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Non-Statistical Effects in the Gas Phase S_N2 Reaction

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The S_N2 reaction occupies a singularly important position in gas-phase ion chemistry.[1,2] Some two decades ago, Brauman and co-workers[3] demonstrated that the S_N2 reaction of Cl^- with CH_3Cl, eq 1, was very slow and that this could be explained by a significant intermediate barrier on a double minimum potential energy surface. Riveros[4] also demonstrated, at this time, that the preparation of the $ClCH_3Cl^-$ ion by chloride transfer from $ClCO^-$ to CH_3Cl resulted in a species in which the two chlorines were distinguishable. Subsequent experimental studies of S_N2 reactions have provided information on the energetic positions of the central barrier[5−8] as well as the stable intermediate complexes for reaction of halide ions with alkyl halides.[8] For reaction 2, the potential

$$^{35}Cl^- + CH_3{}^{37}Cl \rightarrow {}^{37}Cl^- + CH_3{}^{35}Cl \qquad (1)$$

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

energy profile shown in Figure 1 has been obtained experimentally in our laboratory. This experimental potential energy surface is nearly identical to that determined by ab initio calculations.[9−11] Hase has also performed trajectory calculations for reactions 1 and 2[12−14] which showed that the complexes initially formed between the reactant ion and neutral molecule have very short lifetimes (<10 ps). During this lifetime there is very poor energy transfer between the new, so-called, intermolecular vibrational modes, coupling Cl^- and the alkyl halide, and the intramolecular modes, associated with the alkyl halide moiety itself. Complex formation thus results in vibrational energy localized initially in the three new intermolecular modes of the complex, and the poor mode coupling inhibits energy flow to the methyl halide modes, which consequently impedes barrier crossing. Hase's trajectory studies also indicate that neither of these two bimolecular reactions behaves statistically because of the poor mode coupling.[15,16] Experiments by Graul and Bowers,[17] Viggiano and co-workers[18,19] and Ervin and co-workers[20] all strongly supported the occurrence of nonstatistical dynamics in the bimolecular reaction. Hase's calculations[15] have also predicted that if the low-frequency intermolecular modes of the $[Cl^-\cdots(CH_3Br)]$ complex are excited then dissociation should proceed predominantly via Cl^- formation. Conversely, if the higher frequency, intramolecular modes are excited, then the Br^- product will become the more important reaction channel because barrier crossing is facilitated. The experiments described below provide a means of assessing this prediction.

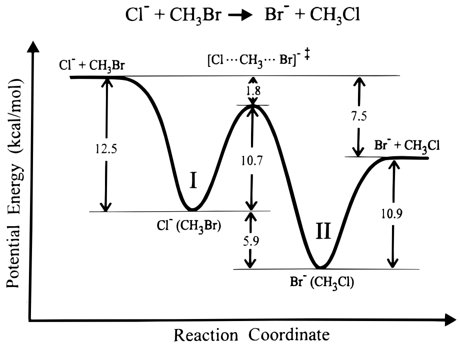

Figure 1. Experimentally determined potential energy surface for the gas-phase reaction of Cl^- with CH_3Br.

All experiments were performed on a Fourier transform ion cyclotron resonance (FTICR) spectrometer to which a high-pressure external source has been mated. The features of this apparatus,[21] as well as FTICR techniques in general,[22] have been described in detail previously. Using the capability of trapping weakly bound cluster ions for long periods of time, we have shown that it is possible to study unimolecular dissociation of ions resulting from absorption of blackbody radiation emitted by the cell walls.[23] More recently, we have also demonstrated that sequential infrared, multiphoton dissociations (IRMPD) can be effected via the introduction of a low power CW CO_2 laser beam into the FTICR cell through a bistable shutter.[24]

The $[Cl^-\cdots CH_3Br]$ complex was synthesized via a route which involved introduction of a ~10-fold excess of benzene, relative to CH_3Br, into the reaction mixture. This resulted in the efficient formation of the intermediate $[Cl^-\cdots C_6H_6]$ complex, eq 3, followed by the soft transfer of Cl^- to CH_3Br, eq 4.

$$Cl^- + C_6H_6 \rightleftarrows [Cl^-\cdots C_6H_6] \qquad (3)$$

$$[Cl^-\cdots C_6H_6] + CH_3Br \rightarrow [Cl^-\cdots CH_3Br] + C_6H_6 \qquad (4)$$

This latter transfer is only ~4 kcal mol^{-1} exothermic,[25] and the S_N2 intermediate thus formed does not have sufficient internal energy, on average, to dissociate, either via loss of Cl^- or by crossing the central barrier to give Br^-. The $[Cl^-\cdots CH_3Br)]$ ion represented only ~1% of the total ion population arriving at the FTICR cell, however, using rf ion ejection techniques, all ions except the desired S_N2 intermediate could be eliminated from the ICR cell. Following isolation of this S_N2 reaction intermediate, the blackbody radiation induced dissociation was investigated. The complex was allowed to undergo thermalizing collisions for up to 15 s with background CH_4 in the ICR cell, after which time any products formed were ejected again. The unimolecular dissociation kinetics of the re-isolated complex were then deter-

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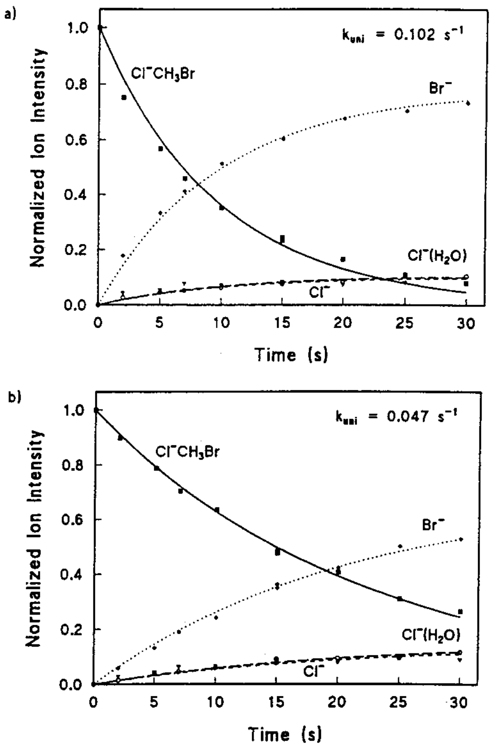

Figure 2. (a) Variation of relative ion intensities with reaction time for the CW CO_2 laser enhanced dissociation of $Cl^-(CH_3Br)$ at 20 °C and a laser power of 9.9 W cm^2. (b) Variation of relative ion intensities with reaction time for the blackbody infrared radiation induced dissociation of $Cl^-(CH_3Br)$ at 20 °C.

mined. As can be seen from the representative data shown in Figure 2b there are three products observed. The first two, eqs 5a and 5b, are the direct unimolecular dissociation products, Cl^- and Br^- respectively, in a ratio of ~1:5. The third product, $[Cl^-\cdots(H_2O)]$, eq 5c, is the result of the exothermic bimolecular chloride transfer reaction from $[Cl^-\cdots(CH_3Br)]$ to background water in the system.

$$[Cl^-\cdots(CH_3Br)] \longrightarrow Cl^- + CH_3Br \qquad (5a)$$

$$[Cl^-\cdots(CH_3Br)] \longrightarrow Br^- + CH_3Cl \qquad (5b)$$

$$[Cl^-\cdots(CH_3Br)] + H_2O \rightarrow [Cl^-\cdots(H_2O)] + CH_3Br \qquad (5c)$$

Assuming that this reaction proceeds near the collision rate, the background H_2O pressure can be estimated to be ~10^{-10} Torr. The complete absence of appearance of any $[Br^-\cdots(H_2O)]$ establishes that there are no exit channel complexes formed in the preparation of the $[Cl^-\cdots(CH_3Br)]$ entrance channel complex, since Br^- transfer from $[Br^-\cdots(CH_3Cl)]$ to H_2O is also exothermic. Separate experiments established that the Cl^- product does not arise from blackbody radiation induced dissociation of $[Cl^-\cdots(H_2O)]$. This species is not observed to dissociate to any measurable extent under the present experimental conditions.

Assuming that absorption of blackbody radiation leads to a truncated Boltzmann distribution of internal energies, the analysis of Dunbar,[26] applied to the temperature dependence for the two reaction channels,[27,28] gives a difference in activation energies of 1.3 kcal mol^{-1}. This is very close to the enthalpy difference of 1.8 kcal mol^{-1} obtained both by HPMS experiments[8,28] and ab initio calculations[10] and significantly less than the difference of 4.7 kcal mol^{-1} suggested by the experiments of Seeley et al.[19]

To test the prediction of Hase[15] regarding the effect of exciting different modes of the S_N2 complex, experiments were carried out in which the isolated $[Cl^-\cdots(CH_3Br)]$ intermediate was continuously irradiated during the entire reaction period by the low power output of a CW CO_2 laser. The results of this experiment are shown in Figure 2a. Since the absorption by the complex at 943 cm^{-1} is weak, both blackbody radiation-induced dissociation as well as the CO_2 laser-induced dissociation are occurring. To obtain information on the effect of laser irradiation alone, difference spectra were generated, such as that shown in Figure 3 for 15 s reaction time, in which the spectrum obtained without laser irradiation was subtracted from that obtained with laser irradiation. The resulting spectrum shows only the consequences of irradiation of the S_N2 complex at 943 cm^{-1}. The negative going peaks corresponding to the various isotopic $[Cl^-\cdots(CH_3Br)]$ species show that the complex is dissociated by the laser irradiation. The positive going Br^- peak indicates that Br^- is produced by the laser induced dissociation of the $[Cl^-\cdots(CH_3Br)]$ complex. Significantly, no Cl^- peak is present, indicating that those S_N2 complexes which absorbed radiation into an intramolecular mode, dissociated *exclusively* to give Br^-, exactly as predicted by Hase's trajectory simulations.

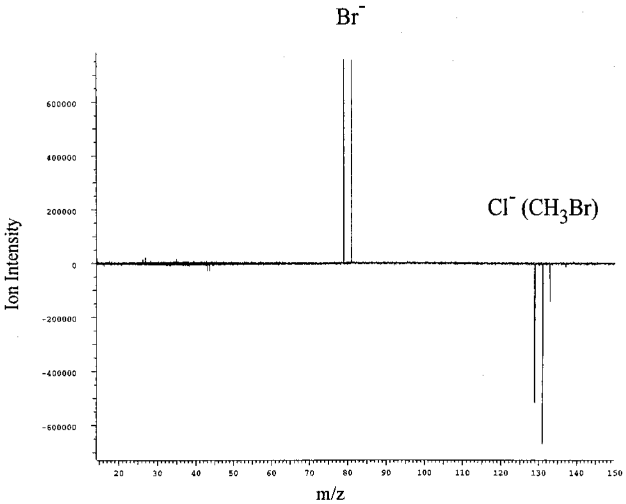

Figure 3. Difference spectrum (laser ON−laser OFF) for $Cl^-(CH_3Br)$ taken at 15 s reaction time in the experiments shown in Figure 2. The sum of the intensities of the three negative peaks is equal to that of the two positive peaks. The small features near *m/z* 26 and *m/z* 44 are due to the third harmonics of Br^- and $Cl^-(CH_3Br)$, respectively.

Recent experiments by Johnson and co-workers[29] also show that resonant absorption into the doubly degenerate C−H stretch modes of the complex leads to selective enhancement of Br^- production. These experiments do not provide any information as to whether the dissociation is nonstatistical, however, because they involve single photon absorption at 3175 cm^{-1} and this provides insufficient energy to give rise to formation of Cl^-.

While the results presented above do not provide definitive proof of non-statistical dynamics in the dissociation of $[Cl^-\cdots(CH_3Br)]$, they are consistent with the prediction of Hase and co-workers that excitation of the CH_3Br intramolecular modes of the $[Cl^-\cdots(CH_3Br)]$ complex should lead to selective enhancement of central barrier crossing on the S_N2 double minimum potential energy surface. The S_N2 reaction thus continues to be one of considerable interest for exploring fundamental aspects of chemical dynamics.

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(28) It is important to note, however, that if the bimolecular reaction does behave non-statistically, then the transition-state theory treatment to derive the enthalpy of activation for the reaction is not valid. The blackbody radiation-induced unimolecular dissociation of $[Cl^-\cdots(CH_3Br)]$ may also arise from a non-Boltzmann distribution. Population of intramolecular and intermolecular modes occurs via absorption from the appropriate region of the blackbody spectrum. While these complexes will then have vibrational energy in each of these types of modes, communication between the modes may be too slow, on the time scale of the experiment, to achieve a Boltzmann like distribution.

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