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Gas-Phase S_N2 Reactions of Chloride Ion with Alkyl Bromides at Atmospheric Pressure. Temperature Dependence of the Rate Constants and Energies of the Transition States

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Abstract: Rate constants for the gas-phase reactions $Cl^- + RBr \rightarrow RCl + Br^-$, where R = Me, Et, and *n*-Bu, have been determined over the temperature range 35–150 °C by a kinetic ion mobility mass spectrometer (KIMMS) at 640 Torr of buffer gas pressure and by a pulsed e-beam high-pressure mass spectrometer (PHPMS) at 3 Torr of buffer gas pressure. For the case of R = Me, different rate constants and different temperature dependencies of the rate constants are observed at 640 versus 3 Torr of buffer gas pressure. This effect of pressure is thought to be due to increased collisional stabilization of the entrance-channel intermediate, $(Cl^-{\cdot}MeBr)$, with increased pressure. Less significant pressure effects observed for the cases of R = Et and *n*-Bu are thought to reflect efficient stabilization of the entrance-channel intermediates of these reaction systems at both buffer gas pressures. If it is assumed that the rate measurement at 640 Torr reflect the high-pressure limit of kinetic behavior, the energies (δE_0) of the S_N2 transition states (TS) of these reactions can be determined from simple transition-state theory (TST); $\delta E_0 = -2.2$, 0.0, and −1.3 kcal/mol for R = Me, Et, and *n*-Bu, respectively. The determination of δE_0 described here for the case of R = Me is particularly significant because δE_0 for this system could probably not be accurately deduced from kinetic measurements made at 3 Torr or lower pressure, where the excited intermediate, $(Cl^-{\cdot}MeBr)^*$, has been shown to behave in a nonstatistical manner.

One of the principal driving forces behind the development of experimental methods for the study of gas-phase ion–molecule (IM) reactions has been to characterize the potential energy surfaces of ionic reactions in the absence of solvent molecules. A point of particular interest has been to determine the nature of the major energy barriers that limit the rate of motion along a reaction coordinate of interest. During the course of these investigations, however, it has also been found that gas-phase ion–molecule reactions carry with them additional complexities, not encountered in the solution phase, that can prevent accurate characterization of their reaction coordinates. These additional difficulties can be attributed to the following combination of factors. The potential energy surface of a given gas-phase IM reaction will be dominated by an electrostatic attraction energy that accompanies the initial approach of the reactant ion and neutral.[1] If the distribution of this association energy within the initially-formed ion complex is not fast relative to its continued motion along the reaction coordinate, then statistical reaction rate theories are not expected to apply. For a reaction system of this type, nonstatistical behavior cannot be avoided under low-pressure buffer gas conditions, where the ion complex is isolated and can only undergo intramolecular energy exchange during its lifetime.

Directly coupled to the problem described above is the fact that the well-established experimental methods for the study of IM reactions operate effectively only at low or moderate total pressures. For example, the ion cyclotron resonance (ICR) and Fourier transform (FT) mass spectrometers operate at pressures of less than about 10^{-5} Torr. In this pressure range, it can probably be assumed that most IM reactions will be in their low-pressure (LP) limit of kinetic behavior where the activated ion complexes suffer no collisions during their lifetimes. The flowing afterglow (FA), selected ion flow tube (SIFT), and pulsed e-beam high-pressure (PHP) mass spectrometers typically operate at pressures from 0.5 to 5 Torr. Over this moderate-pressure (MP) range, it is difficult to predict whether a given reaction system will be operating in its LP limit of kinetic behavior or in another region in which the ion complexes will be either partially or fully thermalized by collisions with buffer gas molecules prior to their continued motion along the reaction coordinate. If only partial thermalization of the ion complexes does indeed occur in the MP range, interpretation of these kinetic data might be expected to be even more difficult than that obtained in the LP range.

As Cacace[2] and Speranza[3] have previously pointed out, considerable simplifications in the interpretation of gas-phase kinetic data can be anticipated if an IM reaction of interest can be observed in its high-pressure (HP) limit of kinetic behavior, where all intermediate species along the reaction coordinate are efficiently thermalized by collisions with the buffer gas molecules prior to their continued motion along the reaction coordinate. In the HP limit, if the rate-limiting step of a slow gas-phase IM reaction is passage over the transition state of interest, theoretical analysis of the HP rate data requires knowledge of only the reactants and the single, rate-limiting transition state of interest. Conveniently, no specific knowledge of the reaction intermediates or other minor transition states along the reaction coordinate are then required. Unfortunately, the development of instrumental methods for the measurement of IM reactions under conditions of very high buffer gas pressures, where essentially any IM reaction of interest would be unambiguously forced into its HP limit of kinetic behavior, have received only a modest level of attention.[4-11]

For this reason, we have recently constructed an instrument called a kinetic ion mobility mass spectrometer (KIMMS) by

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(1) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977,** *99,* 4219.

(2) Cacace, F. *Science* **1990,** *250,* 392.

(3) Speranza, M. *Mass Spectrom. Rev.* **1992,** *11,* 73.

(4) Lee, F. W.; Collins, C. B.; Waller, R. A. *J. Chem. Phys.* **1976,** *65,* 1605.

(5) Collins, C. B.; Lee, F. W. *J. Chem. Phys.* **1978,** *68,* 1391.

(6) Collins, C. B.; Lee, F. W. *J. Chem. Phys.* **1979,** *71,* 184.

(7) Collins, C. B.; Lee, F. W. *J. Chem. Phys.* **1980,** *72,* 5381.

(8) Matsuoka, S.; Nakamura, H.; Tamura, T. *J. Chem. Phys.* **1981,** *75,* 681.

(9) Matsuoka, S.; Nakamura, H.; Takaaki, T. *J. Chem. Phys.* **1983,** *79,* 825.

(10) Matsuoka, S.; Nakamura, H. *J. Chem. Phys.* **1988,** *89,* 5663.

(11) Matsuoka, S.; Ikesoe, Y. *J. Phys. Chem.* **1988,** *92,* 1126.

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which IM reactions can be studied in a buffer gas of 1 atm of pressure.[12,13] This instrument has been shown to be capable of measuring both rate constants[12] and equilibrium constants[13] of ion–molecule reactions to a level of accuracy that compares favorably with that typically obtained with well-established methods of gas-phase ion chemistry that operate at 2 to several orders of magnitude lower pressure. In the present report, we describe the application of a temperature-variable KIMMS instrument to the study of a series of nucleophilic displacement S_N2 reactions between the chloride ion and three primary alkyl bromides (methyl, ethyl, and *n*-butyl bromide). Additional measurements of these reactions by PHPMS in 3 Torr of buffer gas are also reported here.

Several simple S_N2 reactions, including the reaction of Cl^- with MeBr,[1,14–18] have been extensively studied by others and have been shown to be particularly susceptible to nonstatistical behavior[19–24] of the general type referred to in the first paragraph above. Therefore, the present investigation offers an opportunity to obtain a clearer view of the S_N2 transition state of one of these dynamically complex ion–molecule reactions.

Experimental Section

Measurements by the KIMMS. The KIMMS apparatus and its application to the reactions of chloride ion with alkyl bromides at 125 °C have recently been described in detail.[12] For the present study, the only change in the KIMMS instrument has been to make it temperature-variable by the replacement of its original Tyndall ion gate with a Bradbury–Nielson (BN) ion gate. The BN gate is home-built and consists of a set of 40 equally-spaced, coplanar wires (alloy 46, California Fine Wire Co.) of 75-μm diameter, glued (#940 ceramic adhesive, Cotronics Corp., Brooklyn, NY) between two ceramic disks (machinable alumina, Coors, Golden, CO) of 1-in. i.d. Alternate wires are electrically connected so that a differential voltage of about 100 V across the 0.525-mm distance between adjacent wires prevents passage of all ions through the BN gate. This ion gate has proven to be much more rugged than the original Tyndall gate and has allowed variation of temperature at will, without misalignment and electrical shorting of the wires.

In our first description of the KIMMS instrument,[12] several different and mutually consistent methods of determining rate constants were described. In the present study, the method illustrated in Figures 8A and 9 of that report has been used. By this method, chloride ions are produced in the ion source by electron capture of CCl_4. A packet of these Cl^- ions is allowed to enter the drift region of the KIMMS by control of the BN ion gate. By adding an alkyl bromide to the drift gas, the S_N2 reaction of interest is made to occur throughout the length of the drift tube. The resulting ion mobility spectrum, as recorded by a Faraday plate and electrometer, is then analyzed under conditions of four or five different concentrations of the alkyl bromide, as previously described.[12] In order to determine the rate constant at each temperature, this procedure was repeated at least three times. The mass spectrometric function of the KIMMS was used to verify the identity of the reactant and product ions and to ensure that side reactions due to impurities were not important.

Measurements by the PHPMS. The pulsed e-beam high-pressure mass spectrometer (PHPMS) used in this study has also been previously described in detail.[25,26] It has been used in the present study for rate constant determinations in 3 Torr of methane buffer gas by the conventional pulsed mode of operation.[14,26] Typically, measurements of the Cl^- ion decay rate are made at a given temperature using five different concentrations of the neutral RBr reactant added to the buffer gas. The second-order rate constant is obtained from the slope of a plot of Cl^- ion decay rate versus RBr concentration.

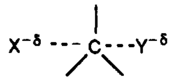
We have found that a significant systematic error is introduced into our PHPMS measurements by an enrichment of the alkyl bromide in the ion source that is caused by preferential diffusion of the lighter buffer gas molecules through the ion exit slit and electron entrance aperture. The magnitude of this effect cannot be easily predicted because the conditions within our source are intermediate between those of molecular and viscous flow. Therefore, we experimentally determined the magnitude of this enrichment by repeating every rate constant measurement in isobutane buffer gas at 3 Torr of pressure. Due to the greater molecular weight of this buffer gas, the enrichment of RBr in isobutane is less than in methane buffer gas and, accordingly, the apparent rate constants were consistently about 30% smaller in 3 Torr of isobutane relative to those observed in 3 Torr of methane. Analysis of all kinetic measurements in both buffer gases led to the conclusion that the true rate constant, k_{obs}, can be obtained from the apparent rate constants, k_{obs}', in either buffer gas at 3 Torr by the following relationship, $k_{obs} = k_{obs}'(MW_{BG}/MW_{RBr})^{1/5}$. Thus, for example, the values of k_{obs} reported here for the Cl^-/MeBr reaction system in methane at 3 Torr have been obtained by multiplication of k_{obs}' by 0.70. These were consistent with those obtained in isobutane multiplied by 0.91. A more comprehensive study of this PHPMS enrichment problem is presently underway in our laboratory in which well-characterized fast IM reactions of fluoride ion[27] with various alkyl halides (such as methyl bromide and methyl iodide) are being observed under varying conditions of the ion source. The results of this study (to be reported separately) have provided additional support for the validity of the correction factors used here.

Results and Discussion

The S_N2 family of reactions has been among the most widely studied of all the elementary chemical processes, in both the solution[28] and gas[17] phases. These reactions, symbolized by reaction 1,occur through backside attack by a nucleophile, X^-,

$$X^- + RY \xrightarrow{\ddagger} RX + Y^- \qquad (1)$$

at the α-carbon atom of a substrate molecule, RY, resulting in the displacement of a leaving group, Y^-. The transition state (‡) for this reaction is thought to be a species in which an X–C bond has been partially formed while the C–Y bond has been weakened, as illustrated by structure I. For the three reaction systems studies here, the possibility that another mechanism, elimination, is competitive with their S_N2 displacement reactions can be discounted due to the significant endothermicity of the elimination reaction for these systems.[17]



I

Reaction of Cl^- with MeBr. In gas-phase investigations of S_N2 reactions, the rate constants will contain information concerning the transition state only if the systems chosen for study are sufficiently slow so that the observed rate constants are not determined simply by the frequency of collisions between the two reactants.[17] The reactions of chloride ion with simple alkyl bromides meet this criteria since their rate constants show rates approximately 2 orders of magnitude slower than the collision rates. In previous studies of the reaction of Cl^- with MeBr, two different ion complexes have been suggested to exist along the reaction coordinate,[1,17] as shown in reaction 2. The potential

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(12) Giles, K.; Grimsrud, E. *J. Phys. Chem.* **1992**, *96*, 6680.

(13) Giles, K.; Grimsrud, E. P. *J. Phys. Chem.* **1993**, *97*, 1318.

(14) Caldwell, G.; Magnera, T. F.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 959.

(15) Tanaka, K.; Mackay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643.

(16) Bohme, D. K.; Raksit, A. B. *Can. J. Chem.* **1985**, *63*, 3007.

(17) DePuy, C. H.; Gronert, S.; Mullin, A.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1990**, *112*, 8650.

(18) Gronert, S.; DePuy, C.; Bierbaum, V. *J. Am. Chem. Soc.* **1991**, *113*, 4009.

(19) Vande Linde, S. R.; Hase, W. L. *J. Phys. Chem.* **1990**, *94*, 6148.

(20) Vande Linde, S. R.; Hase, W. L. *J. Phys. Chem.* **1990**, *94*, 2778.

(21) Vande Linde, S. R.; Hase, W. L. *J. Phys. Chem.* **1990**, *93*, 7962.

(22) Vande Linde, S. R.; Hase, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 2349.

(23) Graul, S. T.; Bowers, M. T. *J. Am. Chem. Soc.* **1991**, *113*, 9696.

(24) Viggiano, A. A.; Morris, R. A.; Paschkewitz, J. S.; Paulson, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 10477.

(25) Knighton, W. B.; Zook, D. R.; Grimsrud, E. P. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 372.

(26) Knighton, W. B.; Grimsrud, E. P. *J. Am. Chem. Soc.* **1992**, *114*, 2336.

(27) Su, T.; Morris, R. A.; Viggiano, A. A.; Paulson, J. F. *J. Phys. Chem.* **1990**, *94*, 8426.

(28) Streitwieser, A. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962.

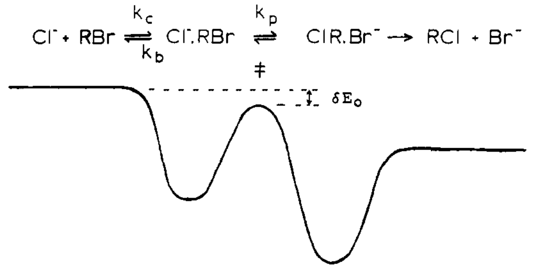

Figure 1. Schematic reaction coordinate diagram for the S_N2 nucleophilic displacement reaction of Cl^- with an alkyl bromide in the gas phase. δE_0 is the energy of the transition state relative to that of the reactants. For the case R = Me, the depth of the first well is thought to be about 10 kcal/mol and the overall reaction exothermicity is thought to be about 6 kcal/mol.[23]

$$Cl^- + MeBr \underset{k_b}{\overset{k_c}{\rightleftharpoons}} \underset{A}{(Cl^-{\cdot}MeBr)} \overset{k_p}{\rightleftharpoons} \underset{B}{(MeCl{\cdot}Br^-)} \rightarrow Br^- + MeCl \qquad (2)$$

energy surface for this reaction is thought to resemble that shown in Figure 1 where the S_N2 transition state of interest (‡) separates the two ion complexes and has an energy somewhat lower than the energy of the reactants.[1,14] After a successful collision of a Cl^- ion and a MeBr molecule (with collision rate constant k_c), the entrance-channel intermediate, A = ($Cl^-{\cdot}$MeBr), is initially formed with a total energy equal to the sum of the thermal energies of the reactants and the enthalpy of the ion–molecule association reaction. This chemically-activated form of the intermediate will be designated as A*.

In the low-pressure (LP) limit of kinetic behavior, A* will remain chemically activated until it either back-dissociates (k_b) to re-form the reactants or undergoes S_N2 inversion (k_p) to form a chemically-activated exit-channel intermediate, B* = ($RCl{\cdot}Br^-$)*. While the S_N2 transition state of interest provides the barrier to forward motion of A*, a second transition state, commonly called the centrifugal barrier,[1] provides an energy barrier for back-dissociation of A*. Once formed, the exit-channel intermediate, B*, can then either move forward to form the final products, RCl and Br^-, or move backward by recrossing the transition-state barrier to reform A*. Assuming that the final products in reaction 2 are stable against back-reaction, the overall observed rate constant, k_{obs}, for reaction 2 will be given by eq 3, where f is the

$$k_{obs} = k_c k_p f/(k_b + k_p) \qquad (3)$$

transmission coefficient[29] and is equal to the fraction of the initial transition-state crossings that successfully lead to final products. While f is often assumed to be unity, recent calculations[19-22] of the Cl^-/MeCl gas-phase S_N2 reaction indicated that f would be less than unity for that system.

In the HP limit of kinetic behavior, both the entrance- and exit-channel intermediates would be envisioned to be efficiently thermalized (that is, A* → A and B* → B) immediately upon their creation and prior to their continued motion along the reaction coordinate. The overall rate constant, k_{obs}, in the HP limit will again be given by eq 3. However, since the micro rate constants, k_b and k_p, can be expected to be different in the LP and HP limits, k_{obs} would also be expected to be different. It is conceivable that the transmission coefficient, f, might also be altered somewhat by a large change in pressure.

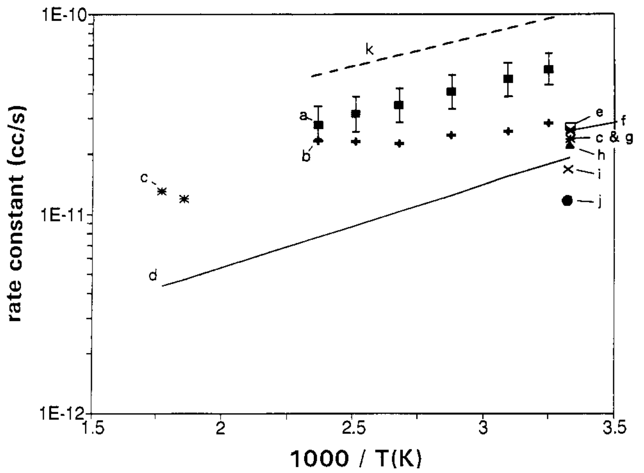

Figure 2. Rate constants observed for the reaction of Cl^- with MeBr under a variety of different temperature and pressure conditions. (a) The present KIMMS measurements at 640 Torr and (b) the present PHPMS measurements at 3 Torr have been plotted in the Arrhenius form. Error bars indicate the estimated uncertainties of the KIMMS measurements (±20%). The estimated uncertainties of the present PHPMS measurements are also ±20%. The Arrhenius parameters thereby determined are listed in Table I. Also shown are previous measurements of this reaction system by the following techniques and pressures: (c) SIFT[24] at 0.5 Torr, (d) PHPMS[14] at 4 Torr, (e) SIFT[18] at 0.5 Torr, (f) FTMS[30] at <10^{-5} Torr, (g) SIFT[17] at 0.5 Torr, (h) FA[15] at 0.5 Torr, (i) FA[16] at 0.5 Torr, and (j) ICR[1] at <10^{-5} Torr. The dashed line (k) provides a theoretical prediction for the rate constants in the HP limit of kinetic behavior (see eq 5 and accompanying text).

In Figure 2 all present rate measurements for the reaction of Cl^- with MeBr are shown along with numerous previous measurements of this reaction system by others. If the measurements near room temperature ($1000/T \approx 3.3$) are considered first, it is seen that the present PHPMS measurements in 3 Torr of methane are in good to excellent agreement with all of the measurements previously reported for this system at 4 Torr or lower pressures. For example, it is seen that three recent SIFT measurements at about 0.5 Torr (17, 18, 24), one FA measurement at 0.5 Torr,[15] and one FTMS measurement at less than 10^{-5} Torr[30] are in near-perfect agreement with the present PHPMS measurements. Two other measurements, one by the PHPMS at 4 Torr[14] and another by the FA at 0.5 Torr,[16] are only about 50% lower than the present PHPMS measurements. The earliest measurement of this rate constant by ICR below 10^{-5} Torr[1] is a factor of 2 lower than the present PHPMS measurements. If the rate constants at elevated temperatures in Figure 2 are considered, it is seen that the present PHPMS measurements at 3 Torr are in good agreement with those recently reported by Viggiano *et al.*[24] by the SIFT at 0.5 Torr, but are significantly larger than those reported by Caldwell *et al.*[14] by the PHPMS at 4 Torr. In both the present study and that of Viggiano,[24] the rate constant measurements for this reaction were repeated many times in order to determine if experimental errors were leading to values higher than those reported by Caldwell at elevated temperatures. No such errors were found in either the present study or that of Viggiano, and we can offer no satisfactory explanation at this time for the discrepancy between these two sets of measurements and that of Caldwell *et al.* for the reaction of Cl^- and CH_3Br at high temperatures. Nevertheless, in the ensuing discussions, it will be tentatively assumed that the two sets of coinciding measurements (the present set and that of Viggiano) provide the more accurate indication of the temperature dependence of this reaction system in the 0.5–4-Torr pressure range.

The present KIMMS measurements for the reaction of Cl^- with MeBr in 640 Torr of nitrogen buffer gas are also shown in Figure 2. It is seen that these measurements are significantly greater than those determined at lower pressures. The effect of elevated pressure is particularly clear near room temperature, where the present measurements at 640 Torr are at least 2 times

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(29) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanisms*; John Wiley and Sons, Inc.: New York, 1953; p 94.

(30) Ingemann, S.; Nibbering, N. M. M. *Can. J. Chem.* **1984**, *62*, 2273.

greater than all present and previous measurements obtained at pressures less than 4 Torr. In addition, the magnitude of the inverse temperature dependence of k_{obs} is significantly greater for the KIMMS measurements at 640 Torr than for the present measurements by PHPMS at 3 Torr or by the SIFT[24] at 0.5 Torr. These data suggest that this reaction system is altered away from the LP limit of kinetic behavior and toward the HP limit by the change in the buffer gas pressure from 3 to 640 Torr.

In principle, all rate constants and temperature dependencies of rate constants shown in Figure 2 contain information concerning the energy of the S_N2 transition state for the $Cl^-/MeBr$ reaction. However, it presently seems unlikely that the rate constants in Figure 2 that were obtained at pressures lower than 4 Torr could be reliably used for accurate characterizations of the transition state. The reasons for this are summarized in the following paragraph.

Several recent experimental and theoretical studies have shown that the intermediate ion complexes involved in simple S_N2 reactions can behave in a nonstatistical manner. Viggiano *et al.*[24] observed that the rate constant for the reaction of Cl^- with MeBr decreases with increased relative kinetic energy of the reactants, but is not affected by increased internal energy of the neutral reactant, MeBr. This suggests inefficient energy transfer between the internal modes of $(Cl^-{\cdot}MeBr)^*$. In addition, Graul and Bowers[23] have found that the kinetic energy imparted to the Br^- ion upon the unimolecular decomposition of $(Cl^-{\cdot}MeBr)^*$ is much less than predicted by statistical phase space theory. This implies that the neutral product of this decomposition, MeCl, is formed in an internally excited state and that the internal energy within the complex was not randomly distributed prior to its decomposition. Also, recent calculations by Vande Linde and Hase[19-22] for the symmetric S_N2 reaction $Cl^-_a + MeCl_b \rightarrow MeCl_a + Cl^-_b$ predict nonstatistical energy distributions within $(Cl^-{\cdot}MeCl)^*$ ion complexes. In these studies, it was predicted that, during the lifetime of the ion complex, very little energy leaks into the internal modes that are associated with forward motion over the S_N2 transition state. In view of these complexities, it appears that the statistical theoretical methods that are presently used for treatment of gas-phase kinetic data would not be expected to lead to an accurate characterization of the transition state for the $Cl^-/MeBr$ system from the kinetic data in Figure 2 that was determined at 4 Torr or lower pressures. In addition, it is possible that the measurements by PHPMS and SIFT in Figure 2 do not strictly represent LP kinetic behavior, since in the low-Torr pressure range it is possible that partial stabilization of the entrance- and exit-channel intermediates is occurring through collisions.

The KIMMS measurements in Figure 2 suggest that the $Cl^-/MeBr$ reaction has been moved toward the HP limit of kinetic behavior by use of 640 Torr of buffer gas. It is not clear, however, whether this reaction system has actually reached the HP limit at 640 Torr or is still in the intermediate MP range of kinetic behavior. In order to experimentally address this question, it would be useful to be able to measure its rate constants at pressures even greater than 640 Torr. While this extended capability of the KIMMS is anticipated, it is not yet available. However, some insight concerning this question can be found in recent calculations by Vande Linde and Hase[19-22] of the kinetic behavior of the closely related ion complex $(Cl^-{\cdot}MeCl)^*$. They predict that, if this complex is formed by collisions at about 300 K, it will have an average lifetime against back-dissociation of approximately 6 ps. Since the time between collisions for an ion in nitrogen buffer gas at 640 Torr of pressure is about 50 ps, these calculations predict that the $Cl^-/MeCl$ reaction system would be near, but not quite within, the HP limit of behavior at a pressure of 640 Torr. However, recent additional calculations by Hase and coworkers[31] of the $Cl^-/MeBr$ reaction system also indicate that the lifetime of the $(Cl^-{\cdot}MeBr)^*$ complex against back-dissociation will be somewhat greater than that of $(Cl^-{\cdot}MeCl)^*$ at 300 K and this would place the $Cl^-/MeBr$ system nearer and possibly within the threshold of the HP limit of kinetic behavior. Therefore, in the present report, it will be tentatively assumed that the KIMMS measurements in Figure 2 represent kinetic behavior of the HP limit for this reaction system and we will proceed accordingly with the determination of the energy of the S_N2 transition state for the $Cl^-/MeBr$ reaction from these KIMMS data.

In the HP limit for reaction 2, all species along the reaction coordinate will be in thermal equilibrium with the buffer gas. Since k_{obs} is about 2 orders of magnitude smaller than the collision rate, k_b is much greater than k_p and the rate-determining step is passage over the S_N2 transition state, k_p. Under these conditions, conventional transition-state theory (TST) and eq 4 should apply.[14]

$$k_{TST} = f(kT/h)(Q_\ddagger/Q_{Cl^-}Q_{MeBr}) \exp(-\delta E_0/RT) \quad (4)$$

By this equation, the rate constant is determined by the transmission coefficient, f, by the partition functions, Q_i, of the reactants and envisioned transition state, and by the energy of the transition state, δE_0. Note that no knowledge of the intermediate ion complex or of the centrifugal barrier is required. Partial evaluation[32] of eq 4 leads to eq 5, where k_{TST} has units of

$$k_{TST} = (8.5 \times 10^{-13}) f T^{-1/2} (I_\ddagger/I_{MeBr})(Q^v_\ddagger/Q^v_{MeBr}) \exp(-\delta E_0/RT) \quad (5)$$

$cm^3\ s^{-1}$, I_i are the moments of inertia (for rotation about the transverse axis) of the TS and MeBr, and Q^v_i are the vibrational partition functions for the TS and MeBr in which the vibration corresponding the motion along the reaction coordinate has been removed from $Q^v_\ddagger$. Because $I_\ddagger$ and $Q^v_\ddagger$ must be estimated from assumed models of the TS and the value of f is unknown, considerable uncertainty would accompany a determination of δE_0 by eq 5 from a single rate constant measurement. A superior determination of δE_0 can be obtained from the temperature dependence of the KIMMS rate constants since the T dependence of k_{TST} can be assumed to be independent of both f and $I_\ddagger$ and will depend only on the low-frequency contributions to $Q^v_\ddagger$. The vibrational frequencies to be used here are the set previously assumed by Olmstead and Brauman[1] for the $Cl^-/MeBr$ system in which the three new low-frequency vibrations of the TS (two bend and one symmetric stretch vibrations of $Cl{-}CH_3{-}Br$) are all assumed to be 200 cm^{-1}. Using these parameters, the preexponential portion of eq 5 is found to have a temperature dependence over the range 35–150 °C that when expressed in the form $\exp(-\alpha/RT)$ is given by $\alpha = 0.8$ kcal/mol. Therefore, the temperature-dependent and -independent contributions to k_{TST} in eq 5 can be separated into the Arrhenius form given by eq 6, in

$$k_{TST} = A \exp(-E_a/RT) \quad (6)$$

which $E_a = (0.8\ \text{kcal/mol} + \delta E_0)$. From the slope of the plot of $\log k_{obs}$ versus $1/T$ for the KIMMS measurement (Figure 2), an experimental Arrhenius activation energy $E_a = -1.4$ kcal/mol is obtained. Therefore, δE_0 is determined from the measured temperature dependence by $\delta E_0 = E_a - 0.8\ \text{kcal/mol} = -2.2$ kcal/mol.

Also shown in Figure 2 is the prediction for the absolute magnitudes of k_{TST} over the temperature range 35–150 °C as calculated from eq 5. For these calculations, f has been set to unity, δE_0 has been set equal to -2.2 kcal/mol, Q^v_i were again calculated from frequencies provided by Olmstead and Brauman,

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(31) Wang, H.; Zhu, L.; Hase, W. L. *J. Phys. Chem.*, submitted for publication.

(32) Skinner, G. B. *Introduction to Chemical Kinetics*; Academic Press: New York, 1974; Chapter 3.

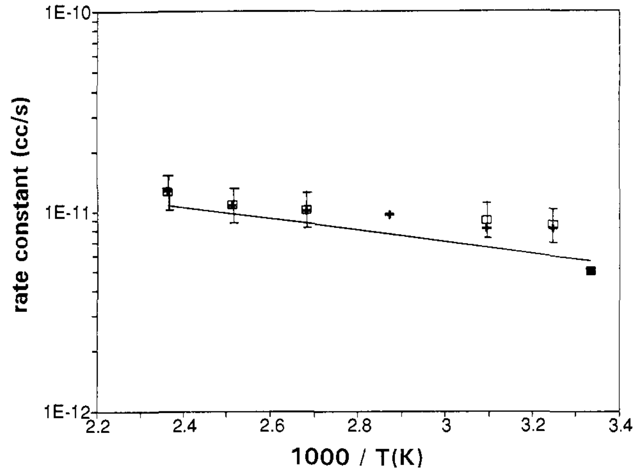

Figure 3. Arrhenius plots of the rate constants for the reaction of Cl^- with EtBr obtained by the KIMMS (□) at 640 Torr and the PHPMS (+) at 3 Torr. Arrhenius parameters obtained are listed in Table I. The solid line represents rate constants for this system previously reported by Caldwell *et al.*[14] using the PHPMS at 4 Torr. The solid square (■) is a room temperature measurement by Gronert *et al.*[18] using the SIFT at 0.5 Torr. Estimated uncertainties of present KIMMS and PHPMS measurements are ±20%, as indicated by error bars included with KIMMS results.

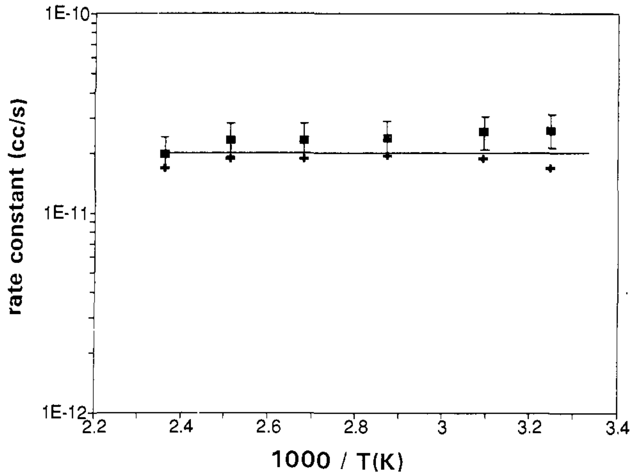

Figure 4. Arrhenius plots of the rate constants for the reaction of Cl^- with *n*-BuBr obtained by the KIMMS (■) at 640 Torr and the PHPMS (+) at 3 Torr. Arrhenius parameters obtained are listed in Table I. The solid line represents rate constants for this system previously reported by Caldwell *et al.*[14] using PHPMS at 4 Torr. Estimated uncertainties of present KIMMS and PHPMS measurements are ±20%, as indicated by error bars included with KIMMS results.

I_{MeBr} was set equal to 53 amu A^2, and $I_{\ddagger}$ was assumed to be 580 amu A^2, a value obtained by assuming that the Cl–C and C–Br bond lengths in the TS will be about 30% greater than in MeCl and MeBr.[20] It is seen that these estimates for k_{TST} are in good agreement with the experimental values determined at atmospheric pressure. By changing the assumed value of f in eq 5 from 1.0 to 0.5 (in view of recent calculations for the closely related Cl^-/MeCl reaction system,[19-22] a value of f less than unity is plausible), the predictions of k_{TST} would be halved and thereby become essentially identical to the KIMMS measurements at all temperatures. Given the accumulated uncertainties in the individual terms in eq 5, however, the near-perfect agreement between TST theory with f set to 0.5 and the KIMMS results is presently considered to be fortuitous.

Reactions of Cl^- with EtBr and *n*-BuBr. Rate constants determined by the PHPMS at 3 Torr and by the KIMMS at 640 Torr for the reactions of chloride ion with ethyl bromide and with *n*-butyl bromide over the temperature range 35–150 °C are shown in Figures 3 and 4, respectively. For both of these reactions, it is seen that the measurements at 640 Torr do not differ significantly from those obtained at 3 Torr. In addition, the present measurements for both of these reaction systems are in good agreement with those of Caldwell *et al.*[14] by PHPMS at 4 Torr. A slight positive temperature dependence is indicated in Figure 3 for all of the measurements of the Cl^-/EtBr reaction, and a slight negative temperature dependence is indicated in Figure 4 for the Cl^-/*n*-BuBr reaction.

An interesting question raised by the data in Figures 3 and 4 is why the rate constants for the reactions of Cl^- with EtBr and *n*-BuBr are not significantly affected by the pressure change from 3 to 640 Torr as were the rate constants in Figure 2 for the corresponding reaction of MeBr. A likely explanation seems to be that these reaction systems are operating in their HP kinetic limits at 3 Torr, as well as at 640 Torr of total pressure. This explanation is feasible if the lifetime of the activated entrance-channel intermediate, $(Cl^-{\cdot}RBr)^*$, against motion along the reaction coordinate is significantly greater for the cases of R = Et and *n*-Bu than for R = Me, due to their increased sizes and greater number of internal modes for energy distribution. The larger ion complexes for the cases R = Et and *n*-Bu might then become efficiently thermalized by collisions prior to their further motion along the reaction coordinate at 3 Torr, as well as at 640 Torr of total pressure. In order to test this hypothesis further, it would be useful to compare the results in Figures 3 and 4 with those obtained by FTMS or ICR, which would reflect the behavior of this system in the LP range. Unfortunately, the reactions of Cl^- with EtBr and *n*-BuBr have not been reported by these methods, to our knowledge. However, support for this explanation can be found in the previous study by Caldwell *et al.*[14] They reported that the clustering reaction in eq 7could be brought into

$$\mathrm{Cl^- + RBr \rightleftharpoons Cl^-{\cdot}RBr} \qquad (7)$$

a state of chemical equilibrium within the PHPMS ion source at 4 Torr of pressure and at room temperature for the cases of R = Et and n-Bu, but not for the case of R = Me. They attributed this result to the longer $(Cl^-{\cdot}RBr)^*$ lifetimes for the cases of R = Et and n-Bu relative to that of R = Me.

It seems reasonable to assume that the KIMMS measurements of the EtBr and *n*-BuBr systems in Figures 3 and 4 represent the HP limit of kinetic behavior for these reactions. The Arrhenius activation energies, determined from these KIMMS measurements, are +0.8 kcal/mol for the Cl^-/EtBr reaction and –0.5 kcal/mol for the Cl^-/*n*-BuBr reaction. The energy of the S_N2 transition states for these reactions can be obtained from these E_a values and the equations of TST in the same manner as described above for the Cl^-/MeBr system. Calculations of α for the Cl^-/*n*-BuBr system using the vibrational frequencies assumed previously for this system by Olmstead and Brauman[1] again lead to α = 0.8 kcal/mol, as for the Cl^-/MeBr system above. This is primarily because three new vibrational modes of $\bar{\nu} \approx 200$ cm^{-1} are again envisioned to be created in the Cl^-/*n*-BuBr TS.[1] Therefore, the TS energy for the Cl^-/*n*-BuBr reaction is $\delta E_0 = E_a - \alpha = -1.3$ kcal/mol. If it is assumed that α is also equal to 0.8 kcal/mol for the Cl^-/EtBr system, δE_0 for the TS of this reaction is equal to 0.0 kcal/mol. Since the PHPMS measurements of the Cl^-/EtBr and Cl^-/*n*-BuBr systems in Figures 3 and 4 are also thought to represent HP kinetic behavior, the Arrhenius and TS energies determined from these PHPMS measurements are also listed in Table I and are seen to be in good agreement with the corresponding measurements by the KIMMS.

Conclusions

It has been demonstrated here that new insight concerning dynamically complex gas-phase ion–molecule reactions can be gained by their kinetic study at greatly elevated pressures. It has

Table I. Values from Arrhenius Plots[a] of Rate Constants $k = A \exp(-E_a/RT)$ for Gas-Phase Reactions $Cl^- + RBr \rightarrow RCl + Br^-$

RBr	pressure[b]	$-\log A$[c]	E_a[d]	δE_0[e]
MeBr	640	11.23	−1.4	−2.2
	3	10.90	−0.5	
EtBr	640	10.52	+0.8	0.0
	3	10.43	+1.0	+0.2
n-BuBr	640	10.95	−0.5	−1.3
	3	10.87	−0.3	−1.1

[a] Shown in Figures 2–4. [b] Experiments at 640 Torr performed by KIMMS, and at 3 Torr, by PHPMS. [c] Units of A are cm^3/s. [d] kcal/mol. [e] δE_0 is defined in Figure 1 and is obtained from $\delta E_0 = E_a - 0.8$ kcal.

been shown that the rate constants and temperature dependence of the rate constants for the reaction of Cl^- with MeBr are significantly different when measured in a buffer gas of 640 versus 3 Torr of pressure. Due to nonstatistical behavior previously reported for the Cl^-/MeBr reaction system when observed under conditions of low buffer gas pressure, the present measurements at elevated pressure appear to offer a superior means of determining the energy of the S_N2 transition state for this reaction. Under the tentative assumption that the Cl^-/MeBr reaction system is within its high-pressure limit of kinetic behavior at 640 Torr, the present KIMMS measurements indicate that the S_N2 transition state for this reaction lies 2.2 kcal/mol below the energy of the reactants. Corresponding KIMMS measurements of the reactions of Cl^- with EtBr and with *n*-BuBr indicate that the transition states for these reactions lie 0.0 and 1.3 kcal/mol, respectively, below the energy of the reactants.

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