Rate Constants for the Gas Phase Reaction of Chloride Ion with Methyl Bromide over the Pressure Range 300 to 1100 Torr

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Rate constants for the reaction of chloride ion with methyl bromide have been determined over a range of buffer gas pressures from 300 to 1100 Torr at 125 °C by ion mobility spectrometry (IMS). The rate constants were found to increase slightly with increased pressure over this range and also increased slightly with a change from nitrogen to methane buffer gas. Parallel measurements for the reaction of chloride ion with *n*-butyl bromide indicated no dependence of the observed rate constants on changes in the pressure or identity of the buffer gas, as expected. The present measurements indicate that the high-pressure limit (HPL) of kinetic behavior is not achieved for the Cl^-/CH_3Br reaction system by use of buffer gases in the near-atmospheric pressure range and are consistent with a recent suggestion by Seeley et al. that this reaction should occur with near-collision frequency in its high-pressure limit.

Introduction

The gas-phase S_N2 reaction of chloride ion with methyl bromide has been extensively studied by a variety of experimental and theoretical methods[1−16] and has become the prototype example of an ion−molecule reaction that is strongly affected by nonstatistical energy distributions within its rate-determining reaction intermediates.[6,10,13,14,16] This reaction is thought to proceed along a double-well potential energy surface with a central barrier that separates the entrance and exit channel ion complexes. Both of these reaction complexes have been shown to behave in distinctly nonstatistical manners and, therefore, are not well-described by conventional statistical theories of reaction rates, such as RRKM theory.[13,14,16] As a result, the rate constants observed for this S_N2 reaction have been difficult to interpret in terms of the potential energy surface for this reaction.

To study this reaction under physical conditions in which the complexities described above would be removed, the use of unusually high buffer gas pressure has been envisioned.[11,12,17] If the buffer gas pressure could be made sufficiently high, a point should eventually be reached where all reaction intermediates would be continuously maintained in a state of thermal equilibrium with the medium during their lifetimes on the reaction coordinates. Under this condition, known as the high-pressure limit (HPL) of kinetic behavior, the reaction complexes could be assumed to have Boltzmann energy distributions and interpretation of the observed rate constants would thereby be greatly facilitated.

In a recent study in our laboratory[12] of the reaction of Cl^- ion with CH_3Br by ion mobility spectrometry (IMS), we reported rate constants observed under the relatively high-pressure conditions of 640 Torr (nitrogen buffer gas) over a range of temperatures from 35 to 150 °C. A significant enhancement (roughly, a doubling) of the observed rate constants was noted at 640 Torr at all temperatures relative to the corresponding rate constants determined by a pulsed high-pressure mass spectrometer (PHPMS) using buffer gas pressures of 3 Torr. At 640 Torr, the efficiency (observed rate constant relative to the calculated ADO collision rate constants) of this reaction increased continuously with a decrease in temperature, from about 1.5% at 150 °C to about 3.5% at 35 °C. In interpreting the significance of these rate constants at near-atmospheric pressure, an unresolved question was whether or not these measurements reflected the HPL of kinetic behavior for the Cl^-/CH_3Br reaction system.

Recent theoretical studies of the $Cl^-(CH_3Br)$ and $Br^-(CH_3Cl)$ reaction complexes by Wang et al.[14] have provided additional insight concerning the question raised above. They predicted distinctly nonstatistical behaviors and exceedingly short lifetimes for both the entrance- and exit-channel complexes. From inspection of the set of mode-specific lifetimes they provided, the average lifetimes of the collision-formed complexes, $Cl^-(CH_3Br)$, might be expected to be even less than the calculated RRKM lifetime of 3 ps. Since the time between collisions of this ion complex with buffer gas molecules at near-atmosphere pressure will be about 50 ps, the theoretical considerations of Wang et al. suggest that the HPL for this reaction could not have been reached in a buffer gas of 640 Torr pressure.

Recent experimental studies of the Cl^-/CH_3Br reaction by Seeley et al.[18] also provide new insight concerning this reaction. They found that when the entrance-channel reaction complex, $Cl^-(CH_3Br)$, was made by the endothermic ligand exchange reaction, $Cl^-(H_2O) + CH_3Br \rightarrow Cl^-(CH_3Br) + H_2O$, in He buffer gas at a pressure of 0.5 Torr, this complex then thermally dissociates primarily in the forward direction to form the Br^- ion and CH_3Cl. Since the observed reaction efficiencies in our previous studies in 640 Torr buffer gas did not exceed 3.5%, the result of Seeley et al. suggests that the entrance channel complexes were not efficiently thermalized by collisions and the HPL had not been reached in our previous study of this reaction[12] using 640 Torr nitrogen buffer gas.

We have recently modified our IMS instrument so that the buffer gas pressure can now be varied from roughly one-half to twice that of local atmospheric pressure, 640 Torr. In the present study, these improvements have enabled us to determine rate constants for the reaction of Cl^- with CH_3Br over the pressure range of 300−1100 Torr at 125 °C. Additional insight into the dynamics of this reaction has thereby been obtained.

Experimental Section

The IMS instrument and the experimental methods used here are almost identical with those used in previous studies in our

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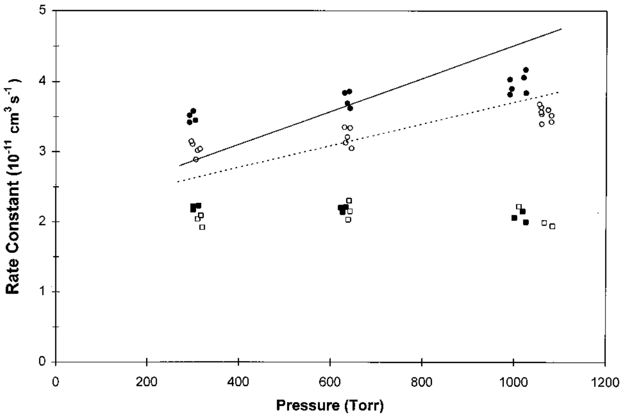

Figure 1. Rate constants observed for the reaction of chloride ion with methyl bromide (circles) and with *n*-butyl bromide (squares) by ion mobility spectrometry at 125 °C as a function of buffer gas pressure. Measurements were made using both nitrogen (open circles and open squares) and methane (solid circles and solid squares) as the buffer gas. The two lines shown are predictions for the pressure dependence of the rate constants for methane (solid line) and nitrogen (dashed line) buffer gases obtained from eq 3 and a simplified model of this reaction.

laboratory of the reactions of chloride ion with methyl bromide and *n*-butyl bromide in nitrogen buffer at 640 Torr.[11,12] In the present study, the only experimental change that has been made is that the buffer gas pressure within the IMS was varied from 300 to 1100 Torr. To accomplish this, the following additions were made to the IMS instrument shown in Figure 1 of ref 11. A mass flow controller (MKS, Type 1179A) replaced the flow meter (f) and leak valve (w). This provided an accurate delivery of buffer gas flow into the IMS that was independent of the pressure selected within the IMS tube. For operation at pressures above the ambient level a stainless steel capillary of 0.76 mm i.d. and 4.5 m length was placed in the gas exit flow line immediately after the pressure transducer (g). A 10 psi safety relieve value (Parker Instruments) was also placed at this point. For operation at pressures below the ambient level, a metering valve (Swagelock) and a mechanical pump were placed immediately after the pressure transducer (g). To eliminate electrical discharges that occurred within the IMS whenever subambient pressures were used, all high-voltage feedthroughs had to be changed to ones rated to 15 kV (Ceramaseal). For successful operation at pressures below the ambient level, much greater care was required to eliminate all microscopic leaks in all external connections of the IMS. The major difficulty caused by such leaks was the introduction of trace levels of water, which tends to cluster to the chloride ion. To ensure that this undesirable effect of trace water was not of importance, a relatively high temperature, 125 °C, was always used in the present study. At this temperature, the ratio of the intensity of the $Cl^-(H_2O)$ ion to that of the Cl^- ion (as determined by an associated mass spectrometer) was always less than 0.005.

Results and Discussion

Rate constant determinations made here for the reaction of chloride ion with methyl bromide and with *n*-butyl bromide are shown in Figure 1. Each point shown has been determined by the standard IMS method illustrated in Figure 9 of ref 11 and is the result of four or more independent IMS measurements using a range of alkyl bromide concentrations. Based on the combined uncertainties of each of the parameters that determine the magnitude of an observed rate constant,[11] the estimated uncertainty of each rate constant measurement is about 15%.

The rate constants determined for the reaction of chloride ion with *n*-butyl bromide are shown in Figure 1 (square data points) and bear no detectable dependence on buffer gas pressure over the pressure range of 300−1100 Torr. Also, these rate constants were not significantly affected by a change from nitrogen (open squares) to methane (solid squares) buffer gas. This result was expected based on our prior observation that a change in buffer gas pressure from 3 Torr (PHPMS) to 640 Torr (IMS) caused no observable change in the rate constant of this reaction (see Figure 4 of ref 12). This lack of buffer gas pressure dependence for the chloride/*n*-butyl bromide reaction system is consistent with either of two potential explanations. One is that this reaction system is operating within its HPL of kinetic behavior at all pressures of 3 Torr or greater. The other is that the rate constants for this reaction system happen to be the same in the high-pressure and low-pressure limits. A third possibility is that a completely different E2 elimination reaction is operative for the chloride/*n*-butyl bromide reaction system. This does not seem likely, however, in view of the fact that this E2 reaction would be endothermic by about 10 kcal/mol.[5] Since the present investigation will focus on the Cl^-/CH_3Br reaction, the set of *n*-butyl bromide measurements provided in Figure 1 serves here primarily to validate the present experimental method. By this method, no significant pressure dependence was noted for a reaction system that was expected to have none, based on the previous rate constant measurements using 3 and 640 Torr buffer gas pressures.

The rate constants for the reactions of chloride ion with methyl bromide are shown in Figure 1 (circles) and indicate a small but significant positive pressure dependence. An increase in the pressure of a given buffer gas from about 300 to 1100 Torr causes an increase in the rate constant of about 15%. In addition, it is noted that a change from nitrogen (open circles) to methane (solid circles) buffer gas also causes an increase of about 15% in the rate constant. Both of these observations suggest that the HPL of kinetic behavior has not been reached for the Cl^-/CH_3Br reaction system in the pressure range near 1 atm.

It is instructive to consider whether the measurements shown in Figure 1 for the Cl^-/CH_3Br reaction system are consistent with the new information concerning this reaction recently reported by Wang et al.[14] and by Seeley et al.[18] (see Introduction). A somewhat more detailed view of the reaction under consideration is provided by reaction sequence 1:

$$\begin{aligned} \mathrm{Cl^-} + \mathrm{CH_3Br} &\underset{k_r}{\overset{k_c}{\rightleftharpoons}} \mathrm{Cl^-(CH_3Br)^*} \xrightarrow{k_p} \mathrm{Br^-} + \mathrm{CH_3Cl} \\ &\underset{k_r}{\overset{k_c}{\rightleftharpoons}} \mathrm{Cl^-(CH_3Br)^*} \xrightarrow{k_q[\mathrm{B}]} \mathrm{Cl^-(CH_3Br)} \rightarrow \\ &\qquad \mathrm{Br^-} + \mathrm{CH_3Cl} \end{aligned} \tag{1}$$

By this sequence, reaction products are envisioned to be formed by two simultaneously operative mechanisms. In both mechanisms, a set of excited entrance channel complexes is first formed at a rate determined by the collisional rate constant k_c. Since the efficiency of this reaction under the present reaction conditions has been observed to be low, it can be assumed that most of the complexes will backdissociate to reform the reactants (k_r). A small fraction of the excited complexes will move forward to form products (k_p). Another small fraction of the excited complexes will undergo collisions with buffer gas molecules and will become thermalized with a pseudo-first-order rate constant for quenching, $k_q[B]$, where [B] is the number density of the buffer gas. In accordance with the recent report of Seeley et al., the principal fate of the thermalized complex shown in reaction sequence 1 will be assumed to be dissociation to the reaction products Br^- and CH_3Cl. From the rate constants for this process also provided by Seeley et al., this step can be assumed to occur very quickly (the half-life of the complex in nitrogen buffer gas at 125 °C will be much less than 1 μs[18]). Therefore, the ion complex will not be detected in the present IMS-based experiments and the dissociation step will not affect the overall observed rate constant for this pathway.

For the sake of this discussion, several simplifications of the detailed reaction dynamics represented by reaction sequence 1 will be made and the possible implications of these assumptions should be pointed out. One of these is that the rate at which the initially formed set of entrance-channel ion complexes undergo backdissociation will be described here by a single rate constant k_r. It is acknowledged, however, that a more rigorous treatment of the backdissociation process would involve a sum of several exponential decay constants representing all of the important mode-specific species initially formed in the ion–molecule collision. In the present study, it is possible that only a subset of the entrance channel complexes that have relatively long lifetimes (smallest k_r's) are being affected by increased buffer gas pressure. Therefore, the simplified model developed here can be expected to provide only a semiquantitative description of the actual events and has validity only to the extent that the relatively long-lived fraction of the collision-formed complexes constitutes a significantly large portion of the total population.

Another point of simplification in reaction sequence 1 is that the passage of $Cl^-(CH_3Br)^*$ over the transition state barrier is shown to lead directly to products. Wang et al.[14] have shown, however, that the exit-channel complex, $Br^-(CH_3Cl)^*$, that is first formed upon passage over the transition state is likely to recross the transition-state barrier to reform $Cl^-(CH_3Br)^*$. In addition, Wang et al. predict that several such recrossings of the central barrier will then occur prior to the dissociation of one of the two complexes to either reactants or to products. Therefore, the rate constant k_p shown in reaction sequence 1 should be viewed to represent the passage over the central barrier only of those entrance-channel complexes that do not recross the barrier. In addition, it is recognized that our use here of a single value for k_p is also a simplification of a much more complex reality in which a set of mode-specific rate constants would actually be required in a rigorous treatment of the forward motion of the excited entrance-channel complexes along the reaction coordinate.

Within this simplified view of reaction sequence 1 and with the reasonable assumption that $k_r \gg (k_p + k_q[B])$ under our experimental conditions, the observed rate constant, k_{obs}, would be given by

$$k_{obs} = k_c k_p / k_r + k_c k_q [B] / k_r \tag{2}$$

Since the rate constant observed for this reaction under buffer gas conditions of relatively low pressure will be given by $k_{LP} = k_c k_p / k_r$, eq 3 can be written as

$$k_{obs} = k_{LP} + k_c k_q [B] / k_r \tag{3}$$

Also shown in Figure 1 are predictions of k_{obs} based on eq 3 where the following values of k_{LP}, k_c, k_q, and k_r were selected. From prior measurements[12] of this reaction by PHPMS in 3 Torr buffer gas at 125 °C, k_{LP} was determined to be equal to 2.2×10^{-11} cm^3 s^{-1}. By ADO theory,[19] k_c is predicted to be equal to 1.42×10^{-9} cm^3 s^{-1} at 125 °C. Accurate predictions of k_q are more difficult to obtain because the efficiency of collisional quenching of the excited complexes by nitrogen and methane buffer gases is not known. If it is first assumed that k_q will be equal to the rate constant for collisions between the ion complex and the buffer gas molecules, Langevin theory[19] predicts $k_q = 1.00 \times 10^{-9}$ cm^3 s^{-1} for methane buffer gas and $k_q = 6.5 \times 10^{-10}$ cm^3 s^{-1} for nitrogen buffer gas. The best fit to the experimental data obtained at 640 Torr was then obtained when the lifetime of the entrance-channel complex was assumed to be about 0.7 ps (i.e., $k_r = 1.5 \times 10^{12}$ s^{-1}). These predictions are shown as the solid (methane) and dashed (nitrogen) lines in Figure 1.

If the efficiency for collisional quenching of the entrance-channel ion complex is less than unity, the value of $k_r = 1.5 \times 10^{12}$ s^{-1} would have been overestimated in the above treatment. For example, if the quenching efficiency of one of the buffer gases is only 10%, then the best fit of k_r to the data in Figure 1 would be about $k_r = 1.5 \times 10^{11}$ s^{-1} (corresponding to a complex lifetime of 7 ps). For this reaction system, it seems reasonable to speculate that the efficiency of quenching by methane buffer gas would be at least 10%.[20] Therefore, it seems reasonable to conclude that the $1/k_r$ lifetime suggested by the present set of measurements and the above simple model for the reaction dynamics operative at 640 Torr is somewhere in the low picosecond range.

If all of the rate constants for the Cl^-/CH_3Br reaction system measured over the entire pressure range between 300 and 1100 Torr (Figure 1) are considered, significant differences between the values measured in both buffer gases and the predictions of the simple model are apparent. Both sets of experimental values form lines of lower slopes than those of the predictions and extrapolate to low-pressure limits that lie significantly above the experimentally determined value of $k_{LP} = 2.2 \times 10^{-11}$ cm s^{-1}. Although the cause of this discrepancy is not presently known, it could result from limitations of the simplified model described above. For example, if the simplified model was altered only slightly in a manner that allowed just 1% of the initially formed complexes in reaction sequence 1 to have distinctly longer lifetimes (i.e., $1/k_r > 50$ ps) against backdissociation, an initial increase of about 1×10^{-11} cm^3 s^{-1} in the rate constant would then be expected for pressures less than 300 Torr. This change would account for the observed extrapolations to higher-than-expected low-pressure limits for the rate constants. Within this modified view, the slopes of the measurements shown in Figure 1 over the pressure range 300–1100 Torr would then lead to deductions for k_r that are about 5 times greater than those derived above from the simplified model (these modified k_r values would apply only to the set of collision complexes that are being affected by the pressure change from 300 to 1100 Torr and not to the set that are affected by lower pressures). To more completely characterize the dynamics of this and other reaction systems, experimental methods that are operative over all pressure ranges of interest are clearly needed. For this purpose, an IMS-based apparatus that will operate over the pressure range from about 10 to 300 Torr is presently being constructed in our laboratory.

Conclusions

The experiments performed here indicate that the reaction of chloride ion with methyl bromide is not moved onto its high-pressure limit of kinetic behavior by use of buffer gas pressures near 1 atm. The pressure dependence of the rate constants observed in this pressure range is qualitatively consistent with predictions by Wang et al.[14] of very short lifetimes for the reaction complexes of this reaction and with the prediction by Seeley et al.[18] that this reaction should proceed with high efficiency in its high-pressure limit.

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