FUNDAMENTAL STUDIES OF GAS PHASE IONIC REACTIONS BY ION MOBILITY SPECTROMETRY

K. Giles, W.B. Knighton, K.E. Sahlstrom and E.P. Grimsrud

Department of Chemistry, Montana State University, Bozeman, MT

ABSTRACT

Ion mobility spectrometry (IMS) provides a promising approach to the study of gas phase ionic reactions in buffer gases at unusually high pressures. This point is illustrated here by studies of the Sn2 nucleophilic displacement reaction, $Cl^- + CH_3Br \rightarrow Br^- + CH_3Br$, using IMS at atmospheric pressure. The equilibrium clustering reaction, $Cl^-(CHCl_3)_{n-1} + CHCl_3 \rightleftharpoons Cl^-(CHCl_3)_n$, where n = 1 and 2, and the effect of clustering on the Sn2 reaction with CH_3Br have also been characterized by this IMS-based kinetic method. Present problems and anticipated improvements in the application of ion mobility spectrometry to studies of other gas phase ionic processes are discussed.

INTRODUCTION

While the field of gas phase ion chemistry (GPIC) has received a great deal of attention during the last 3 decades, kinetic studies of ionic reactions have been successfully performed primarily under conditions in which the total system pressure is relatively low and has rarely exceeding a few torr. In fact, less than 15 reports have appeared in the literature, to date, in which the use of an instrumental method for the kinetic characterization of a gas phase ion-molecule reaction in a buffer gas near atmospheric pressure is described[1-13]. This omission in the field of GPIC is clearly due to instrumental reasons, rather than a lack of interest. The principal methods of GPIC have been based almost exclusively on various forms of mass spectrometry which have been most easily adapted to the study of reactions systems at relatively low pressure.

It is important that we gain increased understanding of the effects of elevated pressures on GPIC for a variety of reasons. One practical reason is that several modern instrumental methods of analysis are based on ionic reactions occurring within an atmospheric pressure buffer gas. These methods include atmospheric pressure ionization mass spectrometry[14], ion mobility spectrometry[15], and the electron capture detector for gas chromatography[16]. In addition, certain lasers depend on the manipulation of ionic reactions under conditions of elevated pressures[1]. Perhaps the most compelling motivation for increased research in GPIC under conditions of elevated pressure, however, is simply that such studies are needed in order to understand more completely the nature of reactions between ions and neutrals in the gas phase. Consider, for example, the following issue which has recently gained much attention in the field of GPIC. Even relatively simple bimolecular ion-molecule (IM) reactions are generally thought to occur by the following set of individual steps in the gas phase[17],

$$A^{\pm} + B \; \rightleftharpoons \; A^{\pm}(B)^* \; \overset{\ddagger}{\rightleftharpoons} \; (A)B^{\pm *} \; \rightleftharpoons \; A + B^{\pm} \qquad (1)$$
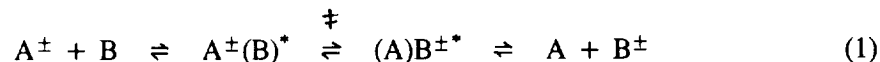
in which the ion and molecule first combined to form an excited entrance-channel ion complex, $A^{\pm}(B)^*$, prior to passing through a transition-state ($\pm$) that leads to an excited exit-channel ion complex, $(A)B^{\pm *}$, and, finally, to the products of the reaction. In interpreting kinetic data obtained under low pressure conditions for reactions of this type, a formidable complexity is becoming increasingly recognized. That is, that the internal energy within the collision

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complex, $A^{\pm}(B)^*$, does not necessarily get rapidly distributed among its vibrational and rotational modes of freedom, prior to its continued motion (either forward or backward) along the reaction coordinate[18-21]. This means that the well-developed statistical theories (RRKM theory, for example) for describing kinetic processes involving excited species are probably not applicable to these systems. For some IM reactions (such as the one to be illustrated below), energy transfer within the entrance-channel complex is actually thought to be the rate-limiting step of the overall reaction when performed under low pressure conditions. Therefore, for these cases, some of the basic parameters of interest in a mechanistic study, such as the structure and energy of the transition state along the reaction coordinate, can not be reliable deduced from low pressure kinetic data and existing theory.

The impasse described above could be avoided if the reaction of interest could be studied under conditions of relatively high pressure where the reaction system is moved to what is known as its high pressure (HP) limit of kinetic behavior. In the HP limit, the entrance- and exit-channel ion complexes shown in Reaction 1 would be brought into thermal equilibrium with the buffer gas by collisions prior to their continued motion along the reaction coordinate. In representing an IM reaction occurring in the HP limit, the asterisks shown in Reaction 1 would be removed, indicating that the entrance- and exit-channel ion complexes do not have the extra internal energy imparted to them by their exothermic formation processes. Instead, these intermediates would have normal Boltzman distributions of energies, that would be determined only by the temperature of the buffer gas and would be continuously maintained by collisions. Kinetic data for systems that are clearly operating in their HP limit should be relatively simple to interpret using well-established transition-state theory.

For the reason highlighted above and for other fundamental reasons[5], as well, new methods for the study of GPIC at elevated pressures are needed. In this paper, we describe recent efforts in our laboratory to apply an ion mobility spectrometer (IMS) to this task. We will focus here on one specific reaction system that has received a great deal of attention by others in recent years. This is the Sn2 nucleophilic displacement reaction of chloride anion with methyl bromide, as shown in Reaction 2.

$$Cl^- + CH_3Br \rightarrow CH_3Cl + Br^- \qquad (2)$$

This reaction is thought to proceed by the general mechanism expressed in Reaction 1, in which the behavior of its entrance-channel ion complex, $Cl^-(CH_3Br)$, is expected to determine the rate of the overall reaction. Others have shown that the entrance- and exit-channel intermediates of this reaction behave in a distinctly non-statistical manner under low pressure conditions[20,21]. Therefore, a comparison of the kinetic behavior of this system under low pressure and high pressure conditions is of considerable interest.

EXPERIMENTAL METHODS

The IMS instrument that we have developed for kinetic studies is shown in Figure 1. Since this instrument has been previously described in detail[10-12], only a brief summary of its operation will be provided here. The instrument consists of an IMS, a mass spectrometer (MS) and a gas handling plant (GHP). The walls of the IMS are defined by a Pyrex glass tube that is terminated at both ends by glass-to-metal seals and stainless-steel flanges. The electric field for the IMS is created by 19 stainless-steel rings (common hose clamps) that are strapped around the glass tube. Ions are created in a movable ion source containing a 15 mCi ^{63}Ni-on-Pt radioactive foil. Nitrogen flows continuously through the ion source (about 50 mL min^{-1}) from a 1-L dilution volume. A movable Bradbury-Nielsen gate is located about 0.5 cm in front of the ion source. A counterflow of nitrogen gas (about 500 mL min^{-1}) enters at the left end of

the IMS. Ions are detected by a stainless-steel Faraday plate that has an MS sampling aperture (50 μm) at its center. By the MS, the ions under any mobility peak of interest can be positively identified. The entire IMS is enclosed in an oven and can be heated up to 175°C. The GHP provides a means of accurately seeding the nitrogen drift gas with the reagent compounds of interest. It includes a 4-L stainless volume that is pressurized to about 2500 torr.

RESULTS AND DISCUSSION

Rate Constants for Ion Molecule Reactions

In Figure 2, typical ion mobility spectra obtained for the purpose of rate constant measurements for Reaction 2 in an atmospheric pressure buffer gas are shown. In Figure 2A, a small amount of CCl_4 was added to the ion source gas so that the Cl^- ion is formed in the ion source by dissociative electron capture. This provides the major ion observed at about $t = 25$ ms. It is also seen in Figure 2A that other ions of minor relative intensity contribute to a broad baseline between 25 and 30 ms. Parallel MS measurements indicate that these unwanted ions are due to the clustering of various protic neutrals to Cl^-. These neutrals include HCl, HCOOH, and CH_3COOH and are thought to be formed by the radiation chemistry occurring within the ion source. These neutrals are not present in the drift region of the IMS.

In Figures 2B-2D, the effects of adding various amounts of CH_3Br to the drift gas are indicated. A new peak is thereby formed due to the formation of Br^- by Reaction 2 at all points along the drift tube. This peak is skewed, has a maximum intensity at about $t = 27$ ms, and is progressively increases in intensity with increased CH_3Br concentration. By analysis of these waveforms, the rate constants for Reaction 2 is obtained. Kinetic determinations such as these have been made over a range of temperatures and are plotted in Figure 3 (solid squares with uncertainty bars). Also shown in Figure 3 are previous measurements of the rate constant for Reaction 2 made under various conditions of lower pressure[17,20,22-27].

It is seen in Figure 3 that the rate constants measured at atmospheric pressure are distinctly greater than those that have been measured at the lower pressures. We believe that this effect with increased pressure is due to changes in the nature of the entrance-channel ion complexes of this reactions, as suggested in the INTRODUCTION. That is, at atmospheric pressure a significant portion of the entrance-channel ion complexes suffer collisions with the buffer gas, thereby altering both the amount of internal energy and the distribution of energy within the vibrational and rotational modes of the entrance-channel ion complexes. It is interesting to note that while the average amount of energy in the entrance-channel ion complexes can be assumed to be decreased by use of higher pressure, the rate of the overall reaction is nevertheless significantly increased at atmospheric pressure. This rate enhancement illustrates the importance of the change in the distribution of energy within complexes that is caused by their increased collisions with buffer gas molecules at atmospheric pressure. Also shown in Figure 3, are predictions of the rate constants for Reaction 2 derived by transition state theory under the assumption that the HP limit has been reached. The fact that the predictions are about twice as great as the measurements at atmospheric pressure suggests that the HP limit for this reaction has not been reached at atmospheric pressure. This suspicion is reinforced by recent calculations by Hase and coworkers[28] indicating that some of the excited entrance-channel ion complexes for this reaction have lifetimes shorter than the time of collisions at atmospheric pressure. Furthermore, their calculations suggest that in order to bring this reaction system clearly into the HP limit, the pressure of the buffer gas would have to be raised to about ten atmospheres. Therefore, it presently appears that the data in Figure 3 indicate the reaction system under study has been moved towards, but not onto, the HP limit

of behavior by the pressure increase to one atmosphere.

Ion Clustering Equilibrium Constants

Ion clustering equilibrium constants can also be measured by IMS as illustrated in Figure 4 for the clustering of Cl^- ion by $CHCl_3$. In this figure, it is noted that the drift time of the major Cl^--containing ion packet is increased by increasing the concentration of the clustering agent, $CHCl_3$. This is because equilibrium Reaction 3 is shifted to the right by increased $CHCl_3$ concentration.

$$Cl^-(CHCl_3)_{n-1} + CHCl_3 \rightleftharpoons Cl^-(CHCl_3)_n \qquad (3)$$
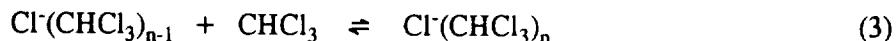
By the analysis of data such as these, equilibrium constants for the individual steps, n = 1 and n = 2 have been determined at three temperatures and these are listed in Table I. Also shown in Table I are other fundamental parameters that were obtained from these measurements, including reduced single ion mobilities and the ion-buffer gas interaction cross sections for the bare and clustered Cl^- ions.

An important advantage of the IMS approach to equilibrium measurements is that a major problem experienced in equilibrium measurements by high pressure mass spectrometric measurements is entirely avoided. That problem is the perturbation of relative ion intensities that can be associated with aperture-sampling of a high pressure ionized gas[29,30].

Rate Constants for Reactions Involving Sets of Clustered Ions

A useful feature of kinetic measurements by the IMS is that the reactions of a set of ions, that are coupled by fast equilibrium reactions, can be observed. In Figure 5, for example, a series of ion mobility spectra are shown which reflect the reaction of a set of $Cl^-(CHCl_3)_n$ cluster ions with CH_3Br. As opposed to the spectra shown previously in Figure 2, it is noted in Figure 5 that the Br^- product ion appears to have a drift time that is less than that of the reactant Cl^- ion. This is due to the fact that clustering of Br^- by $CHCl_3$ is less extensive than clustering of Cl^- under the conditions of this experiment. By analysis of waveforms such as these, the rate constants for the reaction of any selected set of $Cl^-(CHCl_3)_n$ cluster ions with CH_3Br can be determined. Some of these determinations have been plotted in Figure 6 along with a curve indicating the net rate constants that were predicted under the assumption that only the bare Cl^- ion is reactive with CH_3Br. These results indicate that the reaction is essentially shut off by any clustering of the reactant Cl^- ion. This result is interesting in view of the fact that the reaction,

$$Cl^-(CHCl_3)_1 + CH_3Br \rightarrow CH_3Cl + Br^-(CHCl_3)_1 \qquad (4)$$
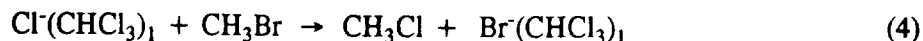
would be exothermic by about 6 kcal/mol. A possible reason why Reaction 4 is not fast is the following. In a concerted Sn2 transition state that might be envisioned for this reaction, the solvent molecule, $CHCl_3$, would have to migrate from one region of decreasing negative charge density at the Cl atom to the other region of increasing negative charge density at the Br atom. Since these two regions would be located at opposite ends of the Sn2 transition state and the $CHCl_3$ molecule has only one proton for interaction with negative charge, migration of the $CHCl_3$ molecule to the Br end of the transition-state probably does not occur during the very short lifetime of this species.

CONCLUSIONS AND FUTURE DIRECTIONS

We have demonstrated here that IMS provides a means of measuring various types of ion molecule processes under conditions of much higher buffer gas pressures than has been possible by the conventional, mass spectrometry-based methods of GPIC. The general procedures described here should be applicable to many reaction systems of interest within the field of GPIC. We have also learned, however, that several formidable problems must be either acknowledged or overcome in future studies of GPIC at very high pressures. One of the most significant of these is that it will be difficult to study the reactions of ions that react readily with ubiquitous buffer gas impurities, such as water, unless the concentration of that impurity can be reduced to about one part per billion. Since the reduction of water to that level is extremely difficult, the reactions of numerous high-energy positive and negative ions that react with water will not be easily studied by the IMS approach. In addition, improved ion sources are needed by which the detrimental effects of the reactive neutrals produced by radiation chemistry within the presently utilized beta sources can be minimized. We have also learned that the internal surfaces of the stainless-steel GHP presently used for our IMS are not sufficiently inert as to allow the quantitative introduction of many compounds. For example, CH_3I and substituted nitrobenezenes have been found to either decompose or adsorb on the surfaces of our GHP. More inert GHP surfaces that are also capable of withstanding superambient pressures (several atmospheres) are needed. Finally, gas phase kinetic measurements are needed over a very wide and continuously varied range of pressures, from about 10 torr to 10 atmospheres. In addressing this need, it presently appears that IMS offers the most promising approach.

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Table I. Results Obtained from IMS Measurents of $Cl^-(CHCl_3)_n$ Clustering Reactions

		Temperature (°C)		
		75°	100°	125°
t_0 [a] (msec)		40.80	36.84	33.99
t_1		63.84	57.88	54.35
t_2		82.64		
$K_{o,0}$ [b] (cm^2 V^{-1} s^{-1})		2.725	2.820	2.883
$K_{o,1}$		1.742	1.795	1.803
$K_{o,2}$		1.346		
Ω_0 [c] (nm^2)		0.919	0.858	0.813
Ω_1		1.168	1.095	1.056
Ω_2		1.461		
K_1 [d] (atm^{-1})		3.7E6	6.1E5	1.41E5
K_2		1.43E4		
ΔH^0_1 [e] (kcal mol^{-1})				-18.1
ΔS^0_1 [f] (cal deg^{-1} mol^{-1})				-21.8

[a] Drift time, t_i, of single ion $Cl^-(CHCl_3)_i$.

[b] Reduced mobility, $K_{o,i}$, of single ion $Cl^-(CHCl_3)_i$.

[c] Ion-buffer gas interaction cross section, Ω_i, for single ion $Cl_i(CHCl_3)_i$.

[d] Equilibrium constant, K_n, for reaction, $Cl^-(CHCl_3)_{n-1} + CHCl_3 = Cl^-(CHCl_3)_n$

[e] Enthalpy of $Cl^-(CHCl_3)_1$ formation determined from temperature dependence of K_1.

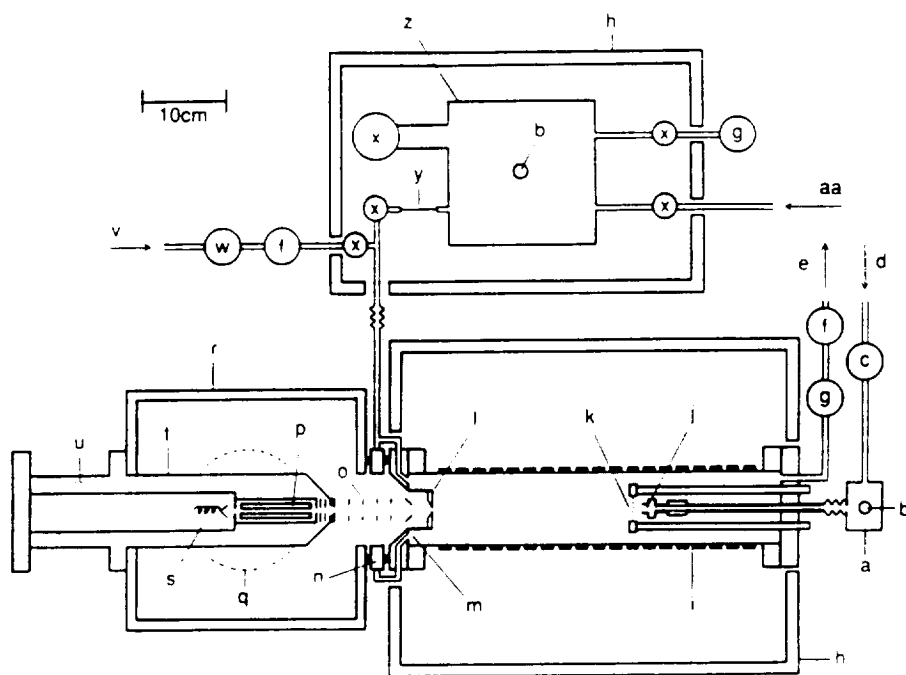[f] Entropy of $Cl^-(CHCl_3)_1$ formation determined from temperature dependence of K_1.

Figure 1. Diagram of the IMS apparatus: (a) stainless-steel source gas dilution volume, (b) septum inlet, (c) needle valve, (d) N_2 source gas supply, (e) source and drift gas exhaust, (f) flow meter, (g) pressure transducer, (h) insulated box, (i) drift tube, (j) ion source, (k) Bradbury-Nielson gate, (l) Faraday plate / MS aperture, (m) drift gas inlet, (n) universal joint, (o) electrostatic lens element, (p) quadrupole mass filter, (q) 6" diffusion pump, (r) first vacuum envelope, (s) channeltron electron multiplier, (t) second vacuum envelope, (u) 3" diffusion pump, (v) N_2 drift gas supply, (w) leak valve, (x) on/off valve, (y) fused silica capillary, (z) 4-liter stainless steel dilution volume, (aa) N_2 gas supply.
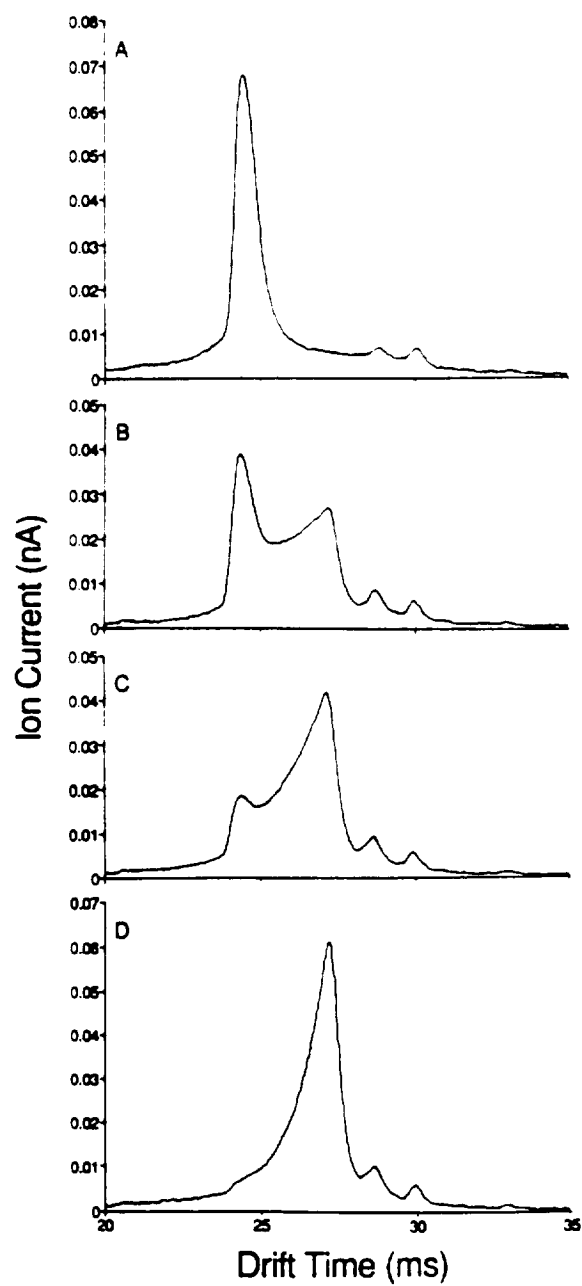
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Figure 2. Ion mobility spectra modified by the reaction, Cl⁻ + CH₃Br → Br⁻ + CH₃Cl, using the following concentrations of CH₃Br in the drift tube: (A) none, (B) 1.29 x 10¹², (C) 2.60 x 10¹², and (D) 5.27 x 10¹² molecules cm⁻³. Temperature is 125°C.
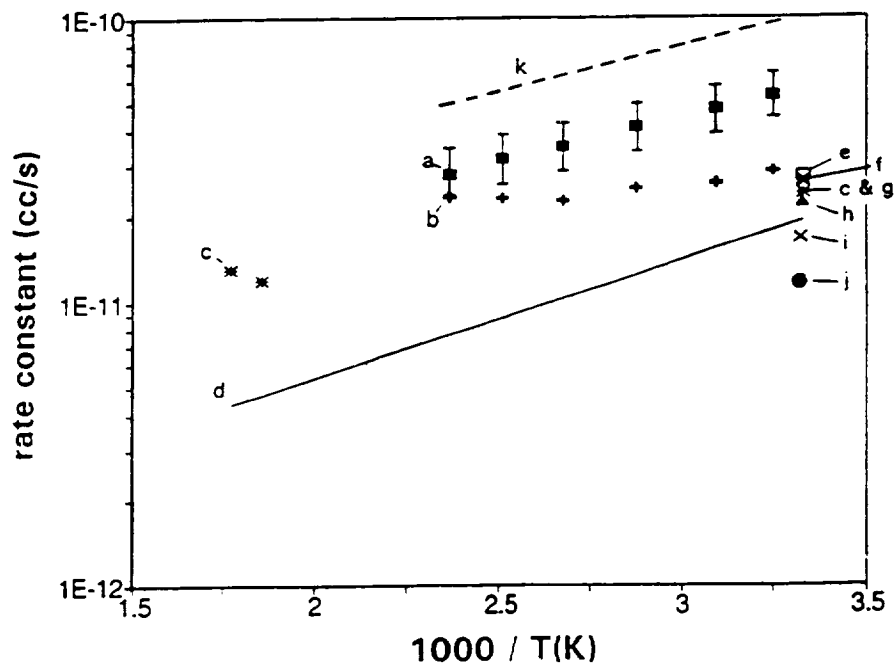
Figure 3. Rate constants observed for the reaction of Cl⁻ with CH₃Br under a variety of different temperature and pressure conditions. The present IMS measurements at 640 Torr (a) and measurements by pulsed high pressure mass spectrometry at 3 Torr also made in our lab (b) have been plotted in the Arrhenius form. Error bars indicate the estimated uncertainties of the IMS measurements ($\pm 20\%$). Also shown are previous measurements of this reaction system by the following techniques and pressures: (c) SIFT (ref. 20) at 0.5 Torr, (d) PHPMS (ref. 22) at 4 Torr, (e) SIFT (ref. 23) at 0.5 Torr, (f) FTMS (ref. 24) at $< 10^{-5}$ Torr, (g) SIFT (ref. 25) at 0.5 Torr, (h) FA (ref. 26) at 0.5 Torr, (i) FA (ref. 27) at 0.5 Torr, and (j) ICR (ref. 17) at $< 10^{-5}$ Torr. The dashed line (k) provides a prediction for the rate constants in the HP limit of kinetic behavior obtained from transition-state theory.
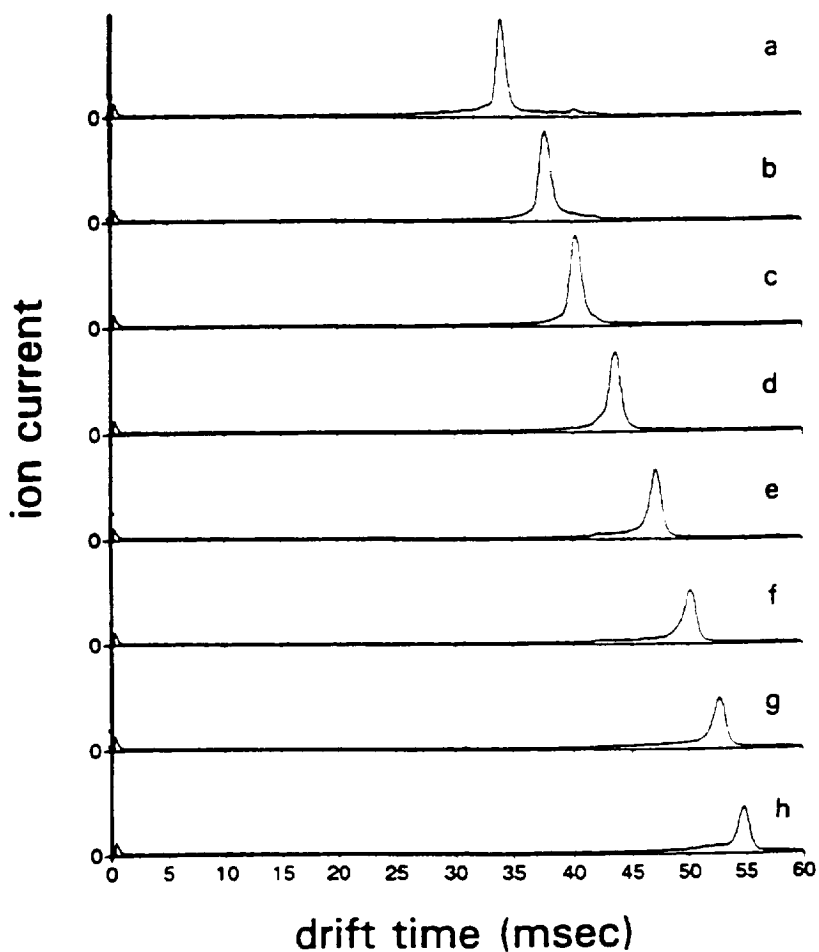
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ion current

drift time (msec)

Figure 4. Ion mobility spectra obtained by the production of Cl⁻ by electron capture to CCl_4 in the ion source with the following partial pressures of $CHCl_3$ added to the drift gas: (a) none, (b) 1.61×10^{-6}, (c) 3.2×10^{-6}, (d) 6.5×10^{-6}, (e) 1.29×10^{-5}, (f) 2.6×10^{-5}, (g) 5.2×10^{-5}, and (h) 1.03×10^{-4} atm. Ion source and drift regions contain nitrogen buffer gas at 640 torr and 125°C.
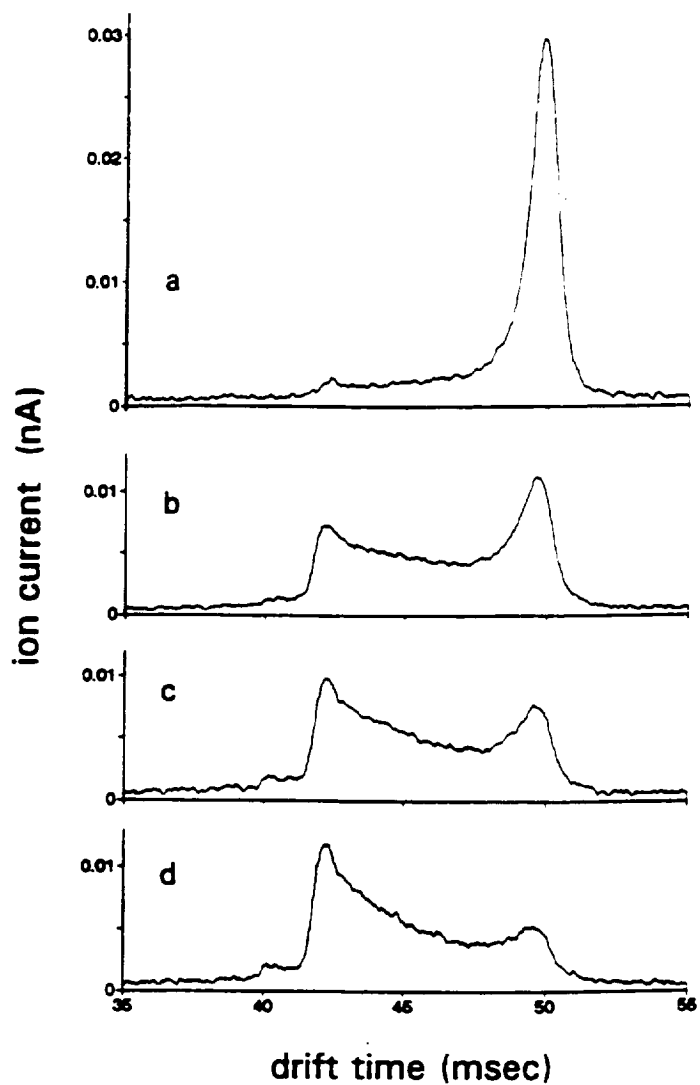
Figure 5. Ion mobility spectra of source-produced Cl⁻ ions with 2.22 x 10⁻⁵ atm of the clustering agent, CHCl₃, present in the drift gas along with the following amounts of the reagent neutral, CH₃Br: (a) none, (b) 2.6 x 10¹², (c) 3.9 x 10¹², and (d) 5.3 x 10¹² molecules cm⁻³. Temperature is 125°C. Under these conditions, only 24% of the reagent ions are present as uncomplexed Cl⁻ ions.
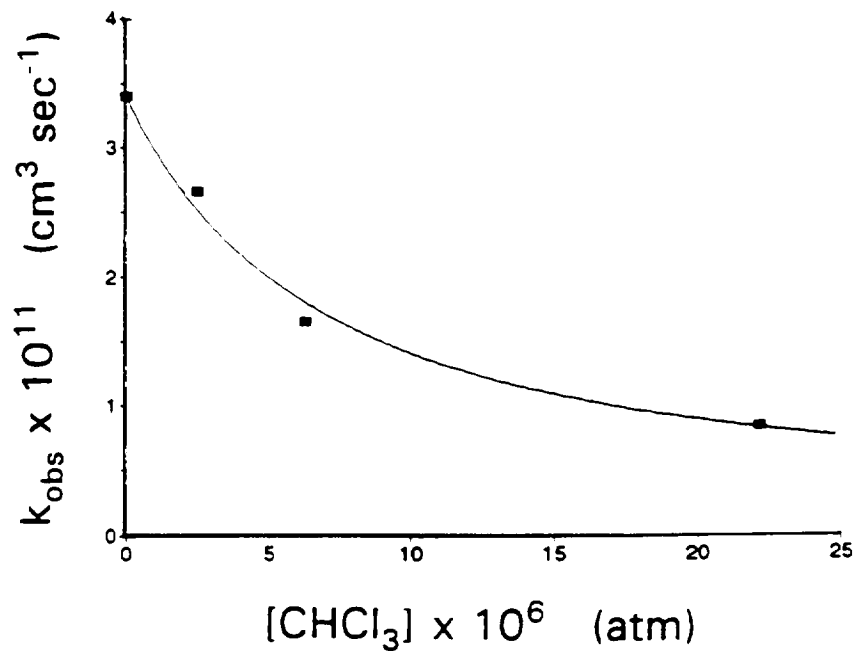
Figure 6. Rate constants observed for the reactions of $Cl^-(CHCl_3)_{0-2}$ ions with CH_3Br as a function of $CHCl_3$ concentration in the drift gas. Temperature is 125°C. The solid line shown is a prediction for k_{obs} based on the assumption that only the uncomplexed Cl^- ion reacts with CH_3Br.