this lower value and their rate constant at 644 K,[47] we calculate the revised 300 K rate coefficient to be 4.5×10^{-12} cm^3 molecule^{-1} s^{-1}. This is in excellent agreement with the present result after consideration of the secondary kinetic isotope effect.

The fact that the previous activation energies for the title reactions may be in error is not overly surprising. The recommended values and all the previous experiments are based on indirect measurements, which may be less reliable and are carried out over temperature ranges with 300 K at or near the lower limit. In addition, simple Arrhenius expressions are known to be inadequate to describe many radical reactions over extended temperature ranges. For example, there is a large amount of low temperature curvature in Arrhenius plots of the isoelectronic F + HX reactions[24] as well as for many OH reactions.[25] The kinetics of the $CH_3 + H_2$ reaction are also poorly described by an Arrhenius expression.[47] One explanation which has been put forward to explain this curvature is the formation of a weakly bound intermediate.[24] At low collision energies, the reaction partners are held together for longer times by the influence of this shallow potential energy minimum; this increases the probability of reaction. In the present context, it is interesting to note that Jacox[48] has observed a hydrogen-bonded $FH\cdots CH_3$ complex in an Ar matrix. The existence of such a complex in the CD_3 + HX systems studied here could result in an enhancement of the reaction rate at lower temperatures. The expected resulting curvature of an Arrhenius plot may help to explain the differences between these and previous determinations.

Another mechanism for low temperature curvature in simple Arrhenius plots of H-atom transfer reactions is tunneling. This mechanism is expected to be important in cases where the activation barrier is too high to be overcome by the reagents. Tunneling may also play some role in the present reactions. However, it is probably not too important since the activation energies lie near or below the available thermal energies.

The dynamics of the reactions of methyl radicals with halogen molecules are understood to be qualitatively similar to the corresponding H + halogen reactions.[49] If the same similarity exists for the CH_3 + HX vs. H + HX series then some recent theoretical results on the H + HX systems[50,51] can provide insight into the dynamics in the present case. The general features of the H + HX series, as X is changed from F to I, are[50] that with increasing exoergicity there is a decreasing barrier height and a large shift in the barrier position toward reactants (i.e. increasingly attractive energy release). The energetics of the CH_3 + HX series are very similar to those of H + HX and the fact that H_3C–H and H–H have similar bond strengths leads to very similar values for the heats of reaction. The qualitative result that the activation energies in CH_3 + HX decrease in going from HCl (2.5 kJ mol^{-1}) to HBr (1.7 kJ mol^{-1}) to HI (0 kJ mol^{-1}) appears to be established.[1]

We now consider the calculated transition-state geometries. In the near-thermoneutral H + HCl, both the HH and the HCl bonds are predicted to be 0.02 nm longer in the transition state than in the diatoms.[50] This is very similar to the transition state estimated for CH_3 + HCl by Heneghan et al.[12b] In that work, the CH_3 + HCl transition state has the C–H–Cl in a collinear arrangement, with the CH and HCl distances both extended 0.03 nm from those of free CH_4 and HCl, respectively. In Dunning's work,[50] H + HBr and H + HI are predicted to have transition-state geometries in which the HH bond length is ~0.05 nm longer than in H_2, but the HX distance is very close to that of the free diatomic. If this early barrier is also a feature of the CH_3 + HBr(HI) systems then it could give rise to substantial vibrational excitation in the products.[52] In addition, the increasingly attractive nature of the energy release through the series CD_3 + HCl, HBr, HI suggests that increasing amounts of the reaction energy are being deposited into product vibrational energy. In this regard it may be noted that the signal intensity observed for the CD_3 + HI reaction is about 5 times larger than that from CD_3 + HBr under similar experimental conditions. The low density of states of CD_3H at energies corresponding to the exoergicities of these reactions[53] raises the intriguing possibility of observing specific energy disposal in polyatomic reaction products. Work is presently under way in this laboratory to explore these possibilities further.

Acknowledgment. This work was supported by the U.S. Department of Energy, D.J.D. thanks N.S.E.R.C. (Canada) for the award of a postdoctoral fellowship.

Registry No. CD_3I, 865-50-9; CD_3, 2122-44-3; HBr, 10035-10-6; HI, 10034-85-2.

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Kinetics of the Reaction of Chlorine Atoms with Hydrogen Bromide

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The kinetics of the reaction Cl + HBr → HCl + Br have been studied over the temperature range 267–333 K by using the very low pressure reactor (VLPR) technique. The measured rate constant is 3.4×10^{-12} cm^3 molecule^{-1} s^{-1}. The reaction rate was found to be independent of temperature. The *A* factor for the reaction is estimated on the basis of a tight transition state and agrees well with the measured rate constant.

Introduction

In recent years the reactions of halogen atoms with hydrogen halides have received much attention. This attention has been directed primarily toward reaction dynamics studies including energy partitioning[1-3] and classical trajectory studies.[4] The overall kinetics of these reactions have received much less attention. Specifically, the temperature-dependent rate constant for the exothermic reaction

$$\mathrm{Cl + HBr \rightarrow HCl + Br} \qquad \Delta H^\circ = 15.7 \text{ kcal mol}^{-1}$$

has been measured by two groups,[8,9] whose results are in only fair

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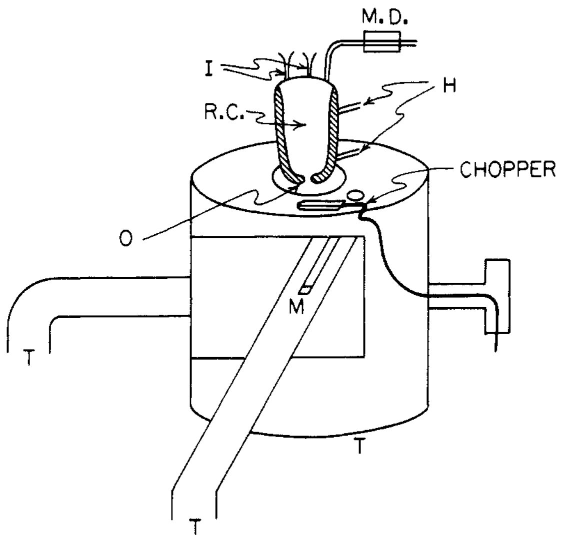

Figure 1. Diagram of apparatus: R.C., reactor cell; M.D., microwave Discharge; I, input capillaries; O, adjustable orifice; C, tuning fork chopper; H, input for heating, cooling liquid; M, mass analyzer; T, turbomolecular pump.

agreement at temperature below about 300 K and in poor agreement above 300 K. Mei and Moore[8] found a non-Arrhenius temperature dependence for the reaction with rate constants increasing more slowly at high temperatures than at low temperatures. Rubin and Persky[9] found a linear Arrhenius plot between 222 and 504 K with an activation energy of slightly less than 1 kcal.

In the present study we have measured the rate constant for the title reaction over the temperature range 267–333 using the very low pressure reactor (VLPR) technique. This technique has been shown to yield reliable rate constants for a wide variety of Cl and Br atom reactions without the complications of unobservable secondary reactions.

Experimental Section

The theory of the very low pressure reactor (VLPR) has been discussed in detail previously.[10,11] Briefly, halogen atoms produced in a microwave discharge are allowed to react for a known length of time in a teflon-coated cell with the other stable reactant to be studied at total pressures less than ~5 mtorr. After reaction the reactants and products are passed through differentially pumped chambers, where they form a molecular beam, and then flow into a quadrupole mass spectrometer. The molecular beam is modulated by a tuning fork chopper and the mass spectrometer signal is fed through a lock-in amplifier and displayed on a chart recorder for analysis.

The VLPR system used in this experiment (Figure 1) is the newest in design of the VLPR series. It differs from previous systems in having three differentially pumped chambers instead of two. This gives us a better collimated molecular beam, lower background, and improved sensitivity. Other improvements include a quickly adjustable orifice size of 2, 3, or 5 mm at the outlet of the reaction cell allowing us to change the residence time of reacting species in the cell and therefore permitting us to measure a wider range of rate constants, all without breaking vacuum.

Gases used in this experiment were a 1% Cl_2/He mixture using Matheson research purity chlorine and ultrahigh-purity helium. The mixture was prepared in a 3-L Pyrex bulk by admitting Cl_2 and performing two freeze–pump–thaw procedures to remove any noncondensible. Helium was passed through a molecular seive at 77 K to remove any hydrocarbon impurities that might be present. HBr was Matheson research grade which was also given two freeze–pump–thaw procedures after admission of its Pyrex storage bulb. Flow rates of the gases were determined by following the pressure drop (measured on a Validyne Model DP 15-30 S/N 56005 ± 1 psitransducer) in a known volume (~500 cm^3) as the gases flowed across a 100-cm capillary with i.d. of 0.020, 0.035, or 0.065 cm. During the experiment the flows were maintained constant by adding gas to the volume by means of a needle valve.

The reactor cell was mounted on a stainless-steel flange containing the adjustable orifice mentioned above. The orifice was machined out of teflon to prevent wall recombination, and the interior of the cell ($V = 238.3$ cm^3) was coated with FEP teflon which also effectively inhibited wall recombinations. HBr was admitted to the cell through a 1 mm × 2 cm capillary to prevent back-diffusion of the reactants. The escape constant of the cell was measured by following the first-order decay curve (as measured by the mass spectrometer) of ethane after the flow was halted. the 3-mm orifice was used in this experiment and k_{em} was found to be 0.5694 $(T/M)^{1/2}$ s^{-1} where T is the absolute temperature (K) and M is the molecular weight (amu).[12]

Chlorine atoms were generated by flowing 1% Cl_2 in helium through a quartz tube coated with phosphoric acid and enclosed in a 2.45-GHz microwave cavity operating at 50 W. The chlorine atoms were admitted to the reaction cell through a 2-cm tapered capillary having approximate diameters of 0.3 and 1 mm at the two ends. The complete dissociation of Cl_2 was checked by mass spectrometry. Our sensitivity to Cl_2 was significantly less than 10^{10} molecules cm^{-3} so that $[Cl_2]/[Cl]$ was established at well under 1%.

The temperature of the reaction cell was held constant by circulating a thermostated liquid (water or ethanol) through an outer jacket surrounding the cell. The temperature was constantly monitored with a copper–constantan thermocouple.

The molecules which exit the aperature of the reaction cell diffused through three differentially pumped chambers thus creating the molecular beam described earlier. The beam was chopped at 200 Hz before entering the ionizer of the mass spectrometer and the ac component was detected with a lock-in analyzer (Ithaco Dynatrac 3). The quadrupole mass spectrometer is a Balzers Model QMG 511 with a cross beam analyzer made specifically for beam work. The choice of electron energy of the ionizer is critical because the appearance of Cl^+ (m/e 35) from HCl (m/e 36) fragmentation would interfere with the chlorine signal from Cl_2 microwave discharge. Checks of HCl fragmentation as a function of electron energy show that there is less than 1% fragmentation at 30 eV. In our experiments the concentration of HCl present is comparable to that of Cl and a 1% fragmentation of HCl would be negligible under these conditions. Therefore all experiments were carried out at 30 eV.

The maximum flow rate of the reactants was limited to about 2×10^{16} molecules s^{-1} (which corresponds to a pressure of about 0.5 mtorr inside the reaction cell) in order to satisfy the Knudsen condition.

This new VLPR system was tested for the first time by measuring the rate constant of a well-characterized reaction, Cl + CH_4. This reaction has been studied by over ten different groups and the NASA Panel for data evaluation recommends a rate constant of 1.0×10^{-13} $molecule^{-1}$ s^{-1}.[13] This reaction has also been measured tin a two-chamber VLPR system.[14] Results from

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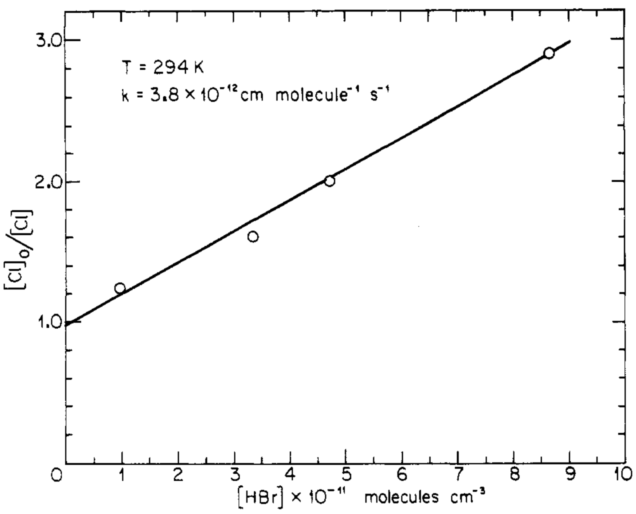

Figure 2. Plot of $[Cl]_0/[Cl]$ vs. [HBr] at 294 K.

this previous VLPR measurement are in excellent agreement with the NASA Panel recommendation.

We measured the rate constant for Cl + CH_4 at 294 K under conditions similar to those used for Cl + HBr. The average rate constant obtained with 1.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, in excellent agreement with the NASA Panel evaluation.

Results

The reaction under study is

$$\mathrm{Cl + HBr \xrightarrow{k} HCl + Br}$$

Steady-state analysis of this system, including the fact that the flow in must equal the flow out, shows that

$$[\mathrm{Cl}] = \frac{k_{\mathrm{eCl}}[\mathrm{Cl}]_0}{k_{\mathrm{eCl}} + k[\mathrm{HBr}]}$$

where k_{eCl} isthe escape constant for chlorine from the reaction cell and $[Cl]_0$ is the concentration of chlorine in the absence of HBr. Upon rearrangement

$$\frac{[\mathrm{Cl}]_0}{[\mathrm{Cl}]} = 1 + \frac{k[\mathrm{HBr}]}{k_{\mathrm{eCl}}} = \frac{I_{\mathrm{Cl0}}}{I_{\mathrm{Cl}}}$$

where I_{Cl0} and I_{Cl} are the mass spectrometer signals at mass 35 for $[Cl]_0$ and [Cl], respectively. We must correct his equation for the fact that we were not under pseudo-first-order conditions: initial concentrations of chlorine ranged from $\sim 2 \times 10^{11}$ to $\sim 8 \times 10^{11}$ atoms cm^{-3}, concentrations of HBr ranged from $\sim 3.6 \times 10^{11}$ to $\sim 1.2 \times 10^{12}$ molecules cm^{-3}. To correct the [HBr] we see that

$$[\mathrm{HBr}] = [\mathrm{HBr}]_0 \frac{[\mathrm{HBr}]}{[\mathrm{HBr}]_0}$$

By using the HBr 80 peak we can measure the ratio $[HBr]/[HBr]_0$ and we calculate $[HBr]_0$ from the flow capillary calibrations and the pressure of HBr before the capillary.

A plot of $[Cl]_0/[Cl]$ vs. [HBr] yields a straight line with an intercept of unity and slope (k/k_{eCl})[HBr]. This allows us to calculate k. A plot of this type is shown in Figure 2 for the reaction at 294 K.

The experiment was carried out at three different temperatures, 267, 294, and 333 K; plots of $[Cl]_0/[Cl]$ vs. [HBr] are shown in Figures 2–4. Our results yield a rate constant of 3.4×10^{-12} cm^3 $molecule^{-1}$ s^{-1} which is independent of temperature.

As a check on the integrity of the VLPR system we performed a mass balance experiment with Cl + HBr where we simultaneously observed mass peaks at Cl, HCl, Br, and HBr at 35, 36, 79, and 80 amu, respectively, under three different conditions. First we scanned these mass regions with only Cl_2/He flowing and the microwave discharge on. The resulting spectrum showed peaks at m/e 35 and 36 only showing the presence of Cl atom and HCl. (HCl is always present in small amounts in the system when Cl_2 is discharged due to the presence of the phosphoric acid coating on the microwave discharge tube.) Then HBr was added to the system. The Cl 35 peak and the HCl 36 peaks changed proportionately, i.e., Cl decreased by the same amount that HCl increased. The peaks for Br and HBr were also observed. The discharge was then turned off and the 35 and 36 peaks disappeared and the 79 and 80 peaks changed proportionately. There was still a small peak (<1/5 the size of the peak at mass 80) at 79 from the fragmentation of HBr by the electron beam. This check showed the system is self-consistent and that there is no mass loss (≤1%) to the walls or by secondary reactions in the experiments.

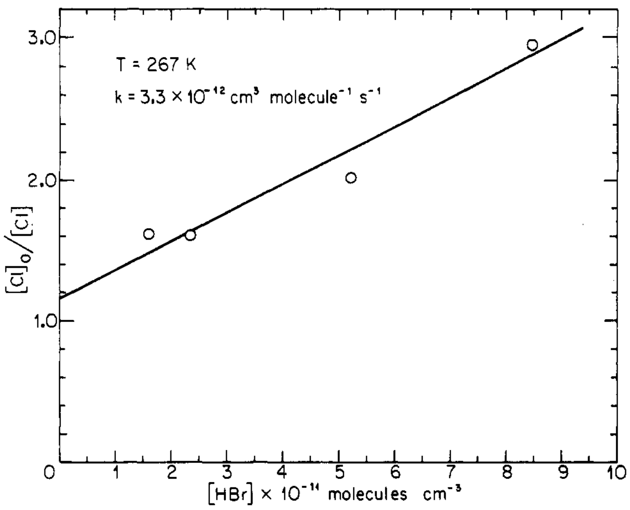

Figure 3. Plot of $[Cl]_0/[Cl]$ vs. [HBr] at 267 K.

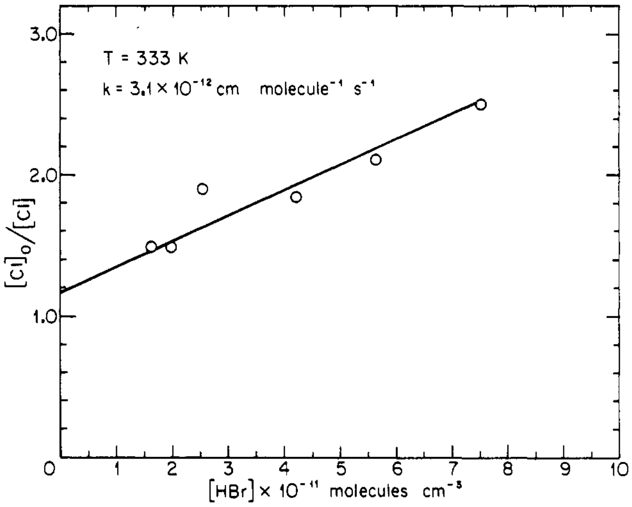

Figure 4. Plot of $[Cl]_0/[Cl]$ vs. [HBr] at 333 K.

Discussion

The rate constants measured by the VLPR method can be compared with those obtained by Mei and Moore[8] and Rubin and Persky.[9] The room temperature rate constant measured by Mei and Moore (8.4×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) is about a factor of 2.5 faster than ours. The room temperature rate constant measured by Rubin and Persky (1.1×10^{-11} cm^3 $molecule^{-1}$ s^{-1}) is about a factor of 3 faster than ours. Mei and Moore also see a non-Arrhenius temperature dependence over a temperature range 218–402 K, while the results of Rubin and Persky show a straight line for the Arrhenius plot over the range 222–504 K, with an activation energy for the reaction of about 0.9 kcal. The activation energy measured in our system is 0 ± 0.4 kcal/mol.

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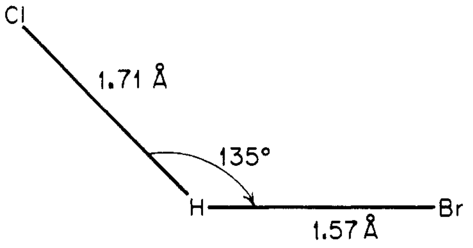

Figure 5. Nonlinear transition state for Cl + HBr.

An A factor for the reaction can be calculated by using Benson's methods,[15] assuming a tight transition state which is nonlinear (Figure 5). The entropy of Cl–H–Br can be calculated readily from the standard equation for translational, rotational, and vibrational entropy.

$$S = 40.2 \text{ (translation)} + 21.4 \text{ (rotation)} + 0 \text{ (vibration)} + 5.0 \text{ (1-D rotor)} + 1.4 \text{ (spin)} = 68.0 \text{ eu}$$

Therefore $\Delta S^{\ddagger} = 68 - 47.5 - 39.5 = -19.0$ eu. This leads to an A factor of 5.8×10^{-12} cm^3 molecule^{-1} s^{-1}, in very good agreement with our experimental results of 3.4×10^{-12} cm^3 molecule^{-1} s^{-1}. Assuming a linear transition state would yield even a slower rate constant, there seems to be no way to bring the experimental results of Mei and Moore and Rubin and Persky into agreement with this calculation.

We see no evidence of a temperature dependence over the range 263 to 333 K. While our range was not as great as that of the two previous groups we could easily see a 30% change in rate constant over that interval as suggested by Rubin and Persky. We estimate that our reported rate constant is accurate to 15%, based on the prior established performance of the VLPR system.

Acknowledgment. J.J.L. gratefully acknowledges the pioneering work of Dr. Peter Papagiannakopoulos for the part he played in designing and building this newest version of the VLPR system. This work has been supported by grants from the National Science Foundation (CHE-(9-26623) and the U.S. Army Research Office (DAAG29-82-K-0043).

Registry No. HBr, 10035-10-6; Cl atomic, 22537-15-1.

Reaction of K Atoms with Oriented CF_3Br

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(Received: September 17, 1985)

A beam of oriented CF_3Br molecules is prepared by passing a randomly oriented beam through an appropriate series of inhomogeneous and homogeneous electric fields. An atomic K beam crosses the beam of oriented CF_3Br and the angular distribution of the reactively scattered KBr is measured with a differential surface ionization detector. The "heads" orientation (Br end closest to incoming K) is about threefold more reactive than the "tails" orientation. The KBr is scattered backward in the "heads" orientation and forward in the "tails" orientation, qualitatively consistent with a "harpoon" type of mechanism in which the orientation affects either the electron jump or the breakup of the dissociating negative ion.

Introduction

Proper orientation of reagents as a prerequisite for chemical reaction seems to be widely accepted on an intuitive level. Almost all theories of reaction rates include "steric factors" in one form or another.[1] However, a detailed understanding of these factors is still lacking. Experimentally, recent advances in molecular beam and laser technology[2] have made possible the direct observation of a variety of steric effects in several reactions.

Polarized laser radiation can be used to prepare beams of *polarized* molecules, which are molecules whose plane of rotation can be oriented with respect to a fixed axis. This technique has been applied, for example, to Sr + HF and "broadside" attack of the plane-of-rotation of HF is observed[3] to yield more SrF (J' = 2) than "edge-on attack", suggesting a bent minumum energy configuration. Similarly, polarized light has been used[4] to produce atoms in which excited p- or d-orbitals are directed parallel or perpendicular to the relative velocity. In the case of Ca + HCl, the direction of the Ca* p-orbital strongly influences the branching into two different CaCl* states.

Electrostatic deflection techniques have been used to prepare beams of *oriented* molecules,[2a,5] which are molecules whose figure axes precess around a space-fixed axis. One "end" of the molecule can be distinguished from another, and can be pointed toward (or away from) an incoming atom so that chemical reactivity can be studied as a function of orientation. Examples of reactions studied using this technique are O_3 reacting with oriented NO,[6] K reacting with CH_3I and CF_3I,[7] and Rb reacting with CH_3I.[8] The latter

TABLE I: Operating Conditions

distances, cm	
K oven–scattering center	12
nozzle–scattering center	70
scattering center–detector	5
nozzle–skimmer	2.6
field length	54
temp, K	
gas nozzle	308
K oven	623
K nozzle	673
nozzle backing pressure, torr	110
hexapole voltage, kV	12
homogeneous field strengths, V/cm	80

[†] Robert A. Welch Predoctoral Fellow.

[‡] Permanent Address: Chemistry Department, University of Canterbury, Christchurch, New Zealand.

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