Rate Constants as a Function of Temperature and Kinetic Energy for the Reactions of Cl^- with C_2H_5Br and *n*-C_3H_7Br

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We have measured the rate constants and branching ratios for the reactions of Cl^- with C_2H_5Br and *n*-C_3H_7Br as a function of temperature and kinetic energy. Both reactions proceed slowly. The reactions proceed mostly to form Br^- at room temperature and above. Both the temperature and kinetic energy dependencies are flat in this regime. At low temperatures a new mechanism becomes important, namely, association followed by thermal dissociation to form both Cl^- and Br^-. This is especially important in the *n*-C_3H_7Br reaction for which the rate constant increases by a factor of 4 between room temperature and 230 K. Not only does the overall rate increase but also the channel-forming Br^-.

Introduction

Gas-phase ion−molecule S_N2 reactions have been an intensive area of research. In particular, the reactions of the halide ions with methyl halides have been extensively studied both experimentally and theoretically (for recent examples, see Raugei et al.,[1] Schmatz and Clary,[2] and Craig et al.[3] and the references within). Much of the interest has focused on whether these reactions behave statistically. The reactions of halide ions with methyl halides have been shown to behave nonstatistically in several experiments. We have contributed to that conclusion by making studies of the rate constants for several reactions as a function of kinetic energy at several temperatures. This allows comparison of how different types of energy affects reactivity. For several halide−methyl halide reactions, we have found that internal energy has little effect on reactivity, even though translational energy makes the reaction slower.[4−6] Wang and Hase[7] have not been able to fit these results using statistical calculations. In contrast, we have found that for other reactions, such as F^- with CF_3Br and CF_3I and Cl^- with $ClCH_2CN$, that all types of energy behave similarly.[8,9] Other evidence for the nonstatistical nature of S_N2 reactions includes the experiments of Graul and Bowers,[10,11] who have found that kinetic energy releases from partially stabilized $X^-(CH_3Y)$ complexes (where X and Y are halogens) cannot be modeled by phase space theory. Knighton et al.[12] have found that the rate constant increases with increasing pressure. Trajectory calculations by Hase and co-workers[13] have found numerous central barrier crossings during the course of one encounter. Craig et al.[14] have found a highly excited complex of $[Cl{\cdot}CH_3OC(O)CF_3]^-$ dissociated faster than what could be predicted by statistical theory.

Our initial goal for the present study is to test whether the reactions of Cl^- with higher alkyl halides behave statistically or not. Unfortunately, the lack of an appreciable temperature dependence in the rate constants ultimately prevents us from making any definitive conclusions on that subject. Instead, we are able to show that at low temperature some of the reactivity can be attributed to a more complex mechanism involving thermal association and dissociation. The presence of the association channel indicates that the lifetime of the complex is long and that the reactions probably could be described by statistical theories.

Experimental Section

The measurements have been made using a variable temperature-selected ion flow drift tube (VT-SIFDT) apparatus. The details of the apparatus have been published elsewhere[4,15] and only those aspects important to the present study will be discussed in detail. Cl^- is made in an electron impact ion source from CF_2Cl_2. The ions are extracted from the source, mass-selected in a quadrupole mass filter, and injected into a flow tube through an orifice surrounded by a Venturi inlet through which the helium buffer gas was added. The mass spectrometer resolution is kept low so that a statistical mixture of the Cl^- isotopes is injected. C_2H_5Br and *n*-C_3H_7Br are added through one of two downstream inlets, and rate constants are measured in the standard manner.[15] The pressure in the experiments was between 0.45 and 0.65 Torr.

Relative and absolute uncertainties are estimated to be ± 15% and ± 25%, respectively.[15] The neutral reactants are liquids and the vapor was used after several freeze−thaw cycles. The limited vapor pressure of the reactants limited the amount of gas that could be added to the flow tube. Freezing of the vapor in our reactant inlet determined the minimum temperature we could study each reaction. For C_2H_5Br this was 220 K, and for *n*-C_3H_7Br this was 230 K. In the past we have used heated inlets to increase the temperature range.[16,17] This is not possible in a drift tube experiment because of the impracticality of heating the ring inlets that are necessary for these types of experiments.[15] Branching fractions were measured by extrapolating to zero reactant flow.

A drift tube is positioned inside the flow tube, and the entire flow tube can be heated or cooled. Heating is done resistively and cooling is accomplished by pulsing liquid nitrogen. Rate constants can therefore be measured as a function of temperature and ion kinetic energy. The average kinetic energy in the ion−neutral center-of-mass system, $\langle KE_{cm} \rangle$, in the drift tube is derived from the Wannier formula[18] as

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$$\langle KE_{cm} \rangle = \frac{(m_i + m_b)m_n}{2(m_i + m_n)} v_d^{\,2} + \frac{3}{2}kT \qquad (1)$$

where m_i, m_b, and m_n are the masses of the reactant ion, buffer gas, and reactant neutral, respectively, v_d is the ion drift velocity, and T is the temperature. A given average center-of-mass kinetic energy, $\langle KE_{cm} \rangle$, is obtained with varying contributions of the temperature term and the drift tube term. Comparing rate constants at a particular $\langle KE_{cm} \rangle$ but with varying contributions from the two terms yields the dependence of the rate constant on the internal temperature of the reactant neutral (if the ion is monatomic, as in the present study). The limited vapor pressure of the reactants coupled with the low rate constants prevented us from studying the reactions over an extended kinetic energy range. In fact, we tried to study the i-C_3H_7Br reaction, but the amount of depletion was too low to make accurate rate constant measurements, consistent with a previous study by DePuy et al.[19]

Results and Discussion

Cl^- + C_2H_5Br. Figure 1 shows the rate constants for the reaction of Cl^- with C_2H_5Br as a function of average kinetic energy calculated according to eq 1. The rate constants are listed in Table 1. The reaction proceeds by two pathways:

$$Cl^- + C_2H_5Br \rightarrow Br^- + C_2H_5Cl + 11.2 \text{ kcal mol}^{-1} \qquad (2a)$$

$$\rightarrow (Cl^-C_2H_5Br) + 13.6 \text{ kcal mol}^{-1\ 20} \qquad (2b)$$

The S_N2 pathway, Br^-, dominates at all temperatures and is the only product observed at 400 and 500 K. For the 220 and 298 K data, both the total rate constant and the rate constant for the S_N2 channel are plotted. The S_N2 rate constant is obtained by multiplying the overall rate constant by the branching fraction for Br^-. We find no appreciable temperature dependence from 298 to 500 K. Similarly, the kinetic energy dependence at 298 K is flat. The slow rate and the limited vapor pressure prevent accurate measurements as a function of kinetic energy at 400 and 500 K. The rate constants are appreciably larger at 220 K, especially at low kinetic energy. Most of the difference is due to the association channel. The rate constants for the S_N2 channel at 220 K and elevated kinetic energy are slightly higher than the pure temperature data at higher temperatures, but the difference is within experimental error. The association fraction decreases with increasing kinetic energy at 220 K, as one would expect. At 298 K, the fraction of association is 5% and is independent of kinetic energy.

Also shown in Figure 1 are results from several previous experiments. The results from Knighton et al.[12] are in very good agreement with the present data. The Knighton et al. data are really the results from two different apparatuses, namely, from a high-pressure mass spectrometer (HPMS) and a high-pressure ion mobility drift tube. The two data sets are identical for all practical purposes and shown as a single line. Their data show no pressure dependence between 3 and 640 Torr. Good agreement with the present results indicates that the lack of a measurable pressure dependence can be extended to 0.4 Torr. In contrast, the other HPMS data set from Caldwell et al.[21] shows a considerably steeper temperature dependence. We have also had a discrepancy when comparing previous data from our laboratory on the reaction of Cl^- with CH_3Br[5] with the Caldwell et al. data. For that reaction, we have argued that the data of Caldwell et al. are in error. The 300 K only point of DePuy et al.[19] is about a factor of 2 lower than the present data and in agreement with the Caldwell et al. data. The DePuy et al. study has also used a selected ion flow tube and we generally have excellent agreement between the two groups.

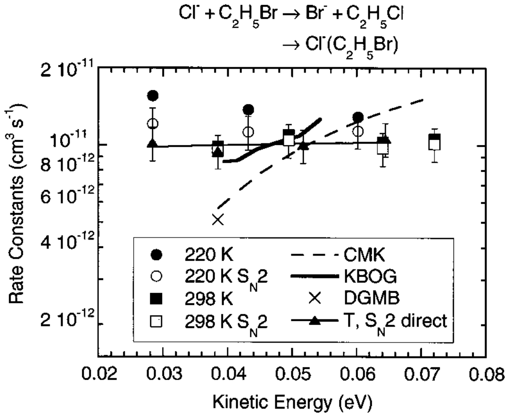

Figure 1. Rate constants in $cm^3\ s^{-1}$ for the reaction of Cl^- with C_2H_5Br as a function of kinetic energy in eV. Closed and open circles represent the total rate constant and the S_N2 only rate constant at 220 K, respectively. Closed and open squares represent the total rate constant and the S_N2 only rate constant at 298 K, respectively. The pure temperature dependent data of the direct S_N2 reaction is given by triangles with a least squares fit line. The triangles include data at 400 and 500 K where no correction is needed. For the correction at low temperature, see the text. The solid line refers to the study of Caldwell et al. (CMK).[21] The dashed line refers to the study of Knighton et al. (KBOG).[12] The X refers to the study of Depuy et al. (DGMB).[19]

TABLE 1: Rate Constants in $cm^3\ s^{-1}$ for the Reaction of Cl^- with C_2H_5Br as a Function of Temperature and Average Center-of-Mass Kinetic Energy Measured in the VT-SIFDT (See Text for Details)

temperature (K)	$\langle KE_{cm} \rangle$ (eV)	total rate constant ($cm^3\ s^{-1}$)	S_N2 rate constant ($cm^3\ s^{-1}$)
220	0.028	1.56×10^{-11}	1.21×10^{-11}
	0.043	1.38×10^{-11}	1.13×10^{-11}
	0.060	1.29×10^{-11}	1.14×10^{-11}
298	0.039	0.99×10^{-11}	0.95×10^{-11}
	0.050	1.10×10^{-11}	1.05×10^{-11}
	0.064	1.03×10^{-11}	0.97×10^{-11}
	0.072	1.06×10^{-11}	1.01×10^{-11}
400	0.052	1.00×10^{-11}	1.00×10^{-11}
500	0.065	1.06×10^{-11}	1.06×10^{-11}

Fast reactant impurities are a potential cause of rate constants that are too fast. We do not believe our experiments suffer from impurities for the following reasons. We have excellent agreement with the two experimental determinations by Knighton et al. Impurities in large enough concentrations to cause the deviation are not present in the reaction of Cl^- with i-C_3H_7Br because the rate constant limit is much smaller than the rate constants measured for the C_2H_5Br reaction. C_2H_5Br has a higher vapor than with i-C_3H_7Br and one can reasonably expect that the higher vapor pressure species would have less contamination in the gas phase. Further argument against a fast-reacting impurity causing the upturn at low temperature is the kinetic energy dependence of the rate constant. Fast reactions usually have little temperature or kinetic energy dependence; therefore, we would not expect a dependence on kinetic energy, in contrast to what is observed. Finally, we have excellent agreement with DePuy et al. for the n-C_3H_7Br reaction. Thus, we have no good explanation for the discrepancy. In any case, an impurity is not likely the cause of the upturn observed at low temperature.

As explained in the Introduction, one of the goals of the study was to examine whether all types of energy affect reactivity

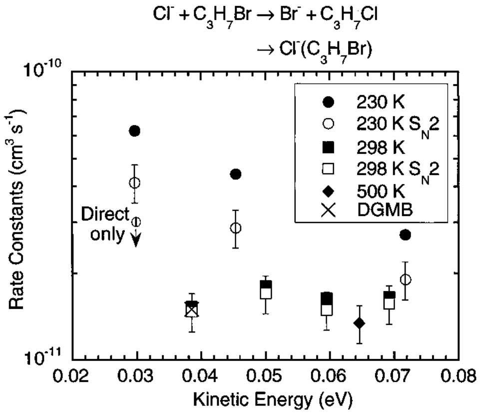

Figure 2. Rate constants in cm^3 s^{-1} for the reaction of Cl$^-$ with n-C_3H_7Br as a function of kinetic energy in eV. Closed and open circles represent the total rate constant and the S_N2 only rate constant at 230 K, respectively. Closed and open squares represent the total rate constant and the S_N2 only rate constant at 298 K, respectively. The diamonds refer to 500 K data. The X refers to the study of Depuy et al. (DGMB).[19] The point labeled "Direct only" is an upper limit to the direct S_N2 reaction at 230 K. See text for details.

TABLE 2: Rate Constants in cm^3 s^{-1} for the Reaction of Cl$^-$ with n-C_3H_7Br as a Function of Temperature and Average Center-of-Mass Kinetic Energy Measured in the VT-SIFDT (See Text for Details)

temperature (K)	$\langle KE_{cm}\rangle$ (eV)	total rate constant (cm^3 s^{-1})	S_N2 rate constant (cm^3 s^{-1})
230	0.030	6.25×10^{-11}	4.12×10^{-11}
	0.045	4.42×10^{-11}	2.87×10^{-11}
	0.072	2.72×10^{-11}	1.90×10^{-11}
298	0.039	1.53×10^{-11}	1.47×10^{-11}
	0.050	1.80×10^{-11}	1.70×10^{-11}
	0.060	1.64×10^{-11}	1.49×10^{-11}
	0.069	1.65×10^{-11}	1.57×10^{-11}
500	0.065	1.34×10^{-11}	1.34×10^{-11}

equally; that is, does the reaction behave statistically? By comparing rate constants at a fixed kinetic energy with differing contributions from the two terms in eq 1, one finds the dependence on the internal temperature of the reactants. The data indicate that adding internal energy has no effect on the rate. However, the kinetic energy dependence is also flat. Normally, we replot the data as a function of total energy, where rotational and vibrational energy are included.[4] If all data fall on one line in the total energy plot, we determine that all forms of energy behave the same. While that is the case here, the weak temperature and kinetic energy dependencies just spread out the data. What we conclude is that no form of energy has a strong influence on the reactivity and that we cannot make a statement on whether the reaction behaves statistically. We can say that adding internal energy, mainly vibrational excitation, does not strongly affect the rate constants.

Cl$^-$ + n-C_3H_7Br. Figure 2 shows the rate constants for the reaction of Cl$^-$ with n-C_3H_7Br as a function of average kinetic energy. The data are listed in Table 2. The reaction also proceeds by two pathways:

$$Cl^- + C_3H_7Br \rightarrow Br^- + C_3H_7Cl + 12.1\ \text{kcal mol}^{-1} \quad (3a)$$

$$\rightarrow (Cl^-C_3H_7Br) + 14.2\ \text{kcal mol}^{-1\ 20} \quad (3b)$$

Again, the S_N2 channel is the predominant channel and both the total rate constant and the S_N2 only rate constant are plotted. The data are similar in magnitude to those for the C_2H_5Br reaction. From 298 to 500 K, the temperature and kinetic energy dependencies are flat within experimental error. There is excellent agreement with the 300 K point of DePuy et al.[19] Good agreement of the 500 K point and 300 K at approximately the same kinetic energy indicate that there is no appreciable dependence on internal temperature and conclusions similar to those found for the C_2H_5Br reaction apply. A 5% association channel is seen at 298 K and no association is seen at 500 K.

In contrast, the total rate constant and the S_N2 rate constant at 230 K are significantly greater than the higher temperature data. The pure temperature dependence has a pronounced kink between 298 and 230 K. The factor of 4 increase is quite large and therefore should be much larger than any potential systematic error. The substantial dependence of the rate constant on kinetic energy should rule out any possible problem with impurities as explained earlier. At the low temperature, a substantial association channel is observed at all kinetic energies. Association goes from 35% of the reactivity at no field to 30% at the maximum field. At the maximum drift field, the S_N2 only rate constant is only slightly higher than the values found at other temperatures. This is not true at low kinetic energies.

Thermal Association/Dissociation vs Direct Reaction. The direct S_N2 mechanism involves a double-well potential. Reactants collide and form a complex, the entrance complex rearranges through a barrier into an exit well complex, and the exit well complex dissociates into products, all in one collision. The odd form of the temperature dependence found in reaction 3 most likely reflects a new mechanism that is operative at low temperature. We postulate that the new mechanism involves the same potential surface but the buffer gas becomes involved by allowing thermal association and dissociation to take place:

$$Cl^- + C_3H_7Br + M \rightarrow (Cl^-\ C_3H_7Br) + M + 14.2\ \text{kcal mol}^{-1} \quad (4a)$$

$$(Cl^-C_3H_7Br) + M \rightarrow Br^- + C_3H_7Cl + M\ (\text{barrier} = 12.9\ \text{kcal mol}^{-1}) \quad (4b)$$

$$\rightarrow Cl^- + C_3H_7Br + M - 14.2\ \text{kcal mol}^{-1} \quad (4c)$$

The thermochemistry and barrier height are from McMahon and co-workers.[20] The barrier height for the formation of Br$^-$ from ($Cl^-C_3H_7Br$) is lower in energy than the dissociation energy to form Cl$^-$, which has no barrier in excess of the thermodynamic one. Thus, once formed, the $Cl^-(C_3H_7Br)$ cluster can add substantially to the S_N2 rate (by dissociation) as well as the overall rate. Thermal dissociation of cluster ions bound by this magnitude are common in our apparatus[22] and have been invoked in the similar dissociation of $Cl^-(CH_3Br)$ when the $Cl^-(CH_3Br)$ complex is formed by the reaction of CH_3Br with $Cl^-(H_2O)$.[23]

It is possible to test for the presence of this mechanism by adding HCl to the flow tube. HCl only reacts slowly with Cl$^-$ to form $Cl^-(HCl)$.[24] However, a ligand switching to form $Cl^-(HCl)$ is fast because it is exothermic by 9 kcal mol^{-1}:[25]

$$Cl^-(C_3H_7Br) + HCl \rightarrow Cl^-(HCl) + C_3H_7Br \quad (5)$$

We have performed this test at 230 K. Isotope exchange is irrelevant because we used low resolution on both of our mass spectrometers so that a statistical mixture of Cl$^-$ is injected and detected as a single broad peak. Only a small amount of HCl is added at a level of 10^{-4} of the helium buffer. This prevents significant depletion of the primary Cl^- primary ion and keeps the energy distribution in the drift tube experiments controlled by the helium buffer. With this level of HCl, all of the complex cannot necessarily be scavenged before dissociating. Nevertheless, it does provide a good test of the mechanism.

Adding HCl changes the kinetics in several ways. First, the $Cl^-(HCl)$ signal increases, showing that we are scavenging some of the $Cl^-(C_3H_7Br)$ complex before it can dissociate; that is, reaction five is fast. We also assume that all of the increase in the $Cl^-(HCl)$ signal is due to nascent $Cl^-(CH_3Br)$. Second, the rate constants increase slightly (~10%). While this increase is small, by taking measurements immediately after each other with only the HCl valve opened or closed, we believe it is a meaningful difference. This indicates that some of the $Cl^-(C_3H_7Br)$ complex is scavenged before it can dissociate into Cl^-, indicating that reaction (4c) is occurring. The branching fraction changes so that Br^- comprises only 46% of the products with HCl added, rather than the 69% observed without HCl. This indicates that reaction (4b) is occurring. Third, the rate constant for Br^- production is 25% lower with HCl added than without, indicating that reaction (5) is preventing reaction (4b) from occurring. This derived rate constant is shown in Figure 2 as direct only and is still higher than the extrapolation of the high-temperature data, which may indicate that we did not scavenge all the $Cl^-(C_3H_7Br)$ with the amount of HCl added. Therefore, we show the point as an upper limit as indicated by the arrow. Larger HCl concentrations interfere with the kinetics by forming significant amounts of $Cl^-(HCl)$ via reaction with Cl^-. Thus, the observations are consistent with the proposed mechanism.

We have done the same test for the C_2H_5Br reaction, although the overall rate constant increase is considerably less. Similar changes but of much smaller magnitude are found. We estimate the direct S_N2 reaction rate (as opposed to the Br^- formed by thermal decomposition) by taking the total rate multiplied by the branching fraction of Br^- produced with HCl added. As indicated above, this may be a slight overestimate because of incomplete scavenging. Assuming the rate constants at higher temperatures are only due to direct reaction, we can estimate the temperature dependence for the direct S_N2 channel as (1) the corrected 220 K point, (2) the 298 K point times the branching fraction, and (3) the 400 and 500 K points. The estimated direct S_N2 channel is shown in Figure 1 as triangles and is very flat.

The energetics of the two reactions are similar. The barrier height for the C_2H_5Br reaction equivalent to (4b) is also 12.9 kcal mol^{-1}.[20] Therefore, the principle difference is in the well depth of the complex and the complexity of the reactants; that is, the n-C_3H_7Br well depth is 0.6 kcal mol^{-1} greater than that for C_2H_5Br and has more degrees of freedom. Both of these differences are small, but they are apparently large enough that the rate constant for the n-C_3H_7Br reaction increases by a factor of 4 at low temperature compared to a factor of 1.5 for the C_2H_5Br reaction. It is not possible to tell whether this is a result of an increased association rate for the n-C_3H_7Br reaction or an increased dissociation rate for the C_2H_7Br reaction. The importance of the thermal association and dissociation mechanism, which ultimately leads to a S_N2 product, therefore depends on a delicate balance between well depth and barrier height and/or the number of degrees of freedom.

We have observed thermal dissociation of the $Cl^-(CH_3Br)$ complex previously.[23] This complex dissociates almost exclusively into Br^- with the estimate for production of Cl^- as 0.3%−4.8% (the higher number refers to higher temperature). The barrier in that reaction is lower than those for the C_2H_5Br and n-C_3H_7Br reactions. In fact, we estimate it to be only 5.4 kcal mol^{-1}. The well depth is considerably greater (12.5 kcal mol^{-1})[20] than the barrier height, so the Cl^-/Br^- ratio is not surprising. Other estimates of the barrier height are larger and are summarized in Li et al.[20] We have speculated that the low barrier in the $Cl^-(CH_3Br)$ dissociation may only be an effective barrier and tunneling may be occurring.[23] The tunneling would correspond to an umbrella flip of the three hydrogens. In the present reactions, tunneling would presumably be less important because one of the hydrogens in the umbrella motion would be replaced by a heavier CH_3 or C_2H_5 group. For the present reactions, the well depths and the barrier heights are closer in magnitude and more dissociation into Cl^- may be expected. We have observed this in the sense that the rate constant increases with the addition of HCl, indicating back dissociation to the Cl^- primary ion has been quenched by the HCl addition.

The presence of the association channels indicates that the lifetime of the $Cl^-(C_2H_5Br)^*$ and $Cl^-(C_3H_7Br)^*$ complexes must approach the time between helium collisions or $\sim 10^{-7}$ s. This is also much longer than the $Cl^-(CH_3Br)^*$ lifetime, which has been estimated to be on the order of picoseconds.[13] The very short lifetime is an important factor leading to the nonstatistical nature of that reaction. Previously, all studies of S_N2 reactions with association channels have been found to depend only on total energy.[8,9] Therefore, we expect the present reactions also to be statistical. This is consistent with the findings that both internal and translational energy do not effect the reactivity, at least at temperatures where the low-temperature association mechanism is inoperative.

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