

# Gas-Phase Proton-Transfer and Substitution Reactions: Energy Dependence and Dissociation Dynamics

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Received February 16, 1993\*

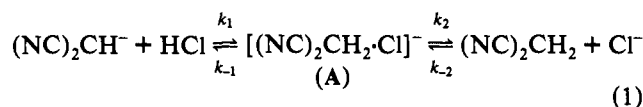
**Abstract:** The energy dependence of the branching ratio for the dissociation of a proton-transfer reaction intermediate,  $[(\text{NC})_2\text{CH}_2\cdot\text{Cl}]^-$ , has been observed in the gas phase using Fourier transform ion cyclotron resonance spectrometry. The intermediate in the near-thermoneutral proton-transfer reaction  $(\text{NC})_2\text{CH}^- + \text{HCl} \rightarrow (\text{NC})_2\text{CH}_2 + \text{Cl}^-$  was formed in two distinct and widely separated energy regimes above the thresholds for either reaction channel. Direct infrared multiple photon activation of the thermalized complex was used to access a low-energy regime (0–3 kcal mol<sup>-1</sup> above threshold). Formation of the intermediate through the S<sub>N</sub>2 reaction  $\text{CN}^- + \text{ClCH}_2\text{CN} \rightarrow [(\text{NC})_2\text{CH}_2\cdot\text{Cl}]^-$  was used to access a high-energy regime (30–33 kcal mol<sup>-1</sup> above threshold). The experimental results of the dissociation branching ratios were found to be qualitatively consistent with a statistical RRKM model. Implications for a general picture for the dynamics of gas-phase S<sub>N</sub>2 reactions are discussed.

## Introduction

The temperature or internal energy dependence of chemical reaction rates in both solution and in the gas phase has been the subject of numerous investigations<sup>1–13</sup> and has been reviewed by Magnera and Kebarle.<sup>14</sup> For gas-phase ion–molecule reactions, the effects of temperature can vary significantly from their solution-phase counterparts. The potential energy surface for gas-phase reactions is often dominated by the electrostatic interaction between the ion and the reacting neutral, and as a result, intermediates and even transition states may lie below the energy of the reactants or the products. Thus, the temperature dependence of these reactions is, in many cases, dictated primarily by the temperature dependence of the competing unimolecular processes following formation of an initial reaction complex. In a bimolecular reaction, both collision dynamics (including angular momentum conservation) and energy transfer can play an important role in the study of these competing unimolecular processes. It is useful, therefore, to study the effects of internal energy on the unimolecular processes of an overall bimolecular reaction in the absence of the collision event. This can be accomplished by studying the unimolecular dissociation of an intermediate proton-transfer complex itself.

We have generated the complex  $[(\text{CN})_2\text{CH}_2\cdot\text{Cl}]^-$ , which corresponds to an intermediate<sup>15</sup> in the proton-transfer reaction

between Cl<sup>-</sup> and malononitrile, eq 1. We have created this complex in two discrete and widely separated energy regimes above the threshold for dissociation and observed the effects of internal energy and angular momentum on the dissociation branching ratio. Infrared multiple photon (IRMP) activation of the initially thermalized intermediate complex in eq 1 was used to access a low-energy, low-angular-momentum regime above threshold (0–3 kcal mol<sup>-1</sup>). Chemical activation, via an S<sub>N</sub>2 displacement reaction, was used to prepare the complex in a much higher energy regime above threshold (30–33 kcal mol<sup>-1</sup>), with both high and low angular momentum. Statistical reaction rate, Rice–Ramsperger–Kassel–Marcus (RRKM), theory<sup>16,17</sup> has been used to interpret the results.



The S<sub>N</sub>2 reaction of CN<sup>-</sup> with ClCH<sub>2</sub>CN (chloroacetonitrile) was used to produce the “chemically activated” proton-transfer intermediate A. The substitution reaction, which produces Cl<sup>-</sup> and (NC)<sub>2</sub>CH<sub>2</sub>, is exothermic by approximately 30 kcal mol<sup>-1</sup>. However, the potential energy surface for the S<sub>N</sub>2 reaction intersects the potential energy surface for the related proton-transfer reaction shown above (eq 1). Specifically, the ion–molecule complex  $[(\text{NC})_2\text{CH}_2\cdot\text{Cl}]^-$  which is formed immediately following the substitution event is the same intermediate complex<sup>18</sup> that is important in the near-thermoneutral proton-transfer reaction between (NC)<sub>2</sub>CH<sub>2</sub> (malononitrile) and Cl<sup>-</sup> (eq 1). Thus, by using the exothermicity of the S<sub>N</sub>2 process, we are able to generate the proton-transfer intermediate complex  $[(\text{NC})_2\text{CH}_2\cdot\text{Cl}]^-$  with a large amount of internal energy in order to study the dissociation branching. The sequence which relates the substitution and proton-transfer reactions is shown in Scheme I.

- \* Abstract published in *Advance ACS Abstracts*, September 15, 1993.
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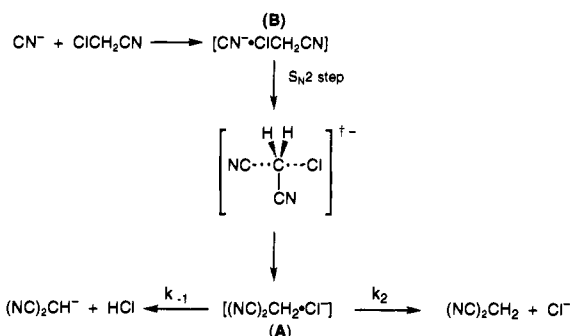
(15) Although there is no evidence to suggest that the proton-transfer reaction should not be described with a double-well potential surface, the barrier to reaction is likely to be small, given the high efficiency of the reaction. Thus, we treat the potential surface as effectively a single well-surface, with a single hydrogen-bound intermediate.

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(18) The expected structures for the S<sub>N</sub>2 and proton transfer complexes may be different. The energy difference is expected to be small, however, and interconversion should be facile.

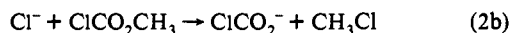
## Scheme 1



The observation that the substitution reaction can produce proton-transfer products also provides valuable information about the dissociation dynamics of ion-molecule complexes in exothermic  $\text{S}_{\text{N}}2$  reactions. The dissociation dynamics of such complexes have been the subject of recent studies, including experimental work by Graul and Bowers<sup>19</sup> Viggiano and co-workers<sup>20,21</sup> and theoretical work by Vande Linde and Hase.<sup>22-25</sup> These papers have focused on issues related to energy transfer within the intermediate complexes, complex lifetimes, kinetic energy release distribution of the products, and statistical modeling. Results on simple  $\text{S}_{\text{N}}2$  systems suggest that energy transfer within the  $\text{S}_{\text{N}}2$  intermediate complexes is slow and that such systems behave nonstatistically. The results presented here on the  $\text{S}_{\text{N}}2$  product branching ratio provide additional information.

## Experimental Section

Experiments were performed with a Fourier transform IonSpec OMEGA ion cyclotron resonance (FT-ICR) spectrometer equipped with impulse excitation.<sup>26</sup> Details of the experimental apparatus can be found elsewhere, along with typical operating conditions.<sup>27</sup> Pressures of the neutral species in the ICR cell were monitored with an ion gauge (Varian 844), which was calibrated against a capacitance manometer when accurate values for the pressure were needed. All chemicals were obtained from Aldrich and subjected to multiple freeze-pump-thaw cycles before introduction into the ICR. For the bimolecular reactions, the primary ion  $\text{CN}^-$  ( $m/z = 26$ ) was generated from HCN [ $(1-5) \times 10^{-7}$  Torr] by dissociative electron attachment and allowed to react with  $\text{ClCH}_2\text{CN}$  [steady-state pressure of  $(2-5) \times 10^{-7}$  Torr]. The stable adduct, corresponding to an intermediate in the gas-phase proton-transfer reaction (A, Figure 1) was synthesized<sup>28</sup> using the method developed by McMahon and co-workers.<sup>29-33</sup> Chloride ion, generated via electron impact (eq 2a), reacted with methyl chloroformate,  $\text{ClCO}_2\text{CH}_3$ , to give the chlorocarbonate anion (eq 2b), which then donated chloride ion to form the desired adduct (eq 2c).



The multimode output of a tunable Lumonics TEA 103-2  $\text{CO}_2$  laser was used for all IRMP-activation experiments. The laser beam was weakly

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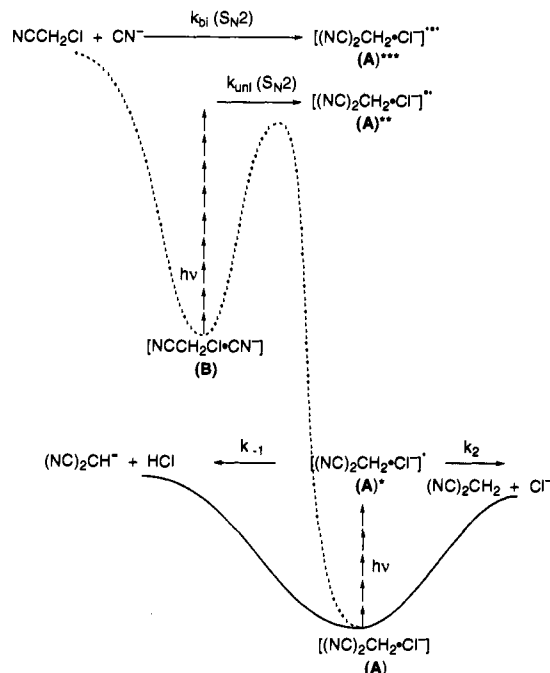


Figure 1. Qualitative potential energy surfaces for  $\text{S}_{\text{N}}2$  (dashed line) and proton-transfer reactions (solid line). See text for details.

focused with a 10-m-radius mirror, reduced to desired spot size using an iris, and allowed to enter the ICR cell through a KCl window. After the beam passed through the ion cloud, a mirror in the back of the ICR cell reflected the pulse back through the ion cloud. The intensity of the laser pulse was attenuated by passing the beam through  $\text{CaF}_2$  flats of varying thickness. Pulse energies were measured using a Scientech 365 power and energy meter with a Scientech 38-0102 volume-absorbing disk calorimeter. Dividing the energy by the measured area of the beam pulse provided the fluence of the incoming beam. This fluence was multiplied by two<sup>34</sup> to determine the effective fluence. For the IRMP experiments, the 9.6- $\mu\text{m}$ , P(18) branch was used, corresponding to a wavelength of 1048.66  $\text{cm}^{-1}$  (3.0  $\text{kcal mol}^{-1}$  photon<sup>-1</sup>).

## Results

The proton-transfer intermediate complex A (eq 1) was prepared via three different routes, and the effect of internal energy on the branching between reactant ( $k_{-1}$ ) and product ( $k_2$ ) channels was observed. IRMP activation of the isolated and thermalized complex A was used to access a low-energy, low-angular momentum regime<sup>35</sup> (0-3  $\text{kcal mol}^{-1}$  above threshold). Chemical activation (CA) via an  $\text{S}_{\text{N}}2$  displacement reaction generated the complex in a much higher energy regime (30-33  $\text{kcal mol}^{-1}$  above threshold) resulting from the exothermicity of the  $\text{S}_{\text{N}}2$  reaction. Figure 1, which shows the relationship between the potential energy surfaces of the  $\text{S}_{\text{N}}2$  and proton transfer reactions, provides a pictorial representation of how the activated intermediates were generated.

**Photochemical Activation (IRMP).** The isolated adduct  $[(\text{NC})_2\text{CH}_2\text{Cl}]$  was formed by the reaction sequence shown above (eqs 2a-c). It was found to transfer  $\text{Cl}^-$  (and not  $\text{CN}^-$ ) to  $\text{ClCH}_2\text{CN}$  readily. In addition, the stability of this intermediate complex was determined by equilibrium measurements and found to be comparable to other known ion-dipole complexes.<sup>32</sup> Together, these data are consistent with a structure in which  $\text{Cl}^-$  is electrostatically (and not covalently) bound. Photochemical activation of this intermediate was accomplished by IRMP

(34) A mirror in the back of the ICR cell reflects the incident laser pulse back through the ion cloud. Thus, the effective fluence is calculated as twice the measured fluence.

(35) For the IRMP experiments, a wavelength of 1048.66  $\text{cm}^{-1}$  (3.0  $\text{kcal mol}^{-1}$ ) was used.

**Table I.** Branching Ratio for the Proton-Transfer Reaction<sup>a</sup> CH<sub>2</sub>(CN)<sub>2</sub> + Cl<sup>-</sup> → CH(CN)<sub>2</sub><sup>-</sup> + HCl as a Function of Internal Energy

method	energy above threshold <sup>b</sup>	expt	stat theory predict <sup>c</sup>
		k <sub>-1</sub> /k <sub>2</sub>	k <sub>-1</sub> /k <sub>2</sub>
chemical activation	30–35	15 ± 3	25–30
IRMP activation of S <sub>N</sub> 2 complex	≈ 30	≈ 10 <sup>d</sup>	20
IRMP activation of PT complex <sup>e</sup>	0–3		0–2.1
(2.8)		0.6	
(3.7)		1.0	
(5.0)		1.4	
(5.5)		2.6	

<sup>a</sup> ΔG<sup>o</sup><sub>298</sub> ≈ 0 and ΔH<sup>o</sup><sub>298</sub> = 2.3 kcal mol<sup>-1</sup> (ref 5). <sup>b</sup> kcal mol<sup>-1</sup>. <sup>c</sup> Statistical RRKM theory was used to determine the branching ratios (see text for details). <sup>d</sup> Only obtained at low fluence due to poor mass balance at higher fluences. <sup>e</sup> Laser fluence in units of J cm<sup>-2</sup> given in parentheses.

activation.<sup>36</sup> Briefly, ions of interest are subjected to infrared radiation and are energized by the absorption of multiple (5–10) photons. If the ions absorb sufficient energy to reach a dissociation threshold and the rate for dissociation competes with the rate of photon absorption, unimolecular decomposition will occur. The absorption rates for pulsed IRMP-activation experiments<sup>27</sup> are estimated to be 10<sup>4</sup>–10<sup>6</sup> photons s<sup>-1</sup>. RRKM calculations, discussed in the Appendix, show that the rate for the dissociation of the intermediate complex is greater than 10<sup>7</sup> s<sup>-1</sup> at or slightly above threshold, indicating that most of the ions which reach energies above threshold dissociate before another photon can be absorbed. Thus, since the energy of a 1048.66-cm<sup>-1</sup> photon is 3.0 kcal mol<sup>-1</sup>, the IRMP-activation experiments are believed to access a similar energy regime roughly 0–3 kcal mol<sup>-1</sup> above the lowest energy threshold for dissociation.

IRMP activation of the intermediate A generates A\* (Figure 1) which undergoes unimolecular dissociation to both the reactants and products of the proton transfer reaction in eq 1. The observed branching ratio between the reactant and the products for the photoactivation experiments is shown in Table I.

**Chemical Activation (S<sub>N</sub>2 reaction).** The S<sub>N</sub>2 reaction which forms the intermediate complex A with excess energy is shown in Scheme I.<sup>37</sup> The S<sub>N</sub>2 reaction sequence was used to form complex A in two different ways. The intermediate complex can be formed with high energy and high orbital angular momentum directly via the bimolecular reaction (A\*\*\*, Figure 1). In the bimolecular reaction, neither complex A nor B is isolated or detected;<sup>28</sup> only the reactant ion (CN<sup>-</sup>) and the product ions (Cl<sup>-</sup> and (CN)<sub>2</sub>CH<sup>-</sup>) are detected. The total ion intensities were measured as a function of time, and first-order decay of the CN<sup>-</sup> ion was observed. The product ion ratio was found to be insensitive to the total pressure over the pressure range studied [(1 to 3) × 10<sup>-6</sup> Torr]; however, it was sensitive to the time of detection. Once formed, the product ions Cl<sup>-</sup> and (NC)<sub>2</sub>CH<sup>-</sup> were found not to react with the neutrals present (and thus change the ratio). However, by measuring the ion loss of the product ions at long time delays, it was established that the change of the product ion ratio with time results from differential ion loss. Thus, to measure the correct product ion ratio accurately and independent of ion loss, the ion intensities were measured at the shortest time delays possible.

The intermediate complex can also be formed with high energy, and low orbital angular momentum (A\*\*, Figure 1) via an IRMP-induced unimolecular reaction of the thermalized complex B through the S<sub>N</sub>2 transition state. The process for formation,

isolation, and activation of the thermalized complex B is analogous to that described above for the thermalized complex A.

In the case of each experiment, the energized complexes A\*\* and A\*\*\* are formed with a distribution of energies; the exact range is, however, somewhat uncertain. For the bimolecular S<sub>N</sub>2 reaction, the heats of formation for all the species are not known experimentally. Therefore, the reaction exothermicity can only be approximated (ΔH<sup>o</sup> ≈ -30 kcal mol<sup>-1</sup>). Moreover, the reactants come together with some distribution of energies. As a result, we estimate the range for A\*\*\* as 30–33 kcal mol<sup>-1</sup> above the k<sub>2</sub> threshold. For the IRMP-induced unimolecular S<sub>N</sub>2 reaction, the range of energies accessed by A\*\* is dependent on the IRMP up-pumping rate and on the height of the S<sub>N</sub>2 barrier relative to those of the separated reactants. The bimolecular S<sub>N</sub>2 reaction rate (CN<sup>-</sup> + ClCH<sub>2</sub>CN) is 2.2 × 10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup> (efficiency = 4.5%). This indicates that the S<sub>N</sub>2 transition state must lie below the separated reactants by approximately 3–5 kcal mol<sup>-1</sup>. We expect the IRMP activation of complex B to generate the complex A\*\* with slightly less energy compared to that of the bimolecular experiment, and we estimate it to be 27–30 kcal mol<sup>-1</sup> above the threshold for the k<sub>2</sub> channel.

The observed product ion branching ratios for the chemical activation experiments are given in Table I. In addition, the branching ratio predicted using statistical RRKM theory is given in Table I for comparison. Due to the ion-loss problem mentioned above, the uncertainty in the reported branching is estimated to be 20–30%.

## Discussion

**Internal Energy of Proton-Transfer Reactions.** Gas-phase proton-transfer reactions represent a fundamental class of reactions from which general principles of chemical reactivity can be obtained. On the basis of early kinetic studies, it was proposed that exothermic proton-transfer reactions should proceed at or very near the collision rate.<sup>38</sup> This was based on the notion that most proton-transfer potential energy surfaces should consist of a deep, single well separating reactants from products, with a negligible barrier to proton transfer. This conceptually pleasing picture found widespread acceptance because a deep potential well resulting from the electrostatic interaction between the ion and the neutral is expected. Early theoretical studies<sup>39–41</sup> based on *ab initio* quantum calculations gave general support to this conclusion.

For a single-well potential surface, the direct relationship between the rates of the forward and reverse reactions and the equilibrium constant is clear. These relationships and the effects of temperature on them have led to an extensive and rapidly growing body of thermodynamic data for proton-transfer systems, including gas-phase acidities, proton affinities, and heats of formation.<sup>42</sup> A recent example of this approach is given by Mautner<sup>5</sup> for proton-transfer reactions involving a large entropy change. Using high-pressure mass spectrometry (HPMS), proton-transfer rates and equilibrium constants were measured as a function of temperature. The reaction enthalpies (ΔH<sup>o</sup>) and entropies (ΔS<sup>o</sup>) were obtained from van't Hoff plots. Mautner showed that reactions which are modestly endothermic may still proceed near the collision rate at high temperatures<sup>43</sup> due to a positive entropy term (TΔS<sup>o</sup>) which renders the reaction exergonic. Included in the group of reactions Mautner studied is the proton-transfer reaction in eq 1. The overall reaction enthalpy (ΔH<sup>o</sup>), and entropy (ΔS<sup>o</sup>) for the reaction as written

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(37) CN<sup>-</sup> could conceivably act as an ambident nucleophile. The nitrogen attack channel is, however, less thermodynamically favored by approximately 16 kcal mol<sup>-1</sup>, based on heats of formation of CH<sub>3</sub>CN and CH<sub>3</sub>NC. Therefore, we would not expect this channel to contribute significantly.

were found to be 2.3 kcal mol<sup>-1</sup> and 8 cal mol<sup>-1</sup> K<sup>-1</sup>, respectively. Therefore, the standard free energy change ( $\Delta G^\circ$ ) at room temperature is very close to zero.

In contrast to these simple reactions, slow proton transfer rates have been observed in several systems,<sup>2</sup> including those involving delocalized anions or sterically hindered species.<sup>4,44</sup> For such systems, a double minimum surface containing an energetic barrier to proton transfer was proposed to rationalize the results. However, recent studies by Mautner and Smith<sup>5</sup> and Lim and Brauman<sup>12,45</sup> suggest that dynamical constraints may also be important. For proton-transfer reactions which occur over more complex potential energy surfaces, the relationships between kinetics, thermodynamics, and their temperature dependencies can become more complicated.<sup>1,14</sup>

In bimolecular reactions, the effects of collision dynamics, including angular momentum conservation, can be important. Thus, it can be advantageous to approach the investigation of the effect of internal energy on proton-transfer reactions by studying the unimolecular decomposition of reactive intermediates. By measuring the unimolecular dissociation branching ratio of an intermediate proton transfer complex as a function of internal energy, one can obtain a measure of the equilibrium constant in the absence of the collision dynamics. This concept has been exploited previously by Cooks and co-workers<sup>10</sup> using collision induced dissociation (CID) techniques and by Brauman and co-workers<sup>46</sup> using IRMPD.

In our experiments, both photoactivation and chemical activation are used to access a very large (30–33 kcal mol<sup>-1</sup> above threshold) energy range. The experimental results are complemented by the use of statistical reaction rate theory to aid in the interpretation of the results, including a microscopic interpretation of the internal energy dependence. The details of the RRKM calculations, including methodology and background, are given in the Appendix.

Table I shows the results for the dissociation branching ratio from the IRMP-activation experiments. An energy regime of approximately 0–3 kcal mol<sup>-1</sup> above threshold is accessed over the laser fluence range studied. In general, the branching ratio is close to unity, consistent with the near-zero free energy change at room temperature. There is, however, a clear trend in the branching ratio as a function of laser fluence. At higher laser fluences (higher internal energy), the branching ratio increases, producing more (NC)<sub>2</sub>CH<sup>-</sup> and less Cl<sup>-</sup>. The RRKM results were found to be qualitatively consistent with the experimental observations, although the calculated increase is more rapid than that observed experimentally.

Table I also shows the observed branching ratio for dissociation of the proton-transfer reaction intermediate when it is prepared in a chemically activated state via the S<sub>N</sub>2 channel described above. These experiments access a range of internal energy between 30–33 kcal mol<sup>-1</sup> above the lowest dissociation threshold. The branching ratio for the IRMP induced chemical activation experiments (B to A<sup>\*\*</sup>, Figure 1) deviates significantly from unity and is approximately [(CN)<sub>2</sub>CH<sup>-</sup>]:[Cl<sup>-</sup>] = 10:1. The branching ratio from the bimolecular chemical activation experiments (forming A<sup>\*\*\*</sup>, Figure 1) also deviates significantly from unity and is approximately [(CN)<sub>2</sub>CH<sup>-</sup>]:[Cl<sup>-</sup>] = 15:1.

The results from both the IRMP and chemical activation

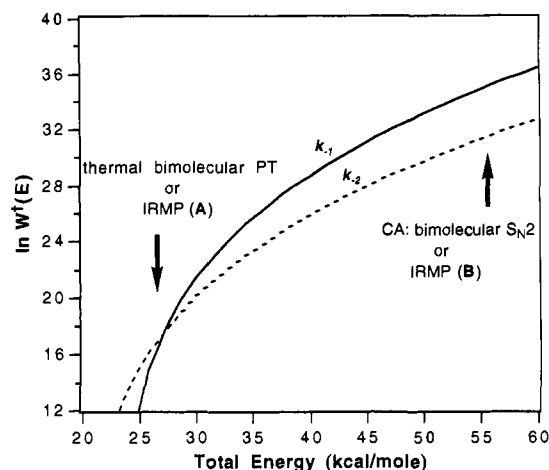


Figure 2. Sum of states versus total energy for the two dissociation channels of the proton-transfer intermediate complex [(NC)<sub>2</sub>CH<sub>2</sub>-Cl]<sup>-</sup>.

experiments demonstrate that with increasing internal energy, the equilibrium for the proton transfer favors channel 1 (reactants in eq 1), which is the endothermic but entropically favored direction. Qualitatively, the energy dependence of the branching ratio can be rationalized using the RRKM theory rate expression (eq a3, Appendix). Due to the two hindered rotational degrees of freedom in channel 1 (dipolar HCl rotating in the electrostatic field of the (CN)<sub>2</sub>CH<sup>-</sup> anion), which develop into free rotations as the complex dissociates, the total sum of states  $W^\ddagger(E)$  increases much more rapidly as a function of energy relative to that in channel 2. These same modes correspond to vibrations in channel 2 which add to the total sum of states more slowly as a function of total internal energy. Figure 2 shows a quantitative representation of this effect. Even though the dissociation threshold for channel 1 lies at a higher energy relative to that for channel 2, the total sum of available quantum states increases more rapidly; within a few kilocalories per mole, the sum of states and hence the unimolecular rates become equal. By the time the system reaches 30 kcal mol<sup>-1</sup> of excess energy, dissociation strongly favors channel 1. This RRKM analysis provides a microscopic description of the dramatic changes which occur in the reactant and product partition functions with increasing energy. These changes in the partition functions, which can be directly related to the familiar macroscopic thermodynamic quantities, are responsible for the observed energy dependence of the reaction.

Although the observed product branching ratios for dissociation of the energized complex [(NC)<sub>2</sub>CH<sub>2</sub>-Cl]<sup>-</sup> appear consistent with expectations based on the product partition functions, there are important qualitative differences between the various experiments (IRMP and CA) in the way energy and orbital angular momentum are transferred to the intermediate complex prior to dissociation. In the case of IRMP activation of the thermalized complex A to form A<sup>\*</sup> as shown in Figure 1, A is trapped for a significant amount of time (500–1000 ms), having the chance to undergo many collisions, before being photolyzed. We would therefore not expect A to be rotationally or vibrationally hot, nor would we expect IRMP activation to significantly increase the rotational angular momentum upon energization. As a result, the contribution of orbital angular momentum to the effective potential should be modest. Moreover, energy is transferred to the thermalized complex in small discrete units (equivalent to 1 photon  $\approx$  3 kcal mol<sup>-1</sup>), and the up-pumping rate is sufficiently slow to allow significant energy randomization among all the modes in the complex. Given these considerations, we would expect the change in the observed product branching ratio to be a function of the energy dependence alone at the low energies accessed in these experiments. We would also expect the results to be consistent, at least qualitatively, with the statistical prediction.

In contrast to the low energy regime, energy transfer during

(43) At high temperatures (500–600 K), the energy distribution is such that most reactants have energies well above the critical energy for reaction. Thus, the behavior of the reaction is dominated by the relative densities of states for each channel and not the relative enthalpies. Since the density of states increases more rapidly for the entropically favored direction, it is possible to observe high efficiencies. This is not true, however, for lower temperatures where the efficiencies will be far from unity. For the proton-transfer reaction discussed here, we have observed 50% efficiency (in the endothermic direction) at approximately 350 K.

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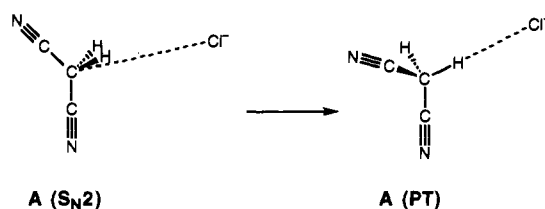
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the formation of the more highly energized intermediate complexes  $A^{**}$  and  $A^{***}$  via the two CA experiments is distinctly different from the experiment described above. In both CA experiments, transfer of energy to the activated complex is more complicated than that in the IRMP activation of A. As shown in Figure 1, the energy which is deposited in the proton-transfer complex  $[(NC)_2CH_2\cdot Cl^-]$  comes from the exothermicity of an  $S_N2$  reaction. Thus, upon substitution, a large amount of energy is transferred to the complex through the  $S_N2$  reaction coordinate. Energy randomization must compete with the rate of dissociation through each exit channel. This raises important questions about the possibility for incomplete intramolecular vibrational energy redistribution, an assumption fundamental to RRKM theory and indeed chemical equilibria. Moreover, although the two CA experiments access a similar, but not identical, range of energies as illustrated in Figure 1, the transfer of orbital angular momentum to the highly energized complex is distinctly different in the two cases. Unlike the IRMP induced unimolecular  $S_N2$  isomerization experiment to form  $A^{**}$  from thermalized B, in the bimolecular  $S_N2$  reaction, large-impact parameter capture events leading to the formation of complex  $A^{***}$  are possible. The activated complex  $A^{***}$  can, therefore, be formed with a large component of orbital angular momentum. The extent to which this factor contributes to the observed difference in the product branching ratio for the two CA experiments is uncertain. The observed results are consistent, however (at least in direction), with the slight difference in energy between  $A^{**}$  and  $A^{***}$  and the expected energy dependence.

Given these factors, it is surprising that the experimental results for the product branching ratio are still qualitatively consistent with the statistical model at such high energies. It should be made clear, however, that at the highest energies, the absolute rates for either channel predicted from RRKM theory approach  $10^{14} s^{-1}$ . A rate of dissociation this fast corresponds to an average lifetime which is on the same time scale as that for a single, low-frequency vibration. Thus, cautious interpretation is indicated at the highest energies.

**$S_N2$  Reaction Dynamics.** The chemical activation experiments also provide information about the dynamics of gas-phase substitution reactions,<sup>47-52</sup> a topic which has recently been the focus of considerable attention.<sup>19-25,53-59</sup> Statistical reaction rate theories<sup>17</sup> such as RRKM theory have been used to model gas-phase substitution reactions. These models assume that energy is statistically distributed among all modes throughout the reaction and that the lifetimes of the intermediates along the reaction path are sufficiently long (and/or that energy transfer is adequately efficient) to allow for the necessary energy redistribution. Although statistical reaction rate theories have been applied in a large number of systems, there has been strong evidence for nonstatistical behavior in  $S_N2$  reactions. In this section, we consider the implications of our result in the context

## Scheme II



of recent experimental and theoretical work on other general  $S_N2$  systems in an attempt to present an integrated picture of the dynamics of  $S_N2$  reactions.

A detailed consideration of our experimental results for the substitution reaction in Scheme I provides valuable information about the lifetimes of intermediate complexes in bimolecular substitution reactions and the energy transfer within them. Following the substitution event, an intermediate species,  $[(NC)_2CH_2\cdot Cl^-]$ , is formed which undergoes proton transfer before it dissociates. Formally, the  $S_N2$  reaction should generate the complex in a "back-side" orientation ( $A(S_N2)$ , Scheme II) if an inversion mechanism is assumed. However, the structure on the minimum energy path of the proton-transfer reaction is a proton-bound structure ( $A(PT)$ , Scheme II). That the intermediate species formed after the substitution event undergoes proton transfer suggests that the lifetime of the intermediate complex is sufficiently long to allow for structural rearrangement and subsequent secondary chemical reaction. This rules out a "direct" mechanism in which the chloride ion is ejected immediately following the substitution event.

The observation of preferential proton transfer prior to dissociation also provides information about energy deposition and exchange within the complex following the substitution event. That proton transfer is the major channel implies that the energy (from the reaction exothermicity) in the post-substitution complex  $[(NC)_2CH_2\cdot Cl^-]$  is partitioned in such a way that insufficient energy is deposited in the modes associated with complex dissociation, such as the loose C-Cl bond stretch. If sufficient energy were deposited directly into these modes, the complex  $[(NC)_2CH_2\cdot Cl^-]$  would probably dissociate in a "direct" process. In fact,  $Cl^-$  is not simply ejected, and proton transfer actually dominates, although the ion-molecule complex is only loosely bound with respect to chloride loss ( $\approx 20 \text{ kcal mol}^{-1}$ ) and the overall reaction is highly exothermic ( $\approx 30 \text{ kcal mol}^{-1}$ ). If little energy is deposited in the loose C-Cl stretching modes of the complex,  $[(NC)_2CH_2\cdot Cl^-]$ , conservation of energy requires that the internal vibrational modes of the neutral must be highly excited. Finally, the dominance of the proton-transfer channel also suggests that energy transfer to the modes related to complex dissociation must be slow; if it were not, energy would transfer to the loose C-Cl bond stretching modes and simple loss of  $Cl^-$  would occur. One plausible explanation is that the coupling between certain vibrational modes of the complex is weak.

These results are consistent with previous work on other  $S_N2$  systems. There have been many experimental and theoretical studies which also suggest inefficient energy transfer within  $S_N2$  ion-molecule complexes. Viggiano and co-workers<sup>21</sup> have studied the energy dependence of the rate for the exothermic  $S_N2$  reaction of chloride ion with methyl bromide. They found that reactants containing a higher component of relative kinetic energy react more slowly compared to reactants with the same total energy but less relative kinetic energy. Thus, species that come together with high relative translational energy simply come apart before reaction can occur. This is consistent with the notion of inefficient energy transfer between the transitional modes, in particular relative translation, and the internal modes of the neutral  $CH_3\cdot Br$ . On the basis of microscopic reversibility arguments, one would expect the same to be true for complex dissociation. Moreover, given that an increased component of relative kinetic

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energy slows down the overall reaction, it is reasonable to assume that most of the products formed come from reactants with a lower component of relative kinetic energy (and thus are internally excited in a relative sense).

Graul and Bowers<sup>19</sup> have also studied the exothermic substitution reaction of chloride with methyl bromide by measuring the kinetic energy release distribution of the metastable [Cl-CH<sub>3</sub>Br] complex. They observed that the relative kinetic energy of the products resulting from substitution and subsequent decomposition to Br<sup>-</sup> + CH<sub>3</sub>Cl is considerably less than that predicted by statistical phase space theory (PST). By conservation of energy arguments, this indicates that the neutral product, CH<sub>3</sub>-Cl, must be internally excited. Again, this observation of nonstatistical energy distribution is indicative of inefficient energy transfer among the internal modes of the neutral and the transitional modes necessary for dissociation of the complex, which are strongly decoupled from one another. This picture suggests that the complex slowly leaks energy from the internal modes of CH<sub>3</sub>Cl to the transitional modes necessary for complex dissociation to produce products with the minimal amount of relative kinetic energy instead of with a statistical distribution. In this way, the results of Viggiano and co-workers and Graul and Bowers are completely consistent with one another and with our observation.

The origin of the less-than-statistical kinetic energy release has an analogy in the behavior of unimolecular reactions at low pressure. Suppose (1) that the reaction products, when formed, are not chemically bonded and have enough total energy to dissociate but not enough energy in the dissociation degree of freedom to dissociate and (2) that energy is transferred to the dissociation reaction coordinate degree of freedom slowly (i.e., energy transfer is inefficient and/or requires numerous collisions of the particles within the complex). Under these conditions, dissociation cannot occur until sufficient energy has been transferred to the dissociation reaction coordinate via collisions between the partners in the complex; as soon as sufficient energy to dissociate has been transferred, the products will dissociate. Since dissociation occurs as soon as the minimum amount of energy has been deposited in the reaction coordinate, the separating products will have essentially no additional kinetic energy (kinetic energy arises only from excess energy in the reaction coordinate for simple ion-molecule dissociations of complexes). By difference, the excess energy will all be in vibrational modes of the products. The process is analogous to activation of unimolecular reactions in the low-pressure limit, where the reaction occurs as soon as the critical energy has been reached, so that the energy of molecules undergoing reaction is less than that observed at high pressures.

The dynamics of S<sub>N</sub>2 reactions have also been recently studied from a theoretical perspective. Vande Linde and Hase<sup>22-25</sup> have carried out classical trajectory calculations on the thermoneutral Cl<sup>-</sup> + CH<sub>3</sub>Cl reaction. Although the potential surface for this thermoneutral reaction is significantly different than that of the exothermic reactions presented above, analysis of the results is informative in light of the present discussion. In a series of studies, Vande Linde and Hase made three important observations. First, they found that for thermal energies, the substitution process is a very unlikely event.<sup>60</sup> Second, they discovered that both the ion-molecule association and dissociation dynamics are distinctly nonstatistical. Intramolecular vibrational energy redistribution is inefficient between the internal modes of CH<sub>3</sub>Cl and the transition modes leading to products. This was evident from the calculated complex lifetimes and the observation that complex formation decreases as the relative kinetic energy of the system increases (resulting in scattering events). Last, trajectories

initiated at the S<sub>N</sub>2 transition state often recross the saddle point numerous times before dissociating, even though there is more than enough total energy to dissociate. Each of these observations is completely consistent with the previous experimental results on exothermic S<sub>N</sub>2 systems presented above. In particular, energy transfer between certain groups of modes within the ion-molecule complexes is inefficient; these modes are strongly decoupled from one another and from the relevant reaction coordinate modes at the S<sub>N</sub>2 transition state, and as a result, the complex lifetimes are longer than those predicted from a statistical model.

Together, these results appear to indicate the following microscopic picture for these substitution reactions in the gas phase. First, energy transfer within the intermediate complexes is inefficient.<sup>61</sup> This, in combination with the inefficiency of energy transfer from kinetic energy to vibrational and rotational energy, means that higher relative kinetic energies of the reactants reduce the rate of reactions.<sup>62</sup> Thus, given a thermal distribution, a greater fraction of the reactants leading to products have low kinetic energies. This is borne out by the observations of Graul and Bowers who find a less-than-statistical product kinetic energy distribution. The observation of a low product kinetic energy distribution is also consistent with our observations that, following the substitution event, little energy is deposited in the vibrational mode for the stretch of the leaving group and energy transfer to this mode is inefficient. This implies that the mode corresponding to the stretch of the leaving-group is poorly coupled to other modes of the reaction. Given the importance of the leaving group stretch in the substitution process, this result is perhaps somewhat counterintuitive.

The generality of this model, however, remains to be established. As with the theoretical work, experimental studies to date have focused largely on small systems with simple nucleophiles and leaving groups. There has been a modest range of reaction exothermicities studies; a full sampling of both thermoneutral and endothermic reactions remains a challenge. In addition, the predictive implications of this model are unclear. While the observation of nonstatistical behavior, which results from inefficient energy transfer, must be considered in the application of statistical theories such as RRKM theory, it is not clear whether it obviates its use. The observable effects of such nonstatistical behavior on chemical reactions may be small. For example, our system, which clearly has nonstatistical elements, when modeled by RRKM theory, gave branching ratios which were qualitatively consistent with the experimental results. Further, other simple reactions, such as the halide/methyl halide systems, have also been successfully modeled. Thus, we conclude that while nonstatistical behavior may play a role in the microscopic picture of reaction dynamics, it does not appear to manifest itself in such a way as to prevent the use of statistical reaction rate theories as a tool for modeling overall reaction kinetics.

**Acknowledgment.** We are grateful to the National Science Foundation for support of this research. J.L.W. gratefully acknowledges the IBM graduate fellowship program for support.

#### Appendix. Application of Statistical Reaction Rate Theory

For most proton-transfer reactions in the gas phase, the potential energy surface is essentially featureless, with a single well separating reactants and products or a double-well surface with a small barrier to reaction.<sup>63</sup> The equilibrium constant for such proton-transfer reactions as represented in eq 1, is simply the ratio of the forward and reverse rate coefficients  $k_f$  and  $k_r$ . Each

(61) This observation is consistent with other experimental work on energy transfer. See, for example: Boering, K. A.; Brauman, J. I. *J. Chem. Phys.* 1992, 97, 5439 and references therein.

(62) Inefficient energy transfer implies that long lifetimes are required for energy exchange. Higher kinetic energies are likely to reduce complex lifetimes.

(63) The potential surface for the proton-transfer reaction in eq 1 may be more complicated, but the experimental evidence would indicate a single well (ref 5).

(60) Mode specific excitation of the CH<sub>3</sub> umbrella modes in the neutral did not significantly increase the efficiency of reaction. However, after mode specific excitation of the C-Cl stretch in the neutral, the likelihood of substitution dramatically increased. This increase, however, was attributed to a direct reaction in which the leaving group was instantly ejected.

of these can be broken down into the component unimolecular steps, eq a1, assuming a sufficiently long complex lifetime to allow for a steady-state approximation.

$$K = \frac{k_f}{k_r} = \frac{k_1 k_{-2} / (k_{-1} + k_{-2})}{k_2 k_{-1} / (k_{-2} + k_{-1})} \quad (\text{a1})$$

The dissociation branching ratio  $\text{BR}(E, J)$  for the intermediate complex, as a function of total energy  $E$  and total angular momentum  $J$ , is simply the ratio of the rates of dissociation for each channel,

$$K(E, J) \simeq \text{BR}(E, J) = \frac{k_{-2}(E, J)}{k_{-1}(E, J)} \quad (\text{a2})$$

To the degree that the association rate coefficients for each channel are the same and independent of total energy (i.e.,  $k_1 \simeq k_2$ ), the branching ratio is also equal to the equilibrium constant for the reaction,  $K(E, J) \simeq \text{BR}(E, J)$ .

The unimolecular dissociation of such an ion-molecule complex can be modeled using statistical reaction rate theory. In particular, Rice-Ramsperger-Kassel-Marcus (RRKM) theory<sup>16,17</sup> can be used to obtain the relative rates between the channels as well as the absolute rates as a function of total internal energy. The standard RRKM expression within the microcanonical variational transition-state ( $\mu$ VTS) approximation, is given by eq a3,

$$k(E, J) = \sigma \frac{\int_0^{\epsilon(J; R^*)} \rho_{\mu\text{VTS}}^\dagger(\epsilon') d\epsilon'}{h\rho[\epsilon(J; R_c)]} = \sigma \frac{W_{\mu\text{VTS}}^\dagger[\epsilon(J; R^*)]}{h\rho[\epsilon(J; R_c)]} \quad (\text{a3})$$

where  $\sigma$  is the reaction path degeneracy,  $R$  denotes the reaction coordinate,  $\epsilon(J; R) = E - V(R) - E_r(J; R) W_{\mu\text{VTS}}^\dagger[E, J]$  is the number of accessible states at the transition state (located at  $R = R^*$ ) for each  $(E, J)$  channel, and  $\rho[\epsilon(J; R_c)]$  is the corresponding density of states for the appropriate ion-molecule complex (for which  $R = R_c$ ).  $V(R)$  and  $E_r(J; R)$  represent the potential energy and orbital rotational energy, respectively, along the reaction coordinate.  $V(R)$  can be modeled using simple electrostatics incorporating the experimental molecular parameter of each neutral (i.e., polarizability and dipole moment).  $E_r(J; R)$  is determined using a diatomic approximation.

On the basis of how the complexes are prepared experimentally, it is not known how much energy is tied up in angular momentum. We do know, however, that since the overall reaction involves transfer of little mass (a single proton), the relative effects of orbital angular momentum will, for the most part, cancel in measuring  $\text{BR}(E, J)$ . Consistent with this notion, the calculated branching ratio was found to be reasonably insensitive to the total angular momentum state  $J$  approximated as the orbital angular momentum  $L$ .

Rigorously, the sum of states  $W^\dagger$  in eq a3 corresponds to that of the transition state for dissociation of each channel, and its position along the reaction coordinate is a strong function of both total energy  $E$  and total angular momentum  $J$ . Ideally, the sum of states and hence the rate coefficient should be determined variationally for each  $E$  and  $J$  state. Little difference was found, however, between the full  $\mu$ VTS theory approach and a simplified model where the rates of dissociation were determined with the transition state taken as separated reactants. A more detailed description of the application of RRKM theory to gas-phase reactions can be found elsewhere.<sup>64</sup>

The RRKM parameters (geometries and harmonic vibrational frequencies) for the separated reactants of both channels and for the intermediate complex were obtained from *ab initio* quantum calculations.<sup>65</sup> Both the optimized geometries and the quadratic force fields of each species were determined at the RHF 6-31+G-(d,p) level of theory. The actual harmonic frequencies used in the RRKM analysis were scaled by 0.9 in accordance with known overestimates at this level of theory. Given in Table I are the branching ratios as a function of internal energy above the threshold expected from the experiment. Also, to help conceptualize the strong energy dependence of BR and hence the equilibrium constant for this reaction, a plot of  $\ln[W^\dagger(E)]$  versus  $E$  (at constant  $L = 100$ ) for both channels,  $k_{-1}$  and  $k_{-2}$ , is given in Figure 2.

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