Inverse Heavy-Atom Kinetic Isotope Effects in Chloroalkanes

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Intramolecular heavy-atom kinetic isotope effects (KIEs) are reported for reactions of some gas-phase ions relevant to atmospheric chemistry. The anionic complexes carbon tetrachloride/Cl^-, chloroform/Cl^-, and methylene chloride/Cl^- ($CH_nCl_{5-n}^-$; $n = 0-2$) were generated by various ionization methods and subjected to single-stage and tandem mass spectrometric analysis in a variety of instruments. Strongly pressure dependent, anomalous chloride abundances were observed in single-stage mass spectra under self-chemical ionization conditions for $CHCl_4^-$ and CCl_5^- in a triple quadrupole and for $CHCl_4^-$ in a quadrupole ion trap. Further examination of these complexes in triple quadrupole MS/MS experiments confirmed the presence of an unusually large inverse kinetic isotope effect. We suggest that the selective loss of $^{37}Cl^-$ is simply due to the difference in centrifugal barriers associated with the competitive reaction channels leading to the two chloride isotopes. This effect is greatly magnified near the threshold for dissociation, and an extreme value of an inverse kinetic isotope effect (0.026 ± 0.01) is displayed by the isotopomeric chloride adduct of chloroform, $CH^{35}Cl_3{}^{37}Cl^-$, under single-collision conditions with xenon at 27 eV lab collision energy. The methylene chloride adduct, $CH_2{}^{35}Cl_2{}^{37}Cl^-$, had a KIE close to unity (0.90 ± 0.05), and the carbon tetrachloride adduct displayed no apparent KIE, under these same conditions. Remarkably, in addition to the heavy-atom KIEs for chlorinated chloroform, (i) substantial H/D isotope effects are associated with chloride loss, (ii) the chlorine KIE values are strongly dependent on the particular isotopomer selected for examination, and (iii) the chlorine KIE for $CHCl_4^-$ is not monotonic with collision energy. In sum, the results are indicative of a complex potential energy surface and of a mixture of dissociating structures or independent dissociation channels of the precursor.

Introduction

Isotope abundances are one of the most widely used tools in the earth, planetary, and geosciences, including those associated with heavy elements in such primitive bodies as meteorites and lunar rock samples.[1] Kinetic isotope effects (KIEs) are a valuable tool for probing chemical structures, reaction mechanisms, and dynamics, both in solution and in the gas-phase. One of the best characterized of all organic reactions, the S_N2 reaction at aliphatic carbon, has been investigated using kinetic isotope effects.[2] For example, the chloride isotope exchange reaction at methyl chloride has been calculated to have an inverse secondary hydrogen/deuterium isotope effect.[3] This has been interpreted, using the double-well potential model, to be a consequence of the intermediate ion−dipole complexes interconverting via a Walden inversion, eq 1[4]

$$Y^- + CH_nX_{4-n} \rightarrow Y^- \cdots CH_nX_{4-n} \rightarrow YCH_nX_{3-n} \cdots X^- \rightarrow YCH_nX_{3-n} + X^- \quad (1)$$

where X and Y denote different isotopes. Despite the great amount of literature on this subject, gas-phase chloride exchange reactions with polychloroalkanes where $n = 0-2$ appear not to have been investigated experimentally.[5] This case is of special interest for its significance to atmospheric and environmental chemistry and for the unusually large *inverse* primary heavy-atom isotope effects ($[^{35}Cl^-]/[^{37}Cl^-]$) associated with eq 2, which are reported here

$$CH_nCl_{5-n}^- \rightarrow CH_nCl_{4-n} + Cl^- \quad (2)$$

The reactions studied are formally simple dissociations corresponding to the second half of particular S_N2 reactions.

Experimental Section

Most of the data discussed here were recorded using a Finnigan TSQ70 triple quadrupole mass spectrometer (Thermo Finnigan, San Jose, CA).[6] The chloride adducts were generated by negative ion self-chemical ionization[7] (CI) according to eqs 3 and 4, and the precursor ions were rigorously checked for correct natural isotopic abundances by recording mass spectra by scanning the first quadrupole.

$$CH_nCl_{4-n} + e^- \rightarrow CH_nCl_{3-n}^+ + Cl^- + e^- \quad (3)$$

$$Cl^- + CH_nCl_{4-n} \rightarrow CH_nCl_{5-n}^- \quad (4)$$

The desired isotopomer(s) or, in some MS/MS experiments, the entire group of chlorine-containing ions was (were) mass-selected in the first quadrupole and subjected to collisional activation[8] at particular collision energies in an rf-only collision quadrupole, and the products analyzed by mass and abundance using the third quadrupole. Data were collected in triplicate, and each set was the result of averaging 100 scans recorded at a rate of 1 Hz. Typical indicated manifold pressures after

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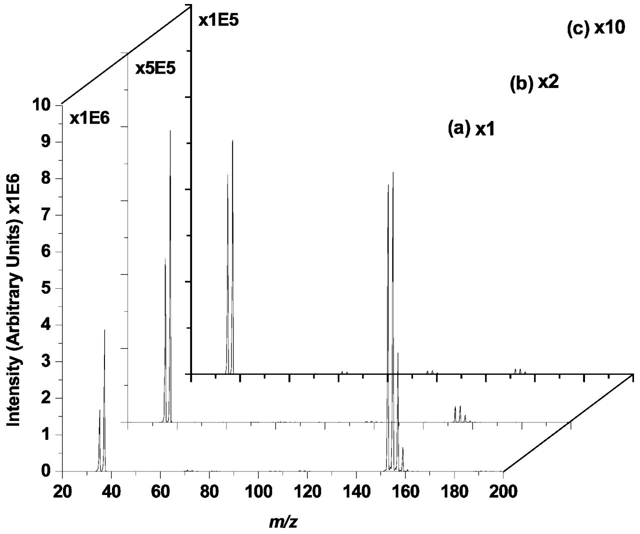

Figure 1. Chloroform single-stage mass spectra recorded in Q3 of a triple quadrupole mass spectrometer at manifold pressures of (a) 3.5, (b) 2.0, and (c) 1.2 × 10^{-6} Torr, 70 eV ionizing electrons and 100 eV q2 offset energy.

addition of sample to the CI source and collision gas to the collision cell were 3 × 10^{-6} and 6 × 10^{-6} Torr; collision cell pressures ranged from 0.2 to 0.6 mTorr (fulfilling the single-collision criterion of less than 20% beam attenuation). Xenon was the target used throughout this study, though argon and helium gave analogous results. Collision energies were varied over a wide range, from nominal zero to 100 eV. The electron energy used was 70 eV unless stated otherwise. Manifold and chemical ionization source temperatures were set to 30 °C.

Experiments were also carried out using a Thermo Finnigan LCQ quadrupole ion trap and a Thermo Finnigan LTQ linear ion trap mass spectrometer, each equipped at different times with atmospheric pressure chemical ionization (APCI),[9] electrospray (ESI),[10] and electro-sonic spray (ESSI)[11] sources. Chloroform was introduced at a flow rate of roughly 10−50 μL/min into a capillary interface at a temperature in the range of 50−80°C. The typical tube lens voltage was 1−100 V, while the injection time was normally 100 ms. In MS/MS experiments, the Mathieu parameter value, q_z, was set to 0.15 during ion activation, whereas the manufacturer's % collision-induced dissociation (CID) parameter representing the energy of activation ranged from 10 to 25. These conditions ensured efficient production and trapping of the chloride fragment ions.

A Thermo Finnigan GCQ quadrupole ion trap, equipped with an external chemical ionization source, permitted formation of chloride clusters in the ion source using conditions similar to those used in the triple quadrupole instrument (ionizing electrons of 70 eV energy). Upon introduction of chloroform, the manifold pressure was allowed to equilibrate at a nominal 1 × 10^{-4} Torr. Helium buffer gas was used in the ion trap and the manifold and inlet temperatures were both roughly 100 °C. All reagents were purchased from Aldrich Chemical Co. (St. Louis, MO) and used without further purification except that the samples were subjected to one freeze−pump−thaw cycle.

Results and Discussion

The mass spectrum of chloroform (Figure 1a), recorded using the third quadrupole of a triple quadrupole instrument (first and second quadrupoles operated in rf-only mode) and with elevated sample pressures in the chemical ionization source (self-chemical ionization conditions), shows two groups of ions, a cluster between m/z 150 and 161, corresponding to the chloride adduct of chloroform, $CHCl_4^-$, and signals at m/z 35 and 37 corresponding to the two isotopes of the chloride anion, Cl^- which is generated both directly from the neutral and as a fragment of the chloride adduct. Remarkably, the chloride signals favor $^{37}Cl^-$ over $^{35}Cl^-$ by a factor of 2.3, corresponding to an isotope effect of 0.14, whereas the chloride adduct shows a natural isotopic distribution. As the pressure in the ion source was decreased (Figure 1b, 1c), the ion/molecule collisions leading to the formation (and collisional stabilization) of the cluster ion became less frequent and the cluster ion abundance decreased rapidly. At a manifold pressure of 1.0 × 10^{-6} Torr, the cluster intensity was comparable to that of the much less abundant ion CCl_3^-, a characteristic feature of the electron impact spectrum. Over this same range of source pressures, the chloride anion abundance changed from 2.3 (^{37}Cl vs ^{35}Cl) to the normal isotopic abundance ratio of 0.32. For clarity, Figure 1 shows only the most unusual part of the range, from 2.3 to approximately 1.0. Similar behavior with a very large inverse and pressure dependent isotope effect was observed for the chloride adduct of carbon tetrachloride. Note that the normal isotope ratios correspond to conditions under which chloride is generated directly from the neutral molecule while the anomalous ratios include large contributions from dissociating clusters.

To confirm the above assignments, tandem mass spectrometry experiments were performed using the triple quadrupole on the chloride adducts of carbon tetrachloride, chloroform, and methylene chloride, using three target gases, He, Ar, and Xe, and a range of collision energies. In each case, chemical ionization was used to prepare the cluster ion which was mass selected using the first quadrupole, collisionally activated under single collision conditions in the second with product ion spectra being recorded using the third quadrupole. The magnitude of the chloroform/Cl^- KIE was measured as 0.026 ± 0.01 for $CH^{35}Cl_3{}^{37}Cl^-$ at a calibrated laboratory collision energy of 27 eV using single collisions with xenon. This remarkably large inverse KIE confirms the result from the single stage mass spectrum, and demonstrates that it is due to the dissociation shown in eq 2. Interest in the chloroform/Cl^- system[12] is increased by a dependence of the KIE on the precursor *isotopomer* selected, the value being 0.042 ± 0.01 for $CD^{35}Cl_3{}^{37}Cl^-$ ($CDCl_3$ reagent gas) and 0.22 ± 0.1 for $CH^{35}Cl_2{}^{37}Cl_2^-$. Isolation and CID of all isotopomers of the chloride complexes of $CHCl_3$ and $CDCl_3$, respectively, give an average KIE of 0.019 ± 0.01 for $CHCl_4^-$ and 0.026 ± 0.01 for the deuterated complex, $CDCl_4^-$, showing that the greater part of the KIE is due to the chlorine isotopes not H/D effects. Data collected for the isotopomers of the methylene chloride/Cl^- complex at nominal 27 eV lab energy showed chlorine KIEs of 0.92 ± 0.05 ($CH_2{}^{35}Cl_2{}^{37}Cl^-$) and 0.90 ± 0.05 ($CH_2{}^{35}Cl^{37}Cl_2^-$), and these values approach unity with increasing collision energy. At 1 eV, these KIEs are 0.69 and 0.70 ± 0.05, respectively. Averaged product ion spectra recorded following CID of all isotopomers of CCl_5^- gave no KIE at 27 eV collision energy.

Figure 2 is a representative MS/MS product ion spectrum recorded for the chloroform/Cl^- complex ($CH^{35}Cl_3{}^{37}Cl^-$) upon CID with xenon target gas. Although the selected precursor ion contains three ^{35}Cl and a single ^{37}Cl atom, the fragment chloride ions have a relative abundance ratio of roughly 1:13 in favor of ^{37}Cl, which makes the isotope effect approximately 1:39 after correction for the numbers of each isotopic atom (i.e. 3:1 for ^{35}Cl:^{37}Cl). Also apparent from Figure 2 is the fact that among the dissociation channels of the mass-selected precursor ion only

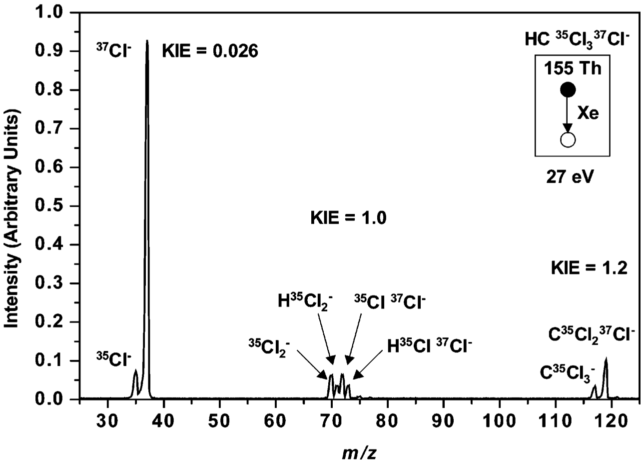

Figure 2. Representative negative ion CID spectrum of $CH^{35}Cl_3{}^{37}Cl^-$ (*m*/*z* 155) taken using a triple stage quadrupole mass spectrometer under single collision conditions with Xe target gas at 27 eV laboratory collision energy. The manifold and CI source were set to 30 °C and the multiplier voltage was 2500 V.

TABLE 1: Instruments, Ion Sources, and Mass Analysis Methods Used to Generate Chloride Complexes, Method of Internal Energy Deposition in the Chloride Adduct and KIE Observed

instrument	ion source	MS^n	energy deposition	$[^{35}Cl^-]/[^{37}Cl^-]$
TSQ70	CI	MS, MS/MS	CI/CID	inverse
TSQ700	APCI/ESI	MS, MS/MS	CID	no effect
GCQ	CI	MS	CI	inverse
LCQ	APCI/ESI	MS, MS/MS	CID	no effect
LTQ	APCI/ESI/ESSI	MS, MS/MS	CID	no effect

this one displays an anomalous isotope effect. The HCl_2^- and Cl_2^- formation reactions showed no significant KIE (1.0 ± 0.1) at the collision energies used, whereas a normal and relatively small (1.2 ± 0.1) KIE is associated with the HCl elimination reaction.

Because of the unexpected nature of these results, the chloride adduct of chloroform was generated by a variety of other methods, including atmospheric pressure chemical ionization APCI, electrospray ionization (ESI), and electro-sonic spray ionization (ESSI), using a number of different mass spectrometers, namely a triple quadrupole mass spectrometer, a quadrupole ion trap mass spectrometer, and a linear ion trap instrument (Table 1). Most of the experiments involved mass-selecting the chloride adduct (either the entire isotopic envelope or a particular isotopomer, as specified) and then performing collision-induced dissociation (an MS/MS experiment). Experiments were done over a wide range of conditions, including the use of different collision gases, different time scales, and different methods of activation to give ions with different amounts of internal energy.[13] Most of the ion trap experiments displayed chloride anions in their natural isotopic abundance ratios, both in the full mass spectra and in the MS/MS experiments. However, in the GCQ ion trap, when using self-CI with 70 eV electrons, chloroform showed a modest inverse KIE (0.80 ± 0.05) in the single-stage mass spectrum. A KIE of 1.00 ± 0.05 was found for carbon tetrachloride.

Before discussing the mechanism(s) associated with chloride formation from the adducts, there are other aspects of the behavior of these systems that are noteworthy. The significant secondary isotope effect associated with D for H substitution noted above was confirmed but again found to be far less pronounced than that associated with ^{37}Cl for ^{35}Cl substitution. At a collision energy at which the chlorine KIEs measured for the different chloroform/Cl^- isotopomers ($CH^{35}Cl_3{}^{37}Cl$ and $CH^{35}Cl_2{}^{37}Cl_2$) differ by *1 order of magnitude*, the KIEs of $CH^{35}Cl_3{}^{37}Cl$ and $CD^{35}Cl_3{}^{37}Cl$ differ by approximately a factor of 2. None of these results are due to isotopic effects operating on the ion/molecule reactions which generate the precursor ions, since their isotopic abundance distributions agree with the statistically expected values: *m*/*z* 152.9 (78), *m*/*z* 154.9 (100), *m*/*z* 156.9 (48), *m*/*z* 158.9 (20), and *m*/*z* 160.9 (1). The fact that the abundances of the ions in the mass spectrum and in other dissociation channels in the MS/MS spectra show natural isotopic distributions means that there is no evidence for hidden effects operating prior to the CID step (viz. a KIE operating on adduct formation, extraction from the source, etc.).

Large but normal (>1) isotope effects associated with isolated ions are readily explained by small excess energies; there are numerous examples of this in the mass spectrometry literature.[14] They are associated with vibrational predissociation near threshold, and in the simplest case, in which the dissociating ion has isotopic atoms of different mass at chemically equivalent positions, they arise simply as a result of differences in zero point energies in the transition states for the competitive dissociations. Large inverse (<1) isotope effects, especially heavy-atom isotope effects, are much more difficult to explain.[15] One possibility is that isomerization occurs under strong isotopic control and that it places $^{37}Cl^-$ at nonequivalent positions in $CHCl_4^-$ ($CCl_3H\cdots Cl^-$ and $CHCl_2Cl\cdots Cl^-$); specifically, the existence of a highly mass-dependent rearrangement to a shallow-well high-energy intermediate could occur as a step in the fragmentation process shown in eq 2. However, although this process might well occur, it cannot account for the KIE effect because carbon tetrachloride shows identical behavior to chloroform in the pressure dependent triple quadrupole single-stage mass spectrum.

There is direct evidence that the present results obtained are associated with rotational effects. It is well recognized that angular momentum effects are nonnegligible in some unimolecular reactions,[16] especially near threshold[17] for loosely bound systems. The ion/molecule complex $CHCl_4^-$ is loosely bound, with a complexation energy of roughly 17 kcal/mol as estimated from a simple linear, point charge dipole model (assuming a dipole moment of 1.0 D for chloroform and an internuclear separation of 2 Å), in agreement with experimental measurements by Kebarle,[18] 15.2 kcal/mol, and Dougherty,[19] 19.1 kcal/mol. The activated complex for dissociation of the cluster is likely even more weakly bound. Given that *intramolecular* KIEs, the type under study here, are solely dependent upon the differences in transition state energies for the competitive dissociation channels, they are therefore dependent upon the relative heights of the centrifugal barriers. If the atoms ^{37}Cl and ^{35}Cl have corresponding positions in the two dissociating complexes the electronic potential energy surfaces for formation of the isotopic chloride products will be identical but the effective potential surfaces will differ because of the centrifugal barriers. Given the greater moment of inertia for the system $^{37}Cl^-(CHCl_2{}^{35}Cl)$ compared to the moment for $^{35}Cl^-(CHCl_2{}^{37}Cl)$, the centrifugal barrier in the exit channel to form $^{37}Cl^-$ will be lower than the corresponding centrifugal barrier to form $^{35}Cl^-$ for the same value of total angular momentum of the complex. As a result, dissociation to form the heavier isotopic product will involve an increased number of rovibrational states for any given state of the competitively dissociating adduct. It is this near-threshold centrifugal effect which we suggest as a plausible mechanism for the observed phenomenon.

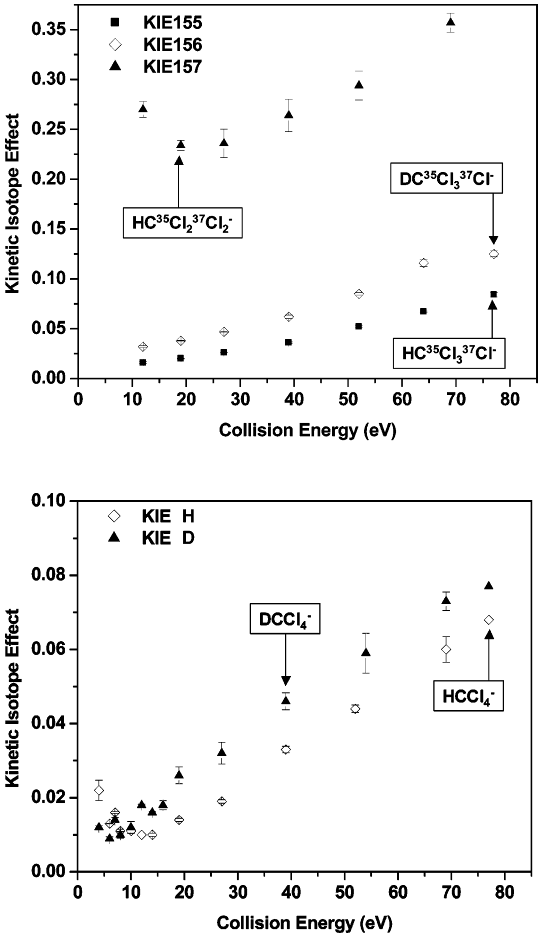

Figure 3. Plot showing the KIE as a function of laboratory collision energy for (a) $CH^{35}Cl_3{}^{37}Cl^-$ (*m/z* 155), $CH^{35}Cl_2{}^{37}Cl_2^-$ (*m/z* 157), and $CD^{35}Cl_3{}^{37}Cl^-$ (*m/z* 156) and (b) $CHCl_4^-$, $CDCl_4^-$. Error bars represent 1σ. A triple stage quadrupole mass spectrometer equipped with a CI source was used. Data were collected under single collision conditions with Xe target gas at 27 eV laboratory collision energy.

The single-stage mass spectral data in Figure 1 demonstrate how changes in experimental parameters can remove the system from this threshold regime, presumably by active manipulation of the angular momentum distribution. We speculate that at the appropriate manifold pressure the difference between angular momenta of the dissociating complexes is negligible. The pressure dependence of centrifugal effects has been examined previously.[20] It is of note that self-CI is essentially a form of chemical activation forming internally, rotationally hot complexes via bimolecular association.[21] Aubanel et al. have pointed out that, though this process of excitation is widely used, the angular momentum distributions resulting from formation of the collision complex are not well understood.[16c]

Briefly, we must mention the chloroform/Cl$^-$ KIE dependence on collision energy shown in Figure 3. These data reveal the energy dependence of the measured KIE for different isotopomers. The corresponding plot for the deuterated species also shows a strong isotope effect. Precursor ion abundances were also measured as a function of collision energy and found to decay exponentially (not shown). Additional features of the data, including the effect of electron energy, will be taken up in full in a later study. These results and the incomplete correspondence in behavior of the chlorine adducts of chloroform, carbon tetrachloride, and methylene chloride point to additional complexities in this system.

Conclusions

We have demonstrated the existence of an anomalous heavy-atom kinetic isotope effect in the decomposition of methylene chloride/Cl$^-$, chloroform/Cl$^-$, and carbon tetrachloride/Cl$^-$ complexes formed in a number of ion sources and analyzed in various mass spectrometers. These effects were explored in more detail using chemical ionization in a triple quadrupole mass spectrometer. We interpret these results in the context of rotational threshold behavior and changing angular momentum distributions due to differing ion source conditions. We also show that small changes in barrier height (associated with examination of particular chlorine isotopomers or with H-for-D substitution) have a large impact on the measured KIE of eq 2. On the other hand, the distinctly different behavior of individual isotopomers and the energy dependence of each isotopomer allow the conclusion that the relevant region of the potential energy surface likely is a complex surface leading to nonmonotonic behavior.

The chloroalkanes and chlorinated solvents studied here are major components of reactive chlorine in the environment.[22] Formation and decomposition reactions such as those described, induced by collisions in the troposphere and stratosphere, could influence the distribution of isotopes in the environment, although no such measurements have been reported.[23] Thus, this large heavy-atom kinetic isotope effect might have significant implications for atmospheric chemistry. It is noteworthy that another crucial atmospheric molecule, ozone, also exhibits a KIE that not only goes to unity at high pressure but is also isotopomer specific.[15,20b] The degree to which the underlying phenomena are similar in the two systems awaits further exploration.

The most significant aspect of this study might be the implication that it is possible to observe either extremely large or extremely small intramolecular isotope effects when the dissociation of a cluster ion containing more than one isotope of an element is examined. The former case (large normal KIEs) is well-known in mass spectrometry and is associated with near-threshold fragmentation by the common vibrational predissociation mechanism. The latter case (extremely large inverse KIEs) has been encountered here and is tentatively assigned to near threshold dissociation of rotationally excited metastable species.

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