# **Energy Disposal in Gas-phase Nucleophilic Displacement Reactions**

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The partitioning of reaction exothermicity into relative translational energy of the products of gas-phase  $S_N 2$ (F<sup>-</sup> + CH<sub>3</sub>Cl) and nucleophilic aromatic substitution (F<sup>-</sup> + C<sub>6</sub>H<sub>5</sub>Cl) reactions has been investigated using kinetic energy release Fourier transform ion cyclotron resonance spectroscopy. The chloride product ion is observed to be highly translationally excited for the  $S_N 2$  reaction, indicating a cold internal energy distribution for the products. For the chlorobenzene reaction the products are not generated with large translational energies. The results are compared with a statistical model. Ion-intensity profiles for the CH<sub>3</sub>Cl reaction deviate significantly from the statistical model whereas the chlorobenzene results are consistent with this model. The kinetic energy release for the CH<sub>3</sub>Cl reaction is compared with energy-disposal results for the photodissociation and dissociative electron-attachment processes of halomethanes. In all three cases a node in the molecular orbital between the carbon atom and the departing halogen results in a repulsive energy release. Ion-retention curves for the nucleophilic aromatic substitution reaction are consistent with the existence of a long-lived ion-dipole complex on the exit channel for this reaction.

## INTRODUCTION

Numerous theoretical and experimental studies have focused on the kinetics of gas-phase nucleophilic substitution reactions in an effort to elucidate details of the potential energy surfaces for these processes.<sup>1-4</sup> In a recent study, VandeLinde and Hase<sup>5</sup> carried out classical trajectory calculations for the chloride exchange reaction between Cl<sup>-</sup> and CH<sub>3</sub>Cl which indicate that mode-specific vibrational excitation of the reactant CH<sub>3</sub>Cl greatly enhances the reaction cross-section. Their work also indicated that the reaction proceeds via a direct mechanism in which most trajectories which are effective in overcoming the intermediate barrier in the reaction are those in which there is no long-lived iondipole complex on the entrance or exit channel. We report here on the disposal of exothermicity into translational energy of the products of the reactions of F with CH<sub>3</sub>Cl and C<sub>6</sub>H<sub>5</sub>Cl determined using Fourier transform ion cyclotron resonance (FT-ICR) spectroscopy. The results show that the  $S_N 2$  reaction with CH<sub>3</sub>Cl proceeds with a large fraction of the exothermicity partitioned into relative translational energy of the products, suggesting that there is no-long lived iondipole complex on the exit channel.

### EXPERIMENTAL

All experiments were performed on a Fourier transform ion cyclotron resonance mass spectrometer recently described in detail.<sup>6,7</sup> The ICR cell used for these experiments consists of solid copper plates of dimen-

0030-493X/91/111003-05 \$05.00 © 1991 by John Wiley & Sons, Ltd. sions 2.75 in (between trap plates)  $\times$  1.375 in  $\times$  1.375 in. This geometry results in an effective potential of  $0.89V_{app}$ , where  $V_{app}$  is the voltage applied to the trapping electrodes. All curves obtained in this study were corrected for the difference in the applied and effective potentials. In order to alleviate problems from contact potentials on the trapping plates, the trap electrodes were coated with 0.32 µm of gold via UHV vapor deposition.

 $F^-$  was generated by dissociative electron capture using NF<sub>3</sub> (0.1 eV electron energy) [reaction (1)]. Reagent pressures were ~1 × 10<sup>-5</sup> Torr (NF<sub>3</sub>) and ~(1.5-2) × 10<sup>-5</sup> Torr (chlorinated reagent) as measured using an uncalibrated ionization gauge (1 Torr = 133.3 Pa). A 25 ms

$$NF_3 + e^- \rightarrow F^- + NF_2 \tag{1}$$

trapping delay was included after the electron beam event to allow ion thermalization and scavenging of stray electrons.  $F^-$  was isolated after the thermalization period by swept double-resonance ejection pulses. Subsequently, F<sup>-</sup> was allowed to react with the chlorinated reagent for  $\sim 75$  ms (CH<sub>3</sub>Cl does not attach thermal energy electrons<sup>8</sup>). During this period, the kinetic energy of the  $Cl^-$  was measured. Briefly, the kinetic energy release experiment involves measuring the ion concentration in the FT-ICR trapping cell as a function of the applied electrostatic potential. If an ion has a component of kinetic energy parallel to the magnetic field lines which is larger than the effective electric field, the ion can overcome the trapping potential with a concomitant decrease in the ion intensity.9,10 For the present work, the reaction was carried out at a series of trapping voltages with the relative abundance of Cl<sup>-</sup> measured as a function of the potential. During detection, the trapping voltage was maintained at a large,

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Figure 1. Experimental pulse sequence for kinetic energy release experiments with corresponding trap-plate potentials.

constant value, which ensures that no high kinetic energy ions can escape the trapping well during detection and no ion-intensity discrimination results from variations in the trapping field. The experimental pulse sequence used is shown in Fig. 1. The overall ion intensity as a function of the effective trapping voltage for an ion population with a distribution of kinetic energies is given by the equation

$$F = \sum_{F_{k}=V_{0}}^{E_{k}(\max)} f_{m} (V_{0}/E_{k})^{1/2} + \sum_{E_{k}=0}^{E_{k}(2)$$

where  $V_0$  is the effective trapping potential,  $f_m$  is the fraction of ions having kinetic energy  $E_k$  and F is the fraction of the product ions trapped in the ICR cell during the reaction period.

The experimental ion-intensity profiles are compared with theoretical distributions based on statistical considerations using the model of Safron et al.<sup>11a</sup> (for a discussion of phase space approaches which account for the conservation of angular momentum, see Refs. 11b and c). This approach only accounts for orbital angular momentum of the collision complex and does not conserve total angular momentum. However, for the present experiments, which only measure relatively high translational energies (>300 meV), the absolute error in the experimentally measurable regime will be significantly smaller than the error in the experimental results. We have used the dissociating ion-dipole complex  $Cl^- \cdots RF$  (R = 'CH<sub>3</sub> and 'C<sub>6</sub>H<sub>5</sub>) as the critical configuration for calculations of the energy partitioning for the reaction. Hence the frequencies for the critical configuration should be very similar to those for the free fluorine containing molecule. The total internal energy of the transition state corresponds to the reaction exothermicity. [Frequencies were taken from Ref. 12; the theoretical ion-intensity profiles shown in Figs 1 and 2 were obtained by convoluting the calculated translational energy distributions with Eqn (2); all thermochemical data were taken from Ref. 13.]

**RESULTS AND DISCUSSION** 

Figures 2 and 3 show the  $Cl^-$  intensity as a function of the effective trapping potential on the ICR cell for the



Figure 2. Kinetic energy release curve for  $F^--CH_3CI$ . The solid line represents the theoretical/statistical distribution.<sup>11</sup>

reactions

$$\mathbf{F}^{-} + \mathbf{C}\mathbf{H}_{3}\mathbf{C}\mathbf{I} \rightarrow \mathbf{C}\mathbf{H}_{3}\mathbf{F} + \mathbf{C}\mathbf{I}^{-} \tag{3}$$

$$\mathbf{F}^- + \mathbf{C_6H_5Cl} \rightarrow \mathbf{C_6H_5F} + \mathbf{Cl}^- \tag{4}$$

Also shown in Figs 2 and 3 are theoretical distributions based on the statistical model with arrows corresponding to the maximum translational energies of  $Cl^{-}$  allowed based on thermochemical constraints. Relevant thermochemical information for both reactions is listed in Table 1.

The Cl<sup>-</sup> generated in reaction (3) rapidly decreases in intensity as the trapping voltage on the ICR cell is decreased below 0.8 V with the ion intensity decreasing nearly linearly as a function of the square root of the trapping potential below  $\sim 0.7$  V. This indicates that the Cl<sup>-</sup> product is highly translationally excited. The distribution has a small positive intercept. This may suggest that a small portion of the ion population has translational energies less than 0.3 eV (the lowest trapping voltage for which a signal was obtainable), but the error in our determination of the *y*-intercept in the plot is large enough to include the origin. Thus, from the uncertainty in our value for the *y*-intercept, we conclude



Figure 3. Kinetic energy release curve for F--C<sub>8</sub>H<sub>5</sub>Cl. The solid line represents the theoretical/statistical distribution.<sup>11</sup>

Table 1. Relevant heats of formation (eV) <sup>a</sup>					
Δ <i>Η</i> , F-	<i>∆н</i> , сн₃сі	<i>Δн</i> , Сн <sub>3</sub> F	∆H, Cl⁻	∆H reaction	Maximum kinetic energy (Cl <sup>-</sup> ) <sup>b</sup>
-2.58	-0.76	~2.56	-2.35	-1.58	0.78
<b>Δ</b> Η, F⁻	∆ <i>H</i> , C <sub>6</sub> H <sub>6</sub> Ci	∆ <i>H</i> , C <sub>6</sub> H₅F	Δ <i>Η</i> , Ci⁻	∆H reaction	Maximum kinetic energy (Cl <sup>-</sup> ) <sup>5</sup>
-2.58	+0.56	-1.20	-2.35	-1.53	1.12
<sup>a</sup> All ther <sup>b</sup> Maxim mass(R-	mochemica um kinetic –F) + mass(	i data from c energy (CI)].	Ref. 13. of Cl <sup>-</sup>	= -ΔH <sub>RXN</sub>	[mass(R—F)/

that >80% of the Cl<sup>-</sup> products from reaction (3) have  $0.8 \pm 0.15$  eV of translational energy. From momentum and energy conservation, these results indicate that the majority of the Cl<sup>-</sup> products are generated with <25 kJ mol<sup>-1</sup> of internal excitation.

It is clear that the experimental data for F<sup>-</sup>-CH<sub>3</sub>Cl deviate significantly from the results expected based on the statistical model. More reaction exothermicity appears as translational energy of the products than is expected from statistical partitioning. Large translational energy releases in gas-phase reactions have previously been rationalized on the basis of repulsive potential energy surfaces, as in the reactions of barium atoms with hydrogen halides and fluorine atoms with alkenes.<sup>14</sup> Stereochemical work on gas-phase  $S_N 2$  reactions indicates inversion of configuration with the mechanism proceeding through a five-coordinate carbon transition state.<sup>15</sup> The  $S_N 2$  reaction coordinate is characterized by a tight transition state, as demonstrated by the inverse kinetic isotope effects observed by Bierbaum and co-workers.<sup>16</sup> Jorgensen and coworkers<sup>17</sup> have performed ab initio calculations of the highly exothermic OH<sup>-</sup>-CH<sub>3</sub>Cl reaction ( $\Delta H_{rxn} =$  $-209 \text{ kJ mol}^{-1}$ ) which indicate that the transition state lies very high in energy relative to the products. It is possible that the energy is statistically distributed at the critical configuration for the reaction but the potential surface is repulsive, resulting in a translational energy release distribution which appears non-statistical. As the reaction proceeds through the five-coordinate transition state, excitation of the modes which evolve into the umbrella mode  $[v_2(a_1)]$  and the C-F stretch  $[v_3(a_1)]^{12}$  of the products might be expected. However, the experimental results suggest little excitation in these vibrations. If all of the remaining available energy were partitioned into the  $v_2(a_1)$  mode of CH<sub>3</sub>F, this would correspond to less than two quanta of energy, whereas less than three quanta could be deposited in the  $v_3(a_1)$ mode of CH<sub>3</sub>F.

The high translational energy release for the present reaction is unexpected when the proposed potential surface for the reaction is considered. Similar  $S_N 2$  reactions have been theoretically calculated to have doublewell potentials along the minimum energy reaction path.<sup>18</sup> If the final ion-dipole complex (FCH<sub>3</sub>…Cl<sup>-</sup>) were long-lived, the energy disposal could be controlled by the small centrifugal barrier on the exit channel. This would result in a small translational energy release. However, the theoretical work of VandeLinde and Hase<sup>5</sup> indicates that most of the trajectories which are successful at overcoming the intermediate barrier to reaction (for  $Cl^--CH_3Cl$ ) proceed via a direct mechanism, i.e. only 1% of the successful trajectories emerge from long-lived complexes in either of the ion-dipole potential wells. Also, classical trajectories for this reaction indicate that three or fewer vibrational modes participate in the intramolecular vibrational energy redistribution of the  $Cl^- \cdots CH_3Cl$ .<sup>5b</sup> For the present reaction, we observe that reactants which overcome the intermediate barrier do not sample the ion-dipole complex which has been proposed to exist along the minimum energy reaction path at the exit channel.

A simple model for the large translational energy release can be found in a comparison with photodissociation and dissociative electron-capture studies of halomethanes. Previous studies of the reactions of hydrogen atoms with halogens [reaction (5)] show a large fraction of the available reaction energy is released in

$$H^{\bullet} + X_2 \to HX + X^{\bullet} \tag{5}$$

$$\mathbf{X}_2 + h\mathbf{v} \to 2\mathbf{X}^{\bullet} \tag{6}$$

$$(X = F, Cl, Br)$$

translation. Similar observations have been made for the photodissociation of the halogens [reaction (6)]. The similarity between the kinetic energy and angular distributions for the products of these two processes has been rationalized on the basis that both involve a transition state in which there is a node in the molecular orbital between the two halogen atoms.<sup>19</sup> This strongly antibonding interaction results in a direct dissociation with large kinetic energy release. A similar argument can be made for the present results. Reactions (7)–(9) show the related processes of nucleophilic activation, dissociative electron

$$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$$
(7)

$$e^{-} + CH_{3}X \rightarrow CH_{3} + X^{-}$$
(8)

$$(\mathbf{X} = \mathbf{Br}, \mathbf{I})$$

$$CH_3X + hv \rightarrow CH_3 + X$$
 (9)

$$(\mathbf{X} = \mathbf{Cl}, \mathbf{Br}, \mathbf{I})$$

capture and photodissociation for the halomethanes. Reactions (8) and (9) have previously been shown to involve a large release of kinetic energy into the products.<sup>20,21</sup> For reaction (8), electron attachment occurs into an antibonding orbital localized on the halogen atom, which results in a node in the molecular orbital between the carbon and halogen atoms. Reaction (9) involves population of an antibonding orbital by vertical excitation of a bonding electron.

For comparison, Fig. 4 shows simple molecular orbitals for reaction (7), including the three resultant orbitals for the collision complex. The intermediate orbital is composed of a superposition of the two orbitals shown. The orbital of reactive interest involves an F-C bonding component and a C-Cl antibonding component. Figure 5 shows a state correlation diagram for the reaction.<sup>22</sup> The ground-state products correlate with an electronically excited state of the reactants



Figure 4. Molecular orbital diagram for the reactants and the intermediate formed in the gas-phase nucleophilic displacement reaction (F--CH<sub>3</sub>Cl).

which contains a node between the C—Cl bond (the high-energy electron attachment process for  $CH_3Cl$  is purely dissociative<sup>8</sup>). Hence, the nucleophilic displacement reaction results in a node in the orbital between the C and Cl atoms in collision complexes which generate products. This node is similar to those involved in reactions (8) and (9), and results in a large translational energy release.

The ion-intensity profile for reaction (4) is shown in Fig. 3. Although experimental limitations prevent the low kinetic energy products to be distinguished, there is not a significant population of highly translationally excited products in this reaction. The available results agree with the statistical model. This is expected based on recent studies of nucleophilic aromatic substitution reactions in the gas phase. Ingemann and co-workers<sup>3c,23</sup> have shown that alkoxide anions react with fluoroanisoles via nucleophilic attack at the



Figure 5. State correlation diagram for the F<sup>-</sup>--CH<sub>3</sub>Cl reaction.

fluorine-bearing carbon followed by elimination of  $F^-$ . However, the leaving group ( $F^-$ ) undergoes nucleophilic attack on the alkoxy groups and proton abstraction prior to decomposition of the ion-dipole complex. Within these ion-dipole complexes significant energy redistribution occurs with statistical partitioning of reaction exothermicity into product internal modes.

#### CONCLUSION

F<sup>-</sup> displacement of Cl<sup>-</sup> from CH<sub>3</sub>Cl and chlorobenzene result in dramatically different product translational energy releases. The  $F^--C_6H_5Cl$  reaction generates products with relatively low kinetic energies whereas the  $F^--CH_3Cl$  reaction generates products with high kinetic energies. The nucleophilic aromatic substitution reaction, which involves elimination of Cl<sup>-</sup> from a sterically uncongested four-coordinate carbon center, results in an energy release which is consistent with a long-lived ion-dipole complex on the exit channel. The CH<sub>3</sub>Cl reaction, which involves elimination of Cl<sup>-</sup> from a highly sterically strained fivecoordinate carbon center, generates products with high kinetic energies, suggesting that any ion-dipole complexes which might exist on the exit channel are not sampled by the majority of the reactive population. The large translational energy release into the products is due to the population of an antibonding orbital with a node between the C and Cl atoms in the collision complex.

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