

(memory of chirality). We believe that this concept can lead to new developments in asymmetric synthesis.

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**Supplementary Material Available:** Analytical and spectral data for **1**, **4a-d**, **13**, and **14** and synthetic procedure for **1** (10 pages). Ordering information is given on any current masthead page.

## The Nonstatistical Dissociation Dynamics of $\text{Cl}^-(\text{CH}_3\text{Br})$ : Evidence for Vibrational Excitation in the Products of Gas-Phase $\text{S}_{\text{N}}2$ Reactions

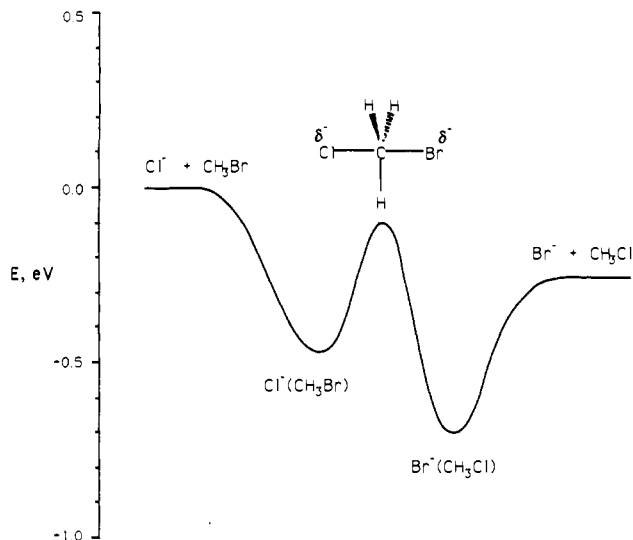
Susan T. Graul and Michael T. Bowers\*

Department of Chemistry, University of California  
Santa Barbara, California 93106

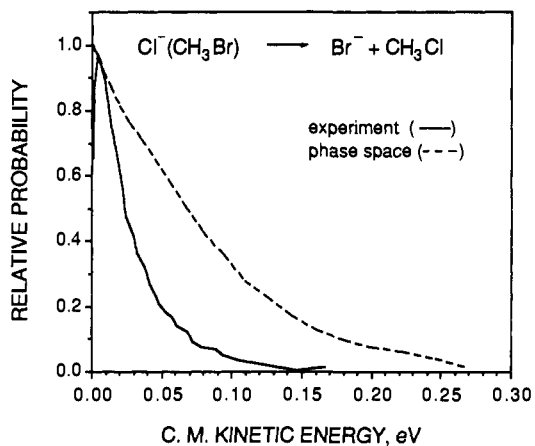
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Gas-phase bimolecular nucleophilic substitution ( $\text{S}_{\text{N}}2$ ) reactions of halide ions with methyl halides have been the subject of numerous experimental<sup>1-10</sup> and theoretical<sup>11-15</sup> studies. Results of recent theoretical studies by Vande Linde and Hase have led to the suggestion that these reactions may exhibit vibrational mode specific reaction rate enhancement.<sup>11</sup> If this is true, then the dynamics of these reactions may display measurable deviations from predictions of statistical theories such as RRKM<sup>16</sup> and phase space theory.<sup>17</sup> One approach to examining the dynamics of

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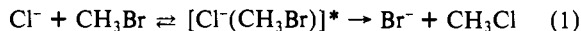


**Figure 1.** The schematic reaction coordinate diagram used to model the  $\text{S}_{\text{N}}2$  reaction  $\text{Cl}^- + \text{CH}_3\text{Br} \rightarrow \text{Br}^- + \text{CH}_3\text{Cl}$ . The energies of the  $\text{Cl}^-(\text{CH}_3\text{Br})$  and  $\text{Br}^-(\text{CH}_3\text{Cl})$  complexes and of the  $\text{S}_{\text{N}}2$  transition state have been determined experimentally.<sup>7,23</sup> The relative energies of the  $\text{Cl}^- + \text{CH}_3\text{Br}$  reactants and the  $\text{Br}^- + \text{CH}_3\text{Cl}$  products are taken from ref 24.



**Figure 2.** Experimental and theoretical kinetic energy release distributions for the metastable displacement reaction  $\text{Cl}^-(\text{CH}_3\text{Br})$ . The theoretical curve is calculated for  $\text{Cl}^-(\text{CH}_3\text{Br})$  complexes with internal energies between 0.4 and 0.5 eV (see text).

reactive bimolecular collisions is to study the unimolecular dissociation of a species that corresponds to the reaction intermediate.<sup>18,19</sup> We have recently succeeded in measuring the kinetic energy release distribution (KERD) for metastable dissociation of the  $\text{Cl}^-(\text{CH}_3\text{Br})$  species, which may serve as a model for the intermediate in the bimolecular reaction (1). Comparison of the



experimental distribution with the distribution predicted by phase space theory reveals significant deviations, which we believe can be attributed to vibrational excitation of the  $\text{CH}_3\text{Cl}$  product.

The KERD measurements were carried out for second field-free region unimolecular dissociations in a reverse geometry sector mass spectrometer (V.G. Analytical ZAB-2F), using methods that have been described previously.<sup>20</sup> The  $\text{Cl}^-(\text{CH}_3\text{Br})$  species are formed by means of thermal energy ( $\sim 300$  K) ion-molecule capture collisions of  $\text{Cl}^-$  (generated by dissociative electron attachment

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to  $\text{CCl}_4$ ) and  $\text{CH}_3\text{Br}$ . 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  $\mu\text{s}$ ) and cannot be detected. However, at source pressures of about 0.1 Torr  $\text{CH}_3\text{Br}$  (collision frequency  $5 \times 10^6 \text{ s}^{-1}$ ), 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  $\mu\text{s}$  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  $\text{Cl}^-(\text{CH}_3\text{Br})$  species dissociates to yield *only*  $\text{Br}^-$  and  $\text{CH}_3\text{Cl}$  (i.e., the  $\text{S}_{\text{N}}2$  displacement products), with an average kinetic energy release of  $30 \pm 10 \text{ meV}$ . Collision-induced dissociation (CID) of  $\text{Cl}^-(\text{CH}_3\text{Br})$  (8-keV laboratory energy collisions, helium target gas) yields both  $\text{Cl}^-$  and  $\text{Br}^-$  ionic products in comparable quantities. By comparison, metastable dissociation is not observed for  $\text{Br}^-(\text{CH}_3\text{Cl})$  generated under conditions of pressure and temperature similar to those used for  $\text{Cl}^-(\text{CH}_3\text{Br})$ .<sup>21</sup> CID of  $\text{Br}^-(\text{CH}_3\text{Cl})$  yields predominantly  $\text{Br}^-$  and only a small amount of  $\text{Cl}^-$  (<5%).<sup>22</sup> These results demonstrate that the  $\text{Cl}^-(\text{CH}_3\text{Br})$  and  $\text{Br}^-(\text{CH}_3\text{Cl})$  species are unique and distinguishable isomers that do not interconvert to a significant extent in the ion source. We have modeled with statistical theory<sup>23</sup> the internal energy dependences of the branching ratios for CID of  $\text{Cl}^-(\text{CH}_3\text{Br})$  and  $\text{Br}^-(\text{CH}_3\text{Cl})$ , 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.<sup>24</sup>

The nascent  $\text{Cl}^-(\text{CH}_3\text{Br})$  collision complexes have internal energies of 0.5 eV or greater (i.e., the cluster bond energy)<sup>25</sup> and, based on our experimental results, lifetimes of less than  $10^{-6} \text{ s}$ . 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  $\text{Cl}^-(\text{CH}_3\text{Br})$  ions. The requirement that the internal energy exceed the intrinsic barrier to displacement provides a lower limit of 0.4 eV.<sup>5,7</sup> We have calculated with phase space theory the kinetic energy release distribution that would result for statistical unimolecular dissociation of  $\text{Cl}^-(\text{CH}_3\text{Br})$  species with internal energies that fall in the range between 0.4 and 0.5 eV. The reaction is modeled<sup>23</sup> with a double-well potential energy surface,<sup>5,6,11–13</sup> shown schematically in Figure 1. These calculations incorporate explicitly the angular momentum constraints imposed by the  $\text{S}_{\text{N}}2$  transition state.<sup>27</sup>

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  $\text{S}_{\text{N}}2$  displacement *must* appear as internal excitation of the  $\text{CH}_3\text{Cl}$  product. Consideration of the  $\text{S}_{\text{N}}2$  reaction mechanism leads us to suggest that this excess internal energy most likely corresponds to excitation of the C–Cl

stretch ( $732 \text{ cm}^{-1}$ )<sup>28</sup> and/or the  $\text{CH}_3$  umbrella ( $1355 \text{ cm}^{-1}$ )<sup>28</sup> vibrational modes. Thus, we believe our experimental results to be evidence of significant vibrational excitation in the products of  $\text{S}_{\text{N}}2$  reactions. From the principle of microscopic reversibility, one might speculate that vibrational excitation in the products of  $\text{S}_{\text{N}}2$  reactions is related to the vibrational mode specific effects in the bimolecular reactions as predicted by Vande Linde and Hase.<sup>11</sup>

We are currently in the process of examining several other aspects of the  $\text{Cl}^-(\text{CH}_3\text{Br})$  metastable and collisionally activated dissociations and have extended the studies to  $\text{Cl}^-(\text{CH}_3\text{I})$  and  $\text{Br}^-(\text{CH}_3\text{I})$ . These results will be reported in a future publication.<sup>29</sup>

**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.**  $\text{Cl}^-$ , 16887-00-6;  $\text{CH}_3\text{Br}$ , 74-83-9;  $\text{CH}_3\text{Cl}$ , 74-87-3.

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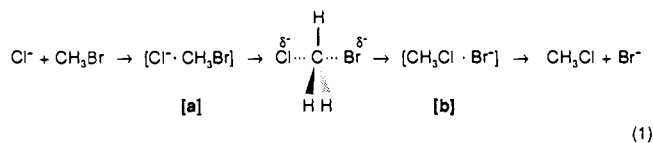
### Collisional Activation of Captured Intermediates in the Gas-Phase $\text{S}_{\text{N}}2$ Reaction $\text{Cl}^- + \text{CH}_3\text{Br} \rightarrow \text{Br}^- + \text{CH}_3\text{Cl}$

Donna M. Cyr, Lynmarie A. Posey,<sup>†</sup> Gregory A. Bishea, Chau-Chung Han,<sup>‡</sup> and Mark A. Johnson\*<sup>§</sup>

Department of Chemistry, Yale University  
225 Prospect Street, New Haven, Connecticut 06511

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The exothermic  $\text{S}_{\text{N}}2$  reaction (reaction 1) is thought to proceed over a double minimum potential energy surface in the gas phase.<sup>1,2</sup> The two minima are common for this class of reactions<sup>3,4</sup> and correspond to the ion-dipole bound complexes [a] and [b], which are separated by the transition state for reaction.<sup>5</sup> The inter-



<sup>†</sup> Current address: Department of Chemistry, Vanderbilt University, Nashville, TN.

<sup>‡</sup> Current address: Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan, Republic of China.

<sup>§</sup> NSF Presidential Young Investigator and Camille and Henry Dreyfus Teacher-Scholar.

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(21) The  $\text{Br}^-$  ions are formed by dissociative electron attachment to  $\text{CH}_2\text{Br}_2$ , and subsequent clustering reactions with  $\text{CH}_3\text{Cl}$  yield the  $\text{Br}^-(\text{CH}_3\text{Cl})$  cluster. No  $\text{CH}_3\text{Br}$  is present.

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