the pre-exponential term (A/T^n) of $3600 \text{ }^\circ\text{K}^2$ at room temperature is unreasonably large as compared to the gas kinetic collision cross section.²⁶ Thus, Eq. (1) does not adequately describe the reaction dynamics.

The temperature dependence of the reaction cross section for $\text{Cl} + \text{DI}$ is similar to that for $\text{Cl} + \text{HI}$ with the maximum at about 345 K. The isotope effect increases from 1.5 to 2.7 as temperature decreases from 400 K to 223 K and a distinct curvature is observed in the semi-log plot, Fig. 3. The decrease in rotational velocity by $\sqrt{2}$ between HI and DI may account for the isotope effect in the proposed reaction mechanism. However, the ratio of the rotational velocity between HI and DI is independent of temperature and the existence of a rotational-barrier is required to explain the temperature dependence of the isotope effect.

The isotope effect can be qualitatively examined with transition-state theory based on the statistical model. An activated complex is assumed in the reaction path before an H (or D) atom is transferred from one halogen atom to the other. The ratio of the rate constants for the reaction $\text{Cl} + \text{HI}$ and $\text{Cl} + \text{DI}$ can be obtained from the general expression:²⁷

$$k_1^{\text{H}}/k_1^{\text{D}} = \left[Q_{(\text{H})}^{\ddagger 3c-1} \cdot Q_{(\text{DI})}^{3c} / Q_{(\text{D})}^{\ddagger 3c-1} \cdot Q_{(\text{HI})}^{3c} \right] \cdot e^{\epsilon_0/RT} \quad (2)$$

where Q and $Q^\ddagger$ are the partition functions of the reactant molecules and the activated complex, respectively; ϵ_0 is a function of the zero-point energies of HI, DI and the complexes involved. Since the ratio of the translational or rotational partition functions is independent of temperature only the ratio of the vibrational partition functions will affect the slope of the semi-log plot of k_1^H / k_1^D vs $1/T$. The general form of the vibrational partition function is $Q_v = 1/(1 - e^{-h\nu/RT})$.

For the reactants HI and DI, $h\nu/RT \gg 1$ and $Q_v = 1$ over the temperature range 200 - 400°K. Thus

$$\frac{k_1^H}{k_1^D} = A \cdot \left[\frac{1 - e^{-h\nu_s^\ddagger(D)/RT}}{1 - e^{-h\nu_s^\ddagger(H)/RT}} \cdot \frac{1 - e^{-h\nu_{ICl}^\ddagger(D)/RT}}{1 - e^{-h\nu_{ICl}^\ddagger(H)/RT}} \right] \cdot e^{\epsilon_0/RT} \quad (3)$$

where A is the temperature independent factor; $\nu_s^\ddagger$ and $\nu_{ICl}^\ddagger$ are the vibrational frequencies for the H-stretching and ICl-stretching modes of the complex respectively, and $\epsilon_0 = (h/2) \cdot [(\nu_{HI} - \nu_{DI}) - (\nu_{s(H)}^\ddagger + \nu_{ICl(H)}^\ddagger - \nu_{s(D)}^\ddagger - \nu_{ICl(D)}^\ddagger)]$. The term in the bracket of Eq. (3) varies from

$$\left(\frac{\nu_{s(D)}^\ddagger}{\nu_{s(H)}^\ddagger} \right) \cdot \left(\frac{\nu_{ICl(D)}^\ddagger}{\nu_{ICl(H)}^\ddagger} \right) \text{ at } h\nu^\ddagger \ll RT \text{ to } 1 \text{ at } h\nu^\ddagger \gg RT. \text{ In this}$$

reaction system, $\nu_{s(D)}^\ddagger \approx \frac{1}{\sqrt{2}} \nu_{s(H)}^\ddagger$ since mainly H and D atoms are moving and also $\nu_{ICl(D)}^\ddagger / \nu_{ICl(H)}^\ddagger \approx 1$. Therefore k_1^H/k_1^D increases with decreasing temperature. The extent of the isotope effect depends mainly on the mass, the zero-point

energy difference, and the location and shape of the energy barrier.^{27, 28} For any $v_s^\ddagger$ and $v_{IC1}^\ddagger$, it can be shown that the isotope effect contributed from the pre-exponential term in Eq. (15) increases by less than 9% as the temperature decreases from 400°K to 223°K. Thus, ϵ_0 is larger than 490 cal/mole (175 cm^{-1}) in the temperature range 300 - 223°K and the upper limit for the H-stretching frequency in the complex ClHI is 1200 cm^{-1} . This implies a highly extended H - I bond in the complex and hence a late barrier in the entrance valley.^{28, 29} For transition state theory a late and high barrier gives a large isotope effect.²⁸ However, the product energy distribution calculated on an LEPS potential surface with a late barrier will deviate from the observed distribution to some extent since the product energy state distribution is essentially determined by the position of the barrier and by the fraction of the energy release taking place along the exit valley.^{15, 30} Thus, Eq. (3) does not provide a satisfactory description of the temperature dependence of the isotope effect.

It is also possible that some quantum-mechanical tunneling²⁸ through the barrier in the rotational coordinate, which favors the lighter H atom, is responsible for the large magnitude and temperature dependence of the isotope effect. For an incident particle of mass M and energy E the probability, $k(E)$, of crossing the barrier V_1 can be determined by solving Schroedinger's equation for a one-dimensional Eckart potential.²⁸

$$k(E) = \frac{\cosh (2\alpha E/V_1)^{1/2} - 1}{\cosh (2\alpha E/V_1)^{1/2} + \cosh (4\alpha^2 - \pi^2)^{1/2}} \quad (4)$$

where $\alpha = 2\pi V_1/hv^*$; $v^* = (1/2\pi)(-F^*/\mu)^{1/2}$ and F^* is the curvature at the potential maximum. For a Boltzmann distribution of incident particles, the ratio of quantum-mechanical barrier-crossing rate to classical-mechanical barrier-crossing rate is

$$\Gamma = k_{qu}/k_{cl} = \exp(V_1/RT) \int_0^\infty k(E) \exp(-E/RT) d(E/RT) \quad (5).$$

The integral is evaluated numerically. The isotope effect is given by k_{qu}^H/k_{qu}^D .

$$k_{qu}^H/k_{qu}^D = (k_{cl}^H/k_{cl}^D) \cdot (\Gamma^H/\Gamma^D) \quad (6).$$

By assuming that there is no classical isotope effect, i.e. $k_{cl}^H/k_{cl}^D = 1$, V_1 and F^* may be fit to the data. The temperature dependence of the isotope effect can be reproduced within 5% error with $V_1 = 2.2$ kcal/mole and $F^* = 1.0 \times 10^5$ dyne/cm. The barrier width L^{28} is calculated to be $0.83 \text{ \AA}$ which roughly corresponds to a 30 degree rotation of the H atom in crossing the barrier.

The inclusion of a tunneling correction in Eq. (1) gives

$$\sigma_1^H(T) = \sigma_h^H + A \cdot \Gamma^H \cdot 1/T^n \cdot e^{-V_1/RT} \quad (7)$$

with V_1 fit to the isotope effect and Γ obtained from Eq. (5), the n factor can be determined from the experimental reaction cross section and Eq. (8) below

$$\log[(\sigma_1^H(T) - \sigma_h^H) \cdot e^{V_1/RT} / \Gamma^H] = \log A + n \log 1/T. \quad (8)$$

Here, $\sigma_h^H = \sigma_{hot}^H(295 \text{ K}) = 3.4 \text{ \AA}^2$. A decrease of σ_h^H from $3.4 \text{ \AA}^2$ to $2.6 \text{ \AA}^2$ (Table III) has almost no effect on the n value and gives only a 2% increase in the A value.

From the slope of the log-log plot, n is found to be 1.4 ± 0.2 which is more reasonable than $n = 4.8$ obtained from Eq. (1) and $A = (8.0 \pm 1.4) \times 10^5 \text{ Å}^2 \text{ K}^{1.4}$. The A/T^n term of 280 Å^2 at room temperature is comparable to the elastic integral cross section for the near isoelectronic Ar - Xe (454 Å^2 at 1 kcal/mole collisional energy) or Cl - Xe (394 Å^2 at 2.5 kcal/mole collisional energy).³¹

The dependence of reaction cross section on rotational energy alone has been measured for the hot atom reaction $\text{Cl} + \text{HI}$. It is found that, at 13.8 kcal/mole collisional energy, the cross section decreases by 1.2 (Table III) as the temperature decreases from 295 to 223°K (a decrease of average rotational energy by 1.3). The larger cross section for $\text{Cl} + \text{HI}$ at 295°K can be accounted for by the increase of the rotational energy in overcoming the rotational barrier and the increase of the ratio of the interaction time to the rotational period.^{1e, 24, 32}

The isotope effect is ~ 1.3 (Table III) for hot atom reactions. It is attributed to the difference in rotational velocities between HI and DI and is comparable to the rotational effect mentioned above. Apparently, both the rotational effect and the isotope effect are less significant at enhanced collision energy than those at thermal energies (Fig. 3). Thus, the argument that the hot atom reaction results mostly from head-on collision¹⁶ is acceptable.

For the $\text{Br} + \text{HI}$ reaction, the cross section decreases

slightly as temperature increases, Fig. 2. The reaction cross section is 12 times smaller than that for $\text{Cl} + \text{HI}$.¹⁶ The van der Waals attraction will be stronger for $\text{Br} + \text{IH}$ than $\text{Cl} + \text{IH}$ but the chemical bonding will be weaker. The smaller cross section for $\text{Br} + \text{HI}$ suggests that the chemical-type attraction is the major factor in promoting the reaction for $\text{Cl} + \text{HI}$. A comparison for all of the measured $\text{Y} + \text{HX}(\text{DX})$ cross sections is shown in Table IV. Both the reaction cross section and the isotope effect are much smaller for $\text{F} + \text{HX}$ ³³ than for $\text{Cl} + \text{HI}$. The chemical attraction between F and IH should be even stronger than that between Cl and HI . One possible explanation is that the rotational barrier is much higher for the $\text{F} + \text{HI}$ system so that barrier crossing is greatly reduced. In fact, the cross section and isotope effect for $\text{F} + \text{HI}$ at room temperature are comparable to those for the hot atom reaction of $\text{Cl} + \text{HI}$. Thus, it is reasonable to speculate that the reaction occurs mainly from the H end of HI for the $\text{F} + \text{HI}$.

Grover et al.⁸ have measured the reaction cross section for $\text{Cl} + \text{HAt}$ at an initial translational energy of 6.5 kcal/mole; it is $26 \pm 4 \text{ \AA}^2$. The cross section for $\text{Cl} + \text{HI}$ at the same collisional energy may be interpolated from the velocity dependence of the cross section and a value in the range $4 - 7 \text{ \AA}^2$ obtained. This is only about 1/4 to 1/7 the value for $\text{Cl} + \text{HAt}$. For $\text{Cl} + \text{HI}$ reaction, the c.m. angular distribution at an initial translational energy of 6 kcal/mole

displays a sharp forward peak and a broad distribution extending to about 125° . This is qualitatively similar to the forward peak for $\text{Cl} + \text{HAt}$.⁸ Unfortunately, 125° is the largest angle for which information is available in the $\text{Cl} + \text{HI}$ reaction and a second peak similar to the backward peak for $\text{Cl} + \text{HAt}$ might also exist. The large difference in reaction cross sections between $\text{Cl} + \text{HI}$ and $\text{Cl} + \text{HAt}$ may be attributed to a stronger attraction and/or a lower barrier in the latter system.

Recently, Muckerman et al.³⁴ have performed three-dimensional trajectory calculations for the $\text{Cl} + \text{HI}$ reaction on a parameterized LEPS surface with a strongly attractive downhill potential for collinear $\text{Cl} - \text{HI}$. The total reaction cross section for $\text{Cl} + \text{HI}$ at room temperature can be reproduced. This alternative model for the reaction dynamics must be tested against other experimental results. The effect of tunneling may need to be quantitatively included in the calculations. The experimental results reported in Ref. 16 and in this work have led to a better understanding of the collision dynamics in halogen-hydrogen-halide reactions. The model proposed is plausible both qualitatively and quantitatively. More detailed experimental information on both elastic and inelastic scattering cross sections from molecular beams will be very useful in constructing a potential energy surface. Extensive theoretical work is required to explore the quantitative features of the surface.

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TABLE I. Summary of the experimental conditions and results for the thermal reaction of Cl + DI from 223 K to 400 K.

T (K)	P _{Ar} (Torr)	P _{Cl} (Torr)	P _{DI} (Torr)	k ₁ ^D x 10 ¹⁰ (cm ³ mole- cule ⁻¹ sec ⁻¹)	σ ₁ ^D = k ₁ ^D /v̄ (Å ²)
400	12.2 - 15.4	0.08 - 0.14	0.03 - 0.17	0.97 ± 0.05	16.7 ± 0.8
345	12.2 - 15.4	0.09 - 0.17	0.02 - 0.14	1.01 ± 0.05	18.8 ± 1.0
295	12.2 - 15.4	0.09 - 0.18	0.02 - 0.24	0.86 ± 0.05	17.3 ± 0.9
274.5	12.2 - 15.4	0.08 - 0.14	0.03 - 0.17	0.72 ± 0.04	15.1 ± 0.8
240	12.2 - 15.4	0.09 - 0.17	0.03 - 0.17	0.50 ± 0.03	11.2 ± 0.7
223	12.2 - 15.4	0.08 - 0.17	0.04 - 0.23	0.38 ± 0.02	8.7 ± 0.5

TABLE II. Summary of the experimental conditions and results for the thermal reaction of Br + HI from 250 K to 374 K.

T (K)	P _{Ar} (Torr)	P _{Br₂} (Torr)	P _{HI} (Torr)	k ₃ x 10 ¹¹ (cm ³ mole- cule ⁻¹ sec ⁻¹)	σ ₃ = k ₃ /v̄ (Å ²)
374	12.3 - 15.8	0.09 - 0.36	0.21 - 0.32	1.16 ± 0.08	2.46 ± 0.17
344	12.3 - 15.8	0.08 - 0.35	0.16 - 0.31	1.12 ± 0.08	2.47 ± 0.17
294	12.3 - 15.8	0.10 - 0.36	0.11 - 0.41	1.09 ± 0.07	2.60 ± 0.18
274	13.1 - 15.7	0.11 - 0.36	0.11 - 0.38	1.10 ± 0.08	2.67 ± 0.18
250	13.1 - 15.7	0.10 - 0.36	0.21 - 0.37	1.11 ± 0.08	2.85 ± 0.20

TABLE III. Rate measurements for Cl atoms with 11.4 kcal/mole relative translational energy.

	T^b (°K)	$\frac{k_1}{k_{\text{hot}}}$	$k_{\text{hot}} \times 10^{10}$ (cm ³ mole- cule ⁻¹ sec ⁻¹)	σ_{hot}^a (Å ²)	$\frac{\sigma_1}{\sigma_{\text{hot}}}$
Cl + HI	295	2.30 ± 0.10	0.67 ± 0.06	3.4 ± 0.3	9.0 ± 0.5
	223	1.95 ± 0.10	0.53 ± 0.05	2.7 ± 0.2	7.4 ± 0.4
Cl + DI	295	1.70 ± 0.10	0.51 ± 0.05	2.6 ± 0.3	6.6 ± 0.4

a) $\sigma_{\text{hot}} = k_{\text{hot}}/v_o$; v_o = initial hot atom velocity.

b) T is the bath temperature and hence the Boltzmann temperature for the rotational degree of freedom of HI (DI).

TABLE IV. Reaction cross sections and isotope effects^a at room temperature.

Atom	Molecule	HI	HBr	HCl
F ^b		4.27(1.29)	5.26(1.29)	1.16(1.38)
Cl ^c		31.2(1.80)	1.63(1.50 ^d)	
Br ^c		2.60		

a) Cross section in Å² followed by (k^H/k^D).

b) Reference 33.

c) This work.

d) Reference 3b.

Figure 1. Semi-log plot of thermal rate constant k_1^D and effective cross section σ_1^D , for the reaction $\text{Cl} + \text{DI}$ vs $10^3/T$. -o-, experimental rate constant. -Δ-, cross section.

Figure 2. Semi-log plot of thermal rate constant k_3 and effective cross section σ_3 , for the reaction $\text{Br} + \text{HI}$ vs $10^3/T$. -o-, experimental rate constant. -Δ-, cross section.

Figure 3. Semi-log plot of the ratio of rate constants vs $10^3/T$ for the reaction $\text{Cl} + \text{HI}$ and DI . -o-, k_1^H/k_1^D vs $10^3/T$. ○, $k_{\text{hot}}^H/k_{\text{hot}}^D$ plotted at the rotational temperature $T = 295 \text{ K}$. Δ, $k_{\text{hot}}^H/k_{\text{hot}}^D$ plotted at $T = \frac{2E_{\text{rel}}}{3R} = 4400 \text{ K}$.

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