to CCl_4) and CH_3Br. The nascent complexes formed in these collisions apparently are too short-lived to survive the flight time from the ion source to the detector (ca. 20 μs) and cannot be detected. However, at source pressures of about 0.1 Torr CH_3Br (collision frequency 5×10^6 s^{-1}), these short-lived complexes can be intercepted within the ion source and "cooled" by third-body collisions, resulting in longer adduct lifetimes. With these source conditions, adducts with lifetimes in excess of the requisite 20 μs can be detected, and a fraction of these adducts undergoes metastable unimolecular dissociation in the second field-free region of the mass spectrometer.

On the time scale of these experiments (tens of microseconds), the metastable $Cl^-(CH_3Br)$ species dissociates to yield *only* Br^- and CH_3Cl (i.e., the S_N2 displacement products), with an average kinetic energy release of 30 ± 10 meV. Collision-induced dissociation (CID) of $Cl^-(CH_3Br)$ (8-keV laboratory energy collisions, helium target gas) yields both Cl^- and Br^- ionic products in comparable quantities. By comparison, metastable dissociation is not observed for $Br^-(CH_3Cl)$ generated under conditions of pressure and temperature similar to those used for $Cl^-(CH_3Br)$.[21] CID of $Br^-(CH_3Cl)$ yields predominantly Br^- and only a small amount of Cl^- (<5%).[22] These results demonstrate that the $Cl^-(CH_3Br)$ and $Br^-(CH_3Cl)$ species are unique and distinguishable isomers that do not interconvert to a significant extent in the ion source. We have modeled with statistical theory[23] the internal energy dependences of the branching ratios for CID of $Cl^-(CH_3Br)$ and $Br^-(CH_3Cl)$, and the results suggest that the observed CID products arise from clusters with internal energies of 1–2 eV. This range is consistent with previous observations of energy deposition for high-energy CID of negative ions.[24]

The nascent $Cl^-(CH_3Br)$ collision complexes have internal energies of 0.5 eV or greater (i.e., the cluster bond energy)[25] and, based on our experimental results, lifetimes of less than 10^{-6} s. Thus, adducts with internal energies in excess of 0.5 eV do not survive long enough to reach the second field-free region, which provides a practical upper limit of about 0.5 eV for the internal energies of the metastable $Cl^-(CH_3Br)$ ions. The requirement that the internal energy exceed the intrinsic barrier to displacement provides a lower limit of 0.4 eV.[5,7] We have calculated with phase space theory the kinetic energy release distribution that would result for statistical unimolecular dissociation of $Cl^-(CH_3Br)$ species with internal energies that fall in the range between 0.4 and 0.5 eV. The reaction is modeled[23] with a double-well potential energy surface,[5,6,11-13] shown schematically in Figure 1. These calculations incorporate explicitly the angular momentum constraints imposed by the S_N2 transition state.[27]

The kinetic energy release distribution calculated assuming a constant probability for internal energies between 0.4 and 0.5 eV is compared in Figure 2 with the experimental result, which is clearly much narrower. Variation of the parameters used in the calculation within physically reasonable limits results in only small changes in the calculated distribution, and under no circumstances does it reproduce the experimental distribution. The balance of the energy released in the S_N2 displacement *must* appear as internal excitation of the CH_3Cl product. Consideration of the S_N2 reaction mechanism leads us to suggest that this excess internal energy most likely corresponds to excitation of the C–Cl stretch (732 cm^{-1})[28] and/or the CH_3 umbrella (1355 cm^{-1})[28] vibrational modes. Thus, we believe our experimental results to be evidence of significant vibrational excitation in the products of S_N2 reactions. From the principle of microscopic reversibility, one might speculate that vibrational excitation in the products of S_N2 reactions is related to the vibrational mode specific effects in the bimolecular reactions as predicted by Vande Linde and Hase.[11]

We are currently in the process of examining several other aspects of the $Cl^-(CH_3Br)$ metastable and collisionally activated dissociations and have extended the studies to $Cl^-(CH_3I)$ and $Br^-(CH_3I)$. These results will be reported in a future publication.[29]

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-88-17201). S.T.G. is grateful to the UC President's Fellowship program for support in the form of a postdoctoral fellowship. We thank Dr. Petra van Koppen for helpful discussions regarding the phase space calculations.

Registry No. Cl^-, 16887-00-6; CH_3Br, 74-83-9; CH_3Cl, 74-87-3.

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Collisional Activation of Captured Intermediates in the Gas-Phase S_N2 Reaction $Cl^- + CH_3Br \rightarrow Br^- + CH_3Cl$

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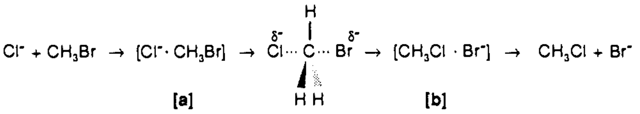
The exothermic S_N2 reaction (reaction 1) is thought to proceed over a double minimum potential energy surface in the gas phase.[1,2] The two minima are common for this class of reactions[3,4] and correspond to the ion–dipole bound complexes [a] and [b], which are separated by the transition state for reaction.[5] The inter-



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mediates [a] and [b] have been isolated previously in the gas phase[2,3] and have been shown to be distinguishable by their halide-transfer chemistry.[1b] We regard [a] and [b] as the entrance and exit channel complexes of the reaction, respectively. Calculations[2,6] support the inference from kinetic data[1,7] that the transition-state potential barrier lies ~1–2 kcal below the energy of separated reactants but well above the ion–dipole minima, completely analogous to the situation discussed in the accompanying paper by Wilbur and Brauman. Because reaction 1 proceeds on only about 1% of the bimolecular encounters,[2,8,9] it is possible to collisionally stabilize the reaction complex in the entrance channel of the potential energy surface. In their accompanying paper, Graul and Bowers capture the entrance channel intermediate [a] with sufficient internal excitation to monitor its unimolecular decay into Br^- product.[10] It should also be possible to access this energy regime by first stabilizing the complex near the potential minimum and then injecting it with an appropriate amount of energy.[11] These cooled intermediates should provide an excellent means of orienting and locking[6] the reagents together prior to initiation of reaction. In this report, we explore the suitability of these complexes for such studies by initiating reaction 1 from the [a] and [b] complexes formed in a cold free jet expansion.

The ionic complexes are formed by electron-impact ionization in the high-density region of a pulsed free jet and analyzed with a tandem time-of-flight mass spectrometer.[12] Although we have no direct evidence in this case, other complexes (e.g., Ne_n^+ and $O_2^-{\cdot}N_2$) formed under these conditions have been shown to be internally cooled,[13] and no appreciable metastable decay is observed from either complex. The UV photodetachment cross sections were determined with a frequency-doubled Nd:YAG pumped dye laser. Collisional activation is performed by passing the high-energy ion beam (2.5 keV) through a second pulsed argon expansion before separation of the parent and daughter ions in a second mass spectrometer.[14] The parent beam attenuation was in the range 10–50%. The [a] and [b] complexes are synthesized by generating Cl^- and Br^- in the presence of excess CH_3Br and CH_3Cl, respectively. The following scheme was used for preparation of [a]:

$$CHCl_3 \xrightarrow{e^-} Cl^- + CHCl_2 \qquad (2)$$

$$CH_3Br \xrightarrow{e^-} Br^- + CH_3 \qquad (3)$$

$$Cl^- + CH_3Br \rightarrow CH_3Cl + Br^- \qquad (4)$$

$$Cl^- + CH_3Br + M \rightarrow [a] + M \qquad (5)$$

$$Br^- + CHCl_3 + M \rightarrow Br^-{\cdot}CHCl_3 + M \qquad (6)$$

so that the complex between Br^- and the Cl^- source (reaction 6) is distinguishable from [a]. Since the $Cl^-{\cdot}CH_3Cl$ complex is not observed in the mass spectrum, we conclude that reaction 4[15] does not build up significant CH_3Cl product to allow formation of [b]. Similarly, we have isolated the [b] complex using the reaction sequence

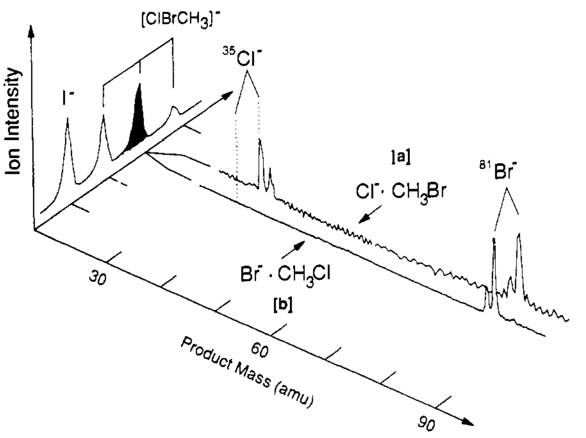

Figure 1. Ionic products from the collisional activation of $Cl^-{\cdot}CH_3Br$ and $Br^-{\cdot}CH_3Cl$ reaction intermediates. The shaded peak identifies the $[^{35}ClCH_3{}^{81}Br]^-$ and the $[^{37}ClCH_3{}^{79}Br]^-$ components of the 131-amu peak, which is collisionally activated to form products Br^- and Cl^-.

$$CHBr_3 \xrightarrow{e^-} Br^- + CHBr_2 \qquad (7)$$

$$Br^- + CH_3Cl + M \rightarrow [b] + M \qquad (8)$$

A typical parent ion mass spectrum is displayed along the depth axis of Figure 1, where a small amount of CH_3I has been added to furnish the I^- mass marker.

The integrity of the syntheses in preparing pure [a] and [b] was checked by monitoring the photodetachment cross sections of the complexes. Because of the greater electron affinity of Cl^- over Br^- *and* the slightly larger binding energy[2,6,3b] anticipated for the entrance [a] complex relative to [b], we expect [a] to have a higher photodetachment threshold than [b] by about 0.32 eV. We therefore scanned the photodetachment spectra of each complex to empirically determine that 312 nm was sufficient to detach an electron from [b] but not [a]. These experiments place an upper bound of 5% on the amount [b] contaminant in the isolated [a].

The results of the collisional-activation experiments are summarized in Figure 1, which displays the ionic products resulting from the unresolved $[^{35}ClCH_3{}^{81}Br]^-$ and $[^{37}ClCH_3{}^{79}Br]^-$ parent ions in the mass-selected 131-amu peak. The two traces along the product mass axis correspond to the breakup of the [a] and [b] complexes in the far and near fields of view, respectively. The pattern from [b] contains only Br^- product ions, indicating that the reverse of reaction 1 is highly unfavorable. The entrance channel complex [a], however, produces both Cl^- reactants and Br^- products in approximately equal abundance (the observed[16] branching ratio for Br^- production is 0.52 ± 0.10), similar to that obtained by Graul and Bowers.[10] Similar results have been obtained for intermediates in the $Br^- + CH_3I$ reaction.[17]

Under our experimental conditions, it is estimated (from high energy collisional activation work[18]) that the ions are excited with a distribution of internal energies peaking at ~0.65 eV with a width on the order of 1 eV. This is sufficient energy to excite the entrance channel complex [a] over the calculated potential barrier (~0.32 eV above the entrance channel minimum[6]). The enhanced reaction efficiency of the activated entrance channel

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complex over that of the low-energy bimolecular collision (~50% vs 1%) is consistent with the transition-state barrier lying below the energy of reactants; that is, a large fraction of the collisionally activated complexes appear to be prepared in an energy range below the entrance channel asymptote and above the transition state. The failure of the exit channel complex [b] to back-react and form Cl^- is anticipated by the high density of states of the Br^- product channel relative to that of the tight transition state for the reaction.

In summary, we have isolated and activated two distinct species captured on the potential energy surface of the gas-phase S_N2 reaction (1). The intermediate corresponding to reactants trapped along the entrance channel reacts to form products with an efficiency of ~50%, far greater than that of the bimolecular reaction, while the intermediate trapped in the exit channel exclusively forms Br^- products upon collisional activation. These results demonstrate the possibility of triggering S_N2 reactions starting from specific configurations along the reactive potential energy surface.

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Registry No. Cl^-, 16887-00-6; Br^-, 24959-67-9; CH_3Cl, 74-87-3; CH_3Br, 74-83-9.

Intermediates and Potential Surfaces of Gas-Phase S_N2 Reactions

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We report the formation of a putative intermediate in an exothermic gas-phase S_N2 reaction (eq 1) and its induced unimolecular dissociation to both products and reactants. To our knowledge, the isolation and energization of a stable S_N2 intermediate to form products has not previously been reported.[1] This is due in part to the paucity of appropriate systems, which require an internal barrier sufficiently high to allow isolation of the adducts but low enough to accommodate conversion of the intermediate to products. Studies of this type provide direct information about the potential surfaces for gas-phase S_N2 reactions and present the opportunity to evaluate existing models experimentally.

$$CF_3CO_2CH_3 + Cl^- \rightarrow [CF_3CO_2CH_3Cl]^- \rightarrow CF_3CO_2^- + CH_3Cl \quad (1)$$

Nucleophilic displacement reactions have been studied extensively in solution,[2] in the gas phase[3] and by theory.[4] An important goal of these investigations has been to obtain an accurate picture of the potential energy surface for gas-phase S_N2 reactions. The double-minimum potential surface (shown schematically in Figure 1) exhibits two ion–dipole complexes as minima separated by a transition state. Such a surface was first proposed to explain the observation that gas-phase S_N2 reactions can proceed at rates below the collision rate.[3e] Subsequent experimental[3e–q] and theoretical[4h–m,p,q] studies have been consistent with the proposed surface. Complexes corresponding to intermediates in gas-phase S_N2 reactions have been generated[3e,k,5] and shown to be unsymmetrical[3e,5a] but have never been converted successfully to products. In isolating an intermediate and inducing its unimolecular decomposition to products, we provide a missing link in the direct characterization of the topology of the potential surface.

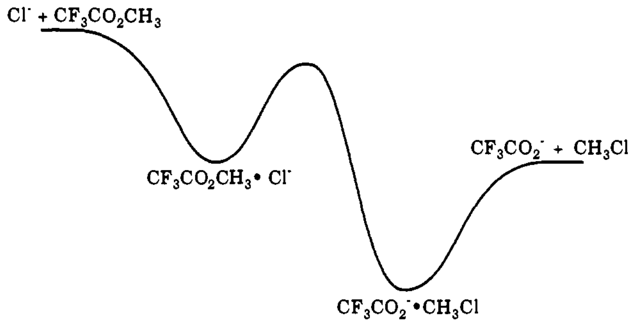

Figure 1. The double-minimum surface for gas-phase S_N2 reaction 1. Minima correspond to complexes bound by electrostatic attractions between the ion and the dipole of the neutral.

All experiments were performed with an IonSpec OMEGA system, equipped with impulse excitation.[6] Other details of the

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