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COMMUNICATIONS

Temperature dependence of the rate constant for the $\text{Cl}^- + \text{CH}_3\text{Br}$ reaction down to 23 K

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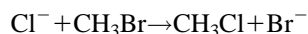
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Rate constants measured for the $\text{Cl}^- + \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{Cl} + \text{Br}^-$ reaction increase by over two orders of magnitude when the temperature is reduced from 300 to 23 K. Calculations done with the rotating bond approximation provide a simple explanation of this unusually strong negative temperature dependence of the rate constant. © 1997 American Institute of Physics. [S0021-9606(97)03527-7]

I. INTRODUCTION

The S_N2 reaction



is a classic example of the simplest substitution reaction in organic chemistry. It has long been postulated that a reaction of this type involves an inversion of the CH_3 "umbrella" mode and the potential energy surface is known to have deep wells corresponding to the formation of ion-dipole complexes placed on either side of a local barrier at which the CH_3 group becomes planar.¹ At 300 K, the rate constant of this exothermic reaction is known to be quite large ($10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$)² and to decrease slightly at higher temperatures, as predicted by simple ion-dipole capture theory.³ However, the magnitude of this rate constant is well below the value ($10^{-9} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$) predicted by this simple theory and the detailed understanding of the rate of this reaction remains uncertain.

We have developed an experimental method for measuring the rate constants of fast gas phase chemical reactions at low temperatures. The method, known as CRESU (a French acronym for Cinétique de Réaction en Ecoulement Supersonique) has been applied to simple reactions of both ion and neutral species down to temperatures as low as 20 K.⁴⁻⁶ Given the interest, alluded to above, in the rate constant for the $\text{Cl}^- + \text{CH}_3\text{Br}$ reaction it is clearly of interest to apply the CRESU method to measure the rate constant for this classic reaction at lower temperatures.

One of us (D.C.C.) has also developed a quantum scattering method for performing calculations on reactions such as $\text{Cl}^- + \text{CH}_3\text{Br}$. This "rotating bond approximation" (RBA) treats explicitly the Cl-C and Br-C bonds and also the umbrella vibration.^{7,8} The method, which follows the reaction all the way from reactants to products, gives state-to-state reaction probabilities and rate constants.⁸ A potential energy

surface already exists for this reaction, which has been calculated from *ab initio* data and has been used in classical trajectory and wave packet calculations.⁹ It is, therefore, of interest to apply the RBA method to this reaction to compare with the experimentally measured rate constants for low temperatures and to give a detailed explanation of the temperature dependence of the rate constant.

Below we briefly describe the application of our experimental and theoretical methods to the $\text{Cl}^- + \text{CH}_3\text{Br}$ reaction. In both theory and experiment, we find a dramatic increase in the rate constant as the temperature is reduced and we describe a simple mechanism for explaining these results that is deduced from the theoretical treatment.

II. EXPERIMENT

First devised by Rowe and co-workers in the early 1980's, the CRESU technique is well-established and documented.⁴⁻⁶ It can be used for the study of a variety of processes such as ion-molecule, radical-molecule, electron attachment, or internal state relaxation reactions at very low temperatures.

The basic concept employs a uniform supersonic flow generated by the isentropic expansion of a buffer gas (nitrogen, helium, or argon) through a Laval nozzle. Since the expansion is isentropic, the resulting temperature of the flow can be made very low, its value being determined by the shape and operating conditions of the nozzle. Details concerning the calculation of the shape and operating conditions required to generate a given Mach number (and therefore a given temperature) can be found elsewhere.¹⁰ The uniformity of the flow in velocity, temperature, and density, downstream of the nozzle exit, can persist for several tens of centimeters, thus making it an ideal reactor for the study of chemical kinetics.

In the experiment,⁴⁻⁶ various nozzles designed for specific flow temperatures and conditions can be easily mounted onto a flange, connected to a movable reservoir located in a large stainless steel chamber which is pumped by powerful roots blowers ($24\,000\text{ m}^3\text{ h}^{-1}$). The flow is very slow in this reservoir, where parent, reactant, and buffer gases are mixed together. Flow rates are established precisely using Tylan flow controllers. The gases expand through the nozzle into a large chamber, and are then intersected at 90° by a high energy (12.5 keV), low intensity ($10\text{ }\mu\text{A}$) electron beam. A low density plasma ($10^8\text{--}10^9\text{ electrons cm}^{-3}$) is thus created, consisting primarily of buffer gas cations and electrons. The parent gas then rapidly converts these species into the reacting ions that are to be studied. Further downstream, the various ions are detected using a quadrupole mass spectrometer that is housed in a chamber, maintained at a much lower pressure ($< 10^{-5}\text{ Torr}$). The ions enter this chamber through a nose cone, having at its tip a very thin disk of molybdenum (0.05 mm in thickness, 5 mm in diam) having a central aperture of diameter 0.05 mm .

In the present study, Cl^- anions are formed through the dissociative attachment of electrons to a parent vapor of CCl_4 , thus



The following reaction is then studied:



The rate coefficient for this reaction is measured at various temperatures using a standard method for flow reactors. The variation of the Cl^- density $[\text{Cl}^-]$ at a given location downstream x of the electron beam is given, as a function of density of the reactant gas, bromomethane $[\text{CH}_3\text{Br}]$, by:

$$[\text{Cl}^-][\text{CH}_3\text{Br}] = [\text{Cl}^-]_0[\text{CH}_3\text{Br}]_0 \exp\left(-\frac{k[\text{CH}_3\text{Br}]x}{v}\right),$$

where v is the flow velocity. The relationship between $\log [\text{Cl}^-]$ and $[\text{CH}_3\text{Br}]$ is therefore linear and the slope yields the rate constant, k .

Since the parent and reactant gases are mixed together in the reservoir, it is important that reaction (1) completely dominates over the electron attachment reaction:



The electron attachment rate to carbon tetrachloride is very large at 300 K [$3.9 \times 10^{-7}\text{ cm}^3\text{ s}^{-1}$ (Ref. 11), $3.7 \times 10^{-7}\text{ cm}^3\text{ s}^{-1}$ (Ref. 12)] and increases with decreasing temperature.¹¹ We have measured the rate at 75 K and found a value of $4.3 \times 10^{-7}\text{ cm}^3\text{ s}^{-1}$, in good agreement with the trend predicted by the higher temperature results of Smith *et al.*¹¹ CH_3Br does not attach electrons efficiently.¹³⁻¹⁵ It was not possible for us to establish the electron attachment rate at lower temperatures because of the presence of trace impurities in the bromomethane used in our experiment (Air Products: 99.5%). We measured its rate at a temperature of 75 K and found an upper limit of $4.5 \times 10^{-11}\text{ cm}^3\text{ s}^{-1}$. The flow rate of CCl_4 was then set at a value sufficient to ensure that reaction (1) always dominated over reaction (3).

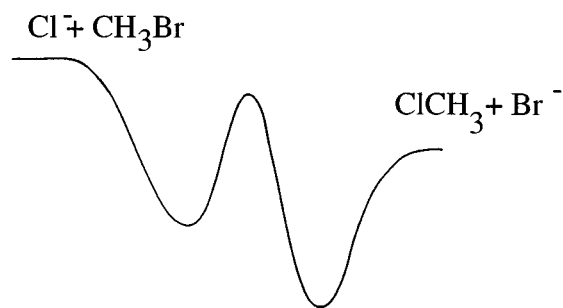
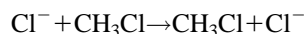


FIG. 1. Reaction path energy profile (Ref. 9) for $\text{Cl}^- + \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{Cl} + \text{Br}^-$. The energy of the barrier is only 2.9 kcal mol^{-1} below the energy of the $\text{Cl}^- + \text{CH}_3\text{Br}$ reactant in its ground state.

III. THEORY

The application of the RBA method to the closely related S_N2 reaction



is described fully elsewhere⁸ and the same technique is used here for the $\text{Cl}^- + \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{Cl} + \text{Br}^-$ reaction. Reaction probabilities as a function of collision energy are calculated for different values of the total angular momentum J and are state selected in the initial C–Br stretching vibration, CH_3 umbrella mode, and product C–Cl stretching vibration. From these J -labeled reaction probabilities, cumulative reaction probabilities (i.e., reaction probabilities summed over all possible final and initial vibrational and rotational states) are calculated by making use of a microcanonical version of reduced dimensionality theory¹⁶ that requires the frequencies of the vibrations of the $\text{Cl}^- - \text{CH}_3\text{Br}$ complex not treated explicitly by the RBA theory.⁸ Boltzmann averaging of the cumulative reaction probabilities over collision energy gives the final rate constant as a function of temperature.

A schematic potential energy profile for this reaction, derived from the *ab initio* calculations of Hase and co-workers is given in Fig. 1.⁹ Of particular note are the ion–dipole wells corresponding to the formation of the complexes $\text{Cl}^- - \text{CH}_3\text{Br}$ and $\text{Br}^- - \text{CH}_3\text{Cl}$. Also, the local barrier in the potential surface, in which the CH_3 group becomes planar, is just below the energy of the $\text{Cl}^- + \text{CH}_3\text{Br}$ reactants. This would suggest that there is no activation energy and the reaction should be fast. However, the height of this local barrier is so close to the reactant energy that the application of capture theory that only includes the long-range part of the potential energy surface is questionable and a theory, such as the RBA, is needed that solves the Schrödinger equation for reaction all the way from reactants to products. In our RBA calculations on the $\text{Cl}^- + \text{CH}_3\text{Br}$ reaction, we used the same potential energy surface as Hase and co-workers with the small modification that the C–Br and C–Cl bonds at the transition state were scaled in the same way as described previously for the $\text{Cl}^- + \text{CH}_3\text{Cl}$ reaction.⁸ This was necessary to bring the geometry of the transition state in closer agreement with the best *ab initio* calculations.

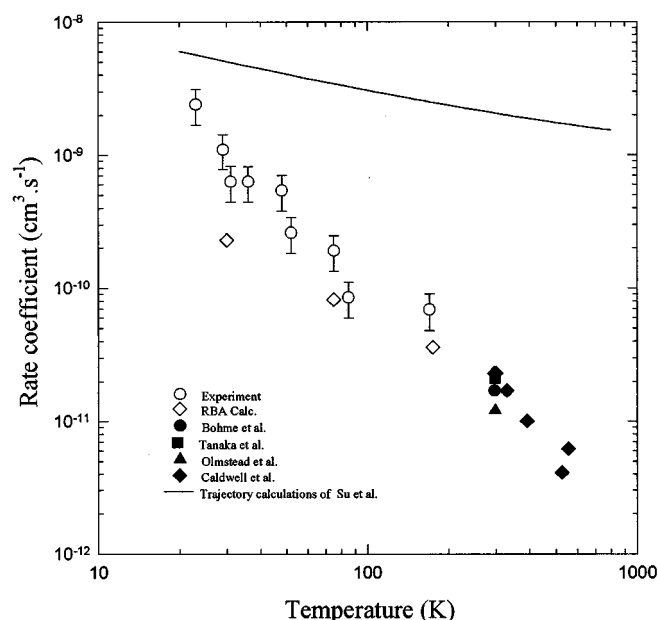


FIG. 2. Rate constants for the $\text{Cl}^- + \text{CH}_3\text{Br}$ reaction as a function of temperature. The present experimental and theoretical (RBA) results are shown as are the rate constants previously measured (Refs. 1, 2, 17, and 18) for 300 K and higher temperatures, and the ion-dipole trajectory capture rate of Su and Chesnavich (Ref. 19).

The RBA reaction probabilities for the $\text{Cl}^- + \text{CH}_3\text{Br}$ reaction show many scattering resonances, as was the case for the $\text{Cl}^- + \text{CH}_3\text{Cl}$ reaction,⁸ but the probabilities do rise to be close to unity at some collision energies close to zero initial kinetic energy.

IV. RESULTS AND DISCUSSION

Our experimental and calculated (RBA) values of the rate constants as a function of temperature are shown in Fig. 2 together with other experimental results^{1,2,17,18} taken at higher temperatures. The consistency between the different sets of experimental data is striking. Also shown is the rate constant obtained from simple ion-dipole capture theory,¹⁹ which should be an upper bound to the exact result.

The most remarkable feature of the experimental and theoretical results is the dramatic increase in the magnitude of the rate constant as the temperature is reduced. Indeed the ratio of the previously measured rate constant at 300 K to that reported here at 23 K is 1:141. The ion-dipole capture rate constant¹⁹ is also shown in Fig. 2 and this has a weaker temperature dependence. However, it is interesting to note that the experimental rate constant does seem to be tending to the ion-dipole limiting value at the lowest temperatures. Although the RBA rate constant does not agree perfectly with experiment, a strong negative temperature dependence is still obtained. Given the several approximations in the theory and potential energy surface, this is a satisfactory agreement.

The calculations and comparison with experiment also give a simple mechanism for explaining the very strong negative temperature dependence of the rate constant. At the

very lowest collision energies, the reaction is fast and follows the potential energy profile as given in Fig. 1 with no activation energy. However, at higher collision energies, excitations of the intermolecular bending modes of the $(\text{Cl}-\text{CH}_3-\text{Br})^-$ transition state are possible and the adiabatic potential energy curves correlating with these excited vibrations can have activation energies. This leads to two types of transition states. One transition state is dominated by the long-range ion-dipole interaction and is appropriate for low temperatures while the other is located close to the barrier in the potential and is appropriate for higher temperatures. This also explains why the measured rate constant is tending to the ion-dipole limit at very low temperatures. In the language of transition state theory, the vibrational partition function arising from the intermolecular modes at the transition state will be relatively small, and will not increase significantly with temperature, while the partition function of the reactants rises very quickly with temperature due to the small rotational constant of the CH_3Br molecule (see also Ref. 20).

We conclude that experimental and theoretical study of the rate constant for the $\text{Cl}^- + \text{CH}_3\text{Br}$ reaction down to low temperatures shows a remarkable increase in the rate constant, with the experimental value at 23 K being over two orders of magnitude larger than that observed at 300 K. As far as we are aware, this negative temperature of the rate constant dependence is much stronger than any that has been observed before for ion-molecule or neutral-neutral reactions. The effect is attributed to the barrier in the potential energy surface being coincidentally just lower than the energy of the $\text{Cl}^- + \text{CH}_3\text{Br}$ reactant so that reaction via excited intermolecular bending vibrations of the $(\text{Cl}-\text{CH}_3-\text{Br})^-$ transition state has a positive activation energy while reaction through the vibrational ground state has no activation energy. It will be interesting to see if other exothermic S_N2 ion-molecule reactions show similar effects.

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