# Application of Marcus Theory to Gas-Phase $S_N 2$ Reactions: Experimental Support of the Marcus Theory Additivity Postulate<sup>†</sup>

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Through the analysis of sufficiently fast identity exchange reactions, the Marcus theory additivity postulate has been tested and verified for two sets of gas-phase  $S_N2$  reactions:  $X^- + RCH_2Y \rightarrow XCH_2R + Y^-$  (where X and Y = Cl and/or Br and R = CN, C<sub>6</sub>H<sub>5</sub>). Statistical RRKM theory, within the microcanonical variational transition state ( $\mu$ VTS) approximation, is used to interpret the experimental kinetic data for each reaction to estimate the activation energies relative to separated reactants. Complexation energies, determined experimentally, are used in conjunction with the data from the RRKM analysis to obtain potential surface energetics. The Marcus expression is then used to determine whether the intrinsic component of the activation energy for the cross reaction is the mean of the activation energies for the two corresponding identity exchange reactions. Good agreement is found for R = C<sub>6</sub>H<sub>5</sub> and CN.

## Introduction

The relationship between kinetics and thermodynamics plays an important role in chemistry. Historically, rate-equilibrium relationships have supplied much of the predictive power that chemists strive for. Since the initial proposal of Bell, Evans, and Polanyi,<sup>1-8</sup> and later Leffler<sup>9</sup> and Hammond,<sup>10</sup> that properties of the transition state should reflect in part those of reactants and products, much work has gone into the refinement of various quantitative formalisms. Our goal is to shed light on one such formalism, namely Marcus theory,<sup>11</sup> as applied to gas-phase nucleophilic substitution (S<sub>N</sub>2) reactions.

In this paper we present direct experimental evidence that verifies the Marcus theory additivity postulate for two gas-phase  $S_N 2$  systems. The rates of substitution for reactions of the type

$$X^- + RCH_2Y \rightarrow XCH_2R + Y^-$$
(1)

where X and Y = Cl and/or Br and R = CN and C<sub>6</sub>H<sub>5</sub>, have been measured in the gas phase using Fourier transform ion cyclotron resonance (FT-ICR) spectrometry. The reaction kinetics were modeled using Rice-Ramsperger-Kassel-Marcus (RRKM) theory within the microcanonical variational transition state ( $\mu$ VTS) approximation to obtain the activation energies. Equilibrium measurements were used to estimate the complexation energies. Finally, the additivity concept is applied to other S<sub>N</sub>2 systems to predict activation energies and approximate rates of substitution near room temperature.

The first rate-equilibrium relationship used to rationalize chemical reactivity quantitatively was that of Brönsted and Pedersen.<sup>12</sup> They proposed an empirical relationship between the rate of proton transfer in solution and the relevant equilibrium constant. Considering a set of structurally similar acids with different ionization constants,  $K_a$ , the rate of proton transfer, k, should vary in a predictable way given by eq 2. Over the years the rate-equilibrium concept and the application of linear free energy relationships expanded in different directions.<sup>13</sup>

$$d\ln k = \alpha \, d\ln K_a \tag{2}$$

An important development in the field came in the mid-1950s from the work of Marcus. Modeling electron-transfer reactions in solution, Marcus derived an expression which relates the activation energy to the thermodynamics. The Marcus expression, eq 3, defines the activation energy,  $\Delta E^{\dagger}$ , as being made up of an

$$\Delta E^{\dagger} = \Delta E_0^{\dagger} + \frac{\Delta E}{2} + \frac{(\Delta E)^2}{16\Delta E_0^{\dagger}}$$
(3)

intrinsic component,  $\Delta E_0^{\dagger}$ , and a component which results solely from the thermodynamic difference between the reactant and the product species,  $\Delta E$ .  $\Delta E_0^{\dagger}$  is the purely kinetic contribution to the activation energy and is the only component in the absence of a thermodynamic driving force. Because the Marcus formalism was originally developed to rationalize a specific solution-phase process, its overall importance and applicability to other systems were initially overlooked. After Haim and Sutin<sup>14</sup> showed that Marcus theory could be successfully applied to atom-transfer reactions, however, the original work of Marcus was reexamined.<sup>15,16</sup> In subsequent years the Marcus equation was rederived in a variety of ways. Dogonadze and Levich,<sup>17-19</sup> as well as others,<sup>20</sup> showed that eq 3 can be obtained using purely geometrical arguments by modeling the reaction coordinate as a set of intersecting parabolas. In an important paper, Murdoch<sup>21</sup> later showed that the Marcus expression can also be derived starting from the original proposal of Leffler, Grunwald, and Hammond by using the Leffler equation. Murdoch's work was of fundamental importance because it established a strong connection between Marcus theory and the earlier rate-equilibrium relationships. Moreover, Murdoch laid the groundwork for the application to other chemical systems. Besides electron- and atomtransfer reactions in solution, proton transfer<sup>15</sup> and methyl group transfer in both solution<sup>22-27</sup> and the gas phase<sup>28-31</sup> have been interpreted using the Marcus formalism. Han and co-workers<sup>32</sup> recently used Marcus theory to analyze gas-phase electron-transfer reactions.

Equation 3 allows us to separate the activation energy into thermodynamic and "intrinsic" components. If the intrinsic activation energy is constant for a class or type of reaction, the Marcus equation can be used directly as a predictive tool to extract the activation energy of all other reactions within the class. The only necessary information is the reaction exothermicity,  $\Delta E$ ,<sup>33</sup> which can be obtained from experimental heats of formation or estimated from bond additivities. To a first approximation this is apparent from systems which give rise to linear Brönstead plots. There are, however, many reaction series whose intrinsic activation energies do vary considerably, for example gas-phase S<sub>N</sub>2 reactions. For such a series, much of the predictive power of eq 3 seems lost since both the thermodynamic and intrinsic components will vary. Therefore, in order for eq 3 to be of value, the intrinsic activation energy for every reaction must be known

<sup>&</sup>lt;sup>†</sup> Dedicated to the memory of Gerhard Closs.

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independently. This can be accomplished if the intrinsic component of the activation energy for each cross reaction in the series is the mean of the activation energies of the corresponding self-reactions. This relationship, the additivity postulate, eq 4, was proposed by Marcus in his original work.<sup>11</sup> Equation 4 allows the Marcus equation to be used as a predictive tool for many reaction series with changing intrinsic activation energies.

$$\Delta E_0^{\dagger}(\mathbf{X}, \mathbf{Y}) = \frac{1}{2} (\Delta E_0^{\dagger}(\mathbf{X}, \mathbf{X}) + \Delta E_0^{\dagger}(\mathbf{Y}, \mathbf{Y}))$$
(4)

The Marcus expression, in conjunction with the additivity postulate, was utilized by Pellerite and Brauman<sup>28,31</sup> and later by Dodd and Brauman<sup>29,30</sup> as a predictive tool in the analysis of kinetic data for  $S_N2$  reactions at methyl centers. By measuring the rates of substitution of various nucleophiles with methyl halides, estimates of the activation energies were made. The Marcus expression and the additivity concept were then used to produce a quantitative scale for intrinsic nucleophilicity. This analysis was critical to understanding of generalized reactivity and has led to some interesting conclusions regarding the intrinsic properties of certain nucleophiles. Although the generality of Marcus theory has been well established, and the application of it to  $S_N2$  reactions in the gas phase has been potentially useful, a test of the additivity postulate was never made. This is the main focus of the work presented here. Our approach is to show that the Marcus theory expression, eq 3, and the additivity postulate, eq 4, are internally consistent with one another. This can be accomplished experimentally by showing that the intrinsic activation energy for some cross reaction obtained from eq 3 is the average of the activation energies for the corresponding identity reactions.

This approach was originally used by Wolfe, Mitchell, and Schlegel;<sup>34,35</sup> *ab initio* quantum calculations rather than experimental techniques were used to determine the molecular properties and energetics. They showed that the original concepts proposed by Bell, Evans, Polanyi, Leffler, and Hammond are borne out, quantitatively. For a series of  $S_N 2$  cross-reactions Wolfe *et al.* found that the calculated geometric parameters of the transition state correlate well with the overall exothermicity of the reaction. More important, almost perfect internal consistency between the Marcus expression and the additivity postulate was found using the *ab initio* energetic data.

## **Experimental Methods**

Materials. All chemicals were available commercially (Aldrich). Both chloroacetonitrile and benzyl chloride were distilled prior to use. All samples were degassed via multiple freezepump-thaw cycles before being introduced into the high-vacuum region.

**Instrumentation.** Experimental measurements were performed using a Fourier transform IonSpec OMEGA ion cyclotron resonance (FT-ICR) spectrometer equipped with impulse excitation.<sup>36,37</sup> Details of the experimental setup along with typical operating conditions can be found in previous papers from this research group.<sup>38</sup> Total pressures within the ICR cell ranged from  $0.2 \times 10^{-6}$  to  $2 \times 10^{-6}$  Torr as measured with an ion gauge (Varian 844), which was calibrated daily against a capacitance manometer (MKS 170 Baratron with a 315BH-1 head). The hydrogen-transfer reaction of methane radical cation with methane (CH<sub>4</sub><sup>+</sup> + CH<sub>4</sub>  $\rightarrow$  CH<sub>5</sub><sup>+</sup> + CH<sub>3</sub><sup>•</sup>), which has a rate coefficient of  $1.1 \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup>,<sup>39</sup> was used to ensure that the absolute pressure readings were sufficiently accurate. All kinetic measurements were carried out at a temperature estimated to be 350 K.<sup>38</sup>

**Kinetic Measurements.** Primary ions (both Cl<sup>-</sup> and Br<sup>-</sup>) were generated directly from dissociative electron attachment via electron impact. For the identity exchange reactions, the neutral reactant also served as the ion source. For the cross-reactions of Cl<sup>-</sup> with the bromide substrates, the corresponding chloride substrate was used to generate the reactive ion. The proper isotope ratios for each ion  $({}^{35}Cl/{}^{37}Cl \approx 3; {}^{79}Br/{}^{81}Br \approx 1)$  were observed at the beginning and end of each kinetic run, indicating that the relative ion intensities were correct. Also, Cl<sup>-</sup> and Br<sup>-</sup> were the only ions observed in all experiments, showing that there were no unwanted side reactions.

Kinetic data collection was slightly different for each of the two types of reactions studied (cross and identity). For the cross reactions, known amounts of both the chlorine and bromine substrates, as determined by their partial pressures, were introduced into the cell. A kinetic run consisted of ion formation (20 ms, which forms both Cl- and Br-) followed by electron and Br-ejection. Absolute ion intensities of both Cl- and Br-were monitored as a function of time (800-2000 ms, depending on the total pressure). Decay of the <sup>35</sup>Cl-ion signal was used to determine the pseudo-first-order rate coefficients. In the case of the identity reactions only one compound was introduced into the cell, and following ion formation, one of the isotopes<sup>40</sup> was ejected. The relative ion intensities of the two isotopes were monitored as a function of time. The method of Eyler and Richardson<sup>41</sup> was used to analyze the ratio data to determine the pseudo-first-order rate coefficients for the identity reactions. By using the Eyler equation, eq 5, to analyze the kinetic data, complications due to ion loss are eliminated.

$$\ln\left[\frac{R_t - R_{\infty}}{R_t + 1}\right] = -k_{\rm obs}Pt \tag{5}$$

In eq 5, P is the total pressure,  $R_t$  is the ratio of ion intensities at time t,  $R_{\infty}$  is the ratio of ion intensities at infinite time (*i.e.*, the nature abundance ratio), and  $k_{obs}$  represents the observed rate coefficient. Details of the raw kinetic data analysis used to obtain the observed rate coefficients for the identity exchange reactions are given in a recent study.<sup>42</sup> Multiple kinetic runs were performed at a variety of different pressures and on different days. Much of the absolute error in the kinetic measurements is believed to be a result of errors in the pressure measurements; We estimate the absolute error in the rate coefficients to be on the order of 20–30%.

Thermodynamic Measurements. Assuming that the stabilities of ion-molecule complexes are dictated by simple electrostatics (see Data Analysis section), it is possible to estimate the complexation energy using established empirical relationships.<sup>43-47</sup> Since an experimental test of Marcus theory additivity postulate is the goal here, an experimental measurement of the complexation energy is desirable. Unfortunately, this is a difficult task.

Ion-molecule complex formation from direct association via three-body stabilization is very slow at the low pressures within the ICR cell, making it impractical to form complexes in this way. At higher pressures, direct ion-molecule complex formation is easier, and a number of thermodynamic measurements have been made using high-pressure mass spectrometry (HPMS) techniques.<sup>48-53</sup> To solve the problems at low pressure, Larson and McMahon<sup>54</sup> developed a technique to form the appropriate complexes using transfer agents. The appropriate methyl formate, CH<sub>3</sub>OCOX, is used to generate XCO<sub>2</sub><sup>-</sup>. Once formed, this ion can transfer X<sup>-</sup> to other neutrals present that have the same or larger X<sup>-</sup> affinities.

$$CH_3OCOX + e^- \rightarrow X^- + CH_3OCO^{\bullet}$$
 (6a)

$$CH_3OCOX + X^- \rightarrow CH_3X + XCO_2^-$$
 (6b)

$$M + XCO_2^{-} \rightarrow [M \cdot X]^{-} + CO_2$$
 (6c)

An equilibrium is set up between species to determine the relative free energy of complexation. By anchoring the results relative to species with known complexation energies, an absolute scale can be developed. Using estimates for the entropy change upon complex formation, the corresponding enthalpies can be calcu-

		$k_1 = k_{\rm cap}{}^{a,b}$				
reaction	$k_{\rm obs}{}^a$	ADO	SC	<b>Φ</b> (%) <sup>c</sup>	$\Delta E^{\operatorname{d} d}$	$\Delta E_0^{d d}$
<ul> <li>(a) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub><sup>35</sup>Cl + <sup>37</sup>Cl<sup>-</sup></li> <li>(b) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub><sup>79</sup>Br + <sup>81</sup>Br<sup>-</sup></li> <li>(c) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br + Cl<sup>-</sup></li> </ul>	$\begin{array}{c} 0.0068 \pm 0.0023 \\ 0.13 \pm 0.022 \\ 2.7 \pm 0.4 \end{array}$	21 15 21	23 17 22	0.030 0.76 12	+0.4 -2.5 -4.5	+0.4 -2.5 -0.8 <sup>f</sup>
(d) <sup>35</sup> ClCH <sub>2</sub> CN + <sup>37</sup> Cl <sup>-</sup> (e) <sup>79</sup> BrCH <sub>2</sub> CN + <sup>81</sup> Br <sup>-</sup> (f) BrCH <sub>2</sub> CN + Cl <sup>-</sup>	$3.3 \pm 0.9^{e}$ 2.6 ± 1.1 <sup>e</sup> 12 $\oplus$ 2.2 <sup>e</sup>	23 17 22	29 20 27	11 13 44	5.9 7.3 9.8	-5.9 -7.3 -6.1 <sup>g</sup>

<sup>a</sup> Units of  $10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>. <sup>b</sup>  $k_1$  is the rate of ion capture associated with the formation of the initial ion-molecule complex. <sup>c</sup> The efficient of reaction,  $\Phi$ , is defined as  $\Phi = k_{obs}/k_1$ . <sup>d</sup> Units of kcal mol<sup>-1</sup> relative to separated reactants (see Figure 1). <sup>e</sup> Bierbaum, DePuy, and co-workers (ref 58) at 300 K reported values of  $3.2 \times 10^{-10}$ ,  $4.0 \times 10^{-10}$ , and  $13 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> for reactions d, e, and f, respectively. <sup>f</sup> Obtained from eq 7 using  $\Delta E^{\circ} \equiv \Delta H^{\circ}$   $= -8.6 \pm 2$  kcal mol<sup>-1</sup> (ref 90) and using the value for the experimental well depth for reaction a,  $\Delta E^{w} \equiv D_0 = 15.1$  kcal mol<sup>-1</sup> (ref 57). <sup>g</sup> Obtained from eq 7 using  $\Delta E^{\circ} \equiv \Delta H^{\circ} = -8.6 \pm 2$  kcal mol<sup>-1</sup> (ref 91) and using the value for the experimental well depth for reaction d,  $\Delta E^{w} \equiv D_0 = 19.4$  kcal mol<sup>-1</sup> (ref 42).

TABLE II:	Experimental	Data and	Predictions f	or Related	S <sub>N</sub> 2 Systems
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		$k_1 = k_{\rm cap}{}^{a,b}$				
reaction	$k_{obs}{}^a$	ADO	SC	Φ (%) <sup>c</sup>	$\Delta E^{\operatorname{d} d}$	$\Delta E_0^{\mathbf{d} \ \mathbf{d}}$
(g) $CH_3^{35}Cl + {}^{37}Cl^{-}$	0.00035 ± 0.00018¢	19	22	0.0008	+2.5	+2.5
(ĥ) CH₃Br + Cl⁻	$0.24 \pm 0.06^{f}$ $0.27 \pm 0.05^{g}$ $0.12^{h}$	17	20	0.58	-1.8	+1.9
(i) $CH_3^{79}Br + {}^{81}Br$	$(0.001)^{t}$					+1.3
(j) ClCH2CN + CN <sup>-</sup> (k) CH2(CN)2 + *CN <sup>-</sup>	2.2 ± 0.4 (≈0) <sup>j</sup>	26	33	4.5	-4.8	+8.0 +21.9/

<sup>a</sup> Units of  $10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>. <sup>b</sup>  $k_1$  is equivalent to the rate of capture or formation of the initial ion-molecule complex. <sup>c</sup> The efficiency of reaction,  $\Phi$ , is defined as  $\Phi = k_{obs}/k_1$  (see text). <sup>d</sup> Units of kcal mol<sup>-1</sup> relative to separated reactants (see Figure 1). <sup>e</sup> References 88 and 89. <sup>f</sup> Reference 87. <sup>s</sup> Reference 58. <sup>h</sup> Reference 72. <sup>f</sup> Value obtained from eq 7 using  $\Delta E^d$  values from reactions g and h and the value of  $\Delta E^\circ = \Delta H^\circ = -8.6 \pm 2$  kcal mol<sup>-1</sup> estimated from thermodynamic data (ref 91). Rate coefficient in parenthesis is an estimate based on the calculated activation energy. <sup>f</sup> Value obtained from eq 7 using  $\Delta E^d$  values from reactions d and j and the value of  $\Delta E^\circ = \Delta H^\circ = -29.5 \pm 5$  kcal mol<sup>-1</sup> estimated from thermodynamic data (ref 90). Rate coefficient in parentheses is an estimate based on the calculated from thermodynamic data (ref 90).

lated. With this technique, Larson and McMahon<sup>54-56</sup> were able to determine complexation energies for a wide variety of compounds complexed to various ions, including F<sup>-</sup> and Cl<sup>-</sup>. We apply this method along with the absolute scale tabulated by Larson and McMahon to determine complexation energies important in the S<sub>N</sub>2 reactions presented here.

One major drawback with this technique is that complexation energies with Br cannot be obtained; the correct recipe for making species with the structure [X·Br], at low pressure, has not yet been found. A few Br complexation energies have been measured using HPMS techniques, including [CH<sub>3</sub>Br·Br] and [CH<sub>3</sub>Cl-Br].<sup>48-50</sup> Far too few have been obtained, however, to be useful in this regard. In addition, substrates that contain reactive sites are often problematic. For example, the ion-molecule complex, [CH<sub>3</sub>Br·Cl<sup>-</sup>], is difficult to form in our apparatus because the thermodynamically favored S<sub>N</sub>2 displacement of Br competes with the reaction responsible for formation of the complex (reaction 6b).

As a result, only the complexation energies of Cl<sup>-</sup> with chloride substrates,  $[C_6H_5CH_2Cl\cdotCl^-]$  and  $[ClCH_2CN\cdotCl^-]$ , have been measured experimentally for this study. We show later that the problems associated with measuring complexation energies introduce little error in the overall analysis and will not affect the final conclusions. A more detailed description of the experimental procedure for the determination of complexation energies in this way can be found in recent studies<sup>42,57</sup> along with the actual experimental data for the complexation energies of  $[C_6H_5CH_2Cl\cdotCl^-]$  and  $[ClCH_2CN\cdotCl^-]$ .

#### Results

The relevant kinetic and thermodynamic data are given in Tables I and II along with previous kinetic results from Bierbaum, DePuy, and co-workers<sup>58</sup> for the nitrile substrates (R = CN). The reported uncertainties represent one standard deviation from the mean of all kinetic runs taken. Tables I and II also contain the calculated capture rates,  $k_{cap}$ , obtained from both average dipole orientation (ADO) theory<sup>45-47,59</sup> and the parametrized



Figure 1. Generalized potential for an exothermic  $S_N 2$  displacement reaction in the gas phase.

trajectory model of Su and Chesnavich (SC),<sup>43</sup> as well as the corresponding efficiency ( $\Phi = k_{obs}/k_{cap}$ ) for each reaction. Finally, activation energies,  $\Delta E^d$ , obtained from the RRKM- $\mu$ VTS analysis of the experimental efficiency data are also given in Tables I and II for each of the reactions studied.

# Data Analysis

A generalized one-dimensional representation of the potential energy surface for an exothermic gas-phase  $S_N2$  reaction is illustrated in Figure 1. As shown, the reactants initially come together to form a chemically activated ion-molecule complex, [RCH<sub>2</sub>Y·X<sup>-</sup>]. This complex can undergo substitution to form a second ion-molecule complex, [RCH<sub>2</sub>X·Y<sup>-</sup>], which simply falls apart to products. This conceptual picture was proposed many years ago and has recently been confirmed experimentally by collision-induced dissociation and photodissociation of the reactive intermediates.<sup>60-62</sup> Moreover, in a recent study,<sup>42</sup> we showed that the stability of these ion-molecule complexes, relative to separated species, can be accounted for by simple electrostatics (i.e., a charge in the multipole and ion-induced fields of the neutral). Therefore, the complexes can be thought of as nonchemically interacting. This confirms that even though gasphase  $S_N2$  reactions are bimolecular overall, the important chemistry occurs in the unimolecular step which converts the reactant complex, [RCH<sub>2</sub>Y·X<sup>-</sup>], to the product complex, [RCH<sub>2</sub>X·Y<sup>-</sup>]. Viewed in this way, many of the problems associated with gas-phase bimolecular  $S_N2$  reactions are obviated, and Marcus theory seems well-suited to interpret the energetics. It is clear that the activation energy as measured from the initial ion-molecule complex,  $\Delta E^{\dagger}$ , is the quantity directly applicable to the Marcus analysis and needed to test the additivity postulate.  $\Delta E^{\dagger}$ , however, is not directly measurable from a single experiment. It must be obtained indirectly by measuring the value of  $\Delta E^{d}$  and  $\Delta E^{w}$  separately (see Figure 1).

In order to test the internal consistency between the Marcus expression and the additivity postulate we used (1) the enthalpy difference between the two ion-molecule complexes in the cross reaction,  $\Delta E$ , which can be approximated as the overall reaction enthalpy,  $\Delta E^{\circ}$ , (2) the ion-molecule complexation energy,  $\Delta E^{w}$ , for both identity exchange reactions and the cross reaction, and (3) the activation energy as measure relative to separated reactants,  $\Delta E^{d}$ , for each reaction.

**Determination of**  $\Delta E^{\circ}$ . When applied to gas-phase S<sub>N</sub>2 reactions, the thermodynamic component of the Marcus expression (eq 2) is related to the energy difference between the two ion-molecule complexes,  $\Delta E$ , as shown in Figure 1. Determination of  $\Delta E$  directly is a difficult task given the problems associated with the determination of complexation energies discussed above.  $\Delta E$  can be approximated as  $\Delta E^{\circ}$ , however, and obtained directly from tabulated thermodynamic data. This approximation is good to the extent that the reactant and product ion-molecule complexation energies are close to one another, since  $\Delta E = \Delta E^{\circ}$ +  $(\Delta E^{w}(X,Y) - \Delta E^{w}(Y,X))$ . Because the complexation energies are dictated by electrostatics, this approximation will begin to break down in systems where the neutral species before and after the substitution event have significantly different electrostatic properties. This is not likely to be a problem here, since the alkyl chlorides and bromides have similar electronic character. This is not the case for all substitution processes, however, as illustrated later in the discussion.

**Determination of \Delta E^{\bullet}.** The complexation energy (*i.e.*, well depth) is a direct experimental observable, unlike the activation energy determination discussed below. The enthalpy of complexation is usually obtained from the experimental equilibrium measurement and an estimate of the entropy change.<sup>54</sup> Problems associated with the formation of certain types of complexes, discussed previously, require us to approximate the values associated with [RCH<sub>2</sub>Br·Cl<sup>-</sup>] as equivalent to [RCH<sub>2</sub>Cl·Cl<sup>-</sup>]  $(i.e., \Delta E^{w}(Br,Cl) \approx \Delta E^{w}(Cl,Cl))$ . Although such an approximation is not ideal, the available experimental and theoretical data suggests that ion-molecule complexes of Cl<sup>-</sup> and Br<sup>-</sup> have very similar relative stabilities. Therefore, we feel this approximation is a reasonable one and preferable to estimating the complexation energies using a simple electrostatic model. Analysis of the experimental data is further complicated by our not knowing the structure of the actual complexes formed during the experimental measurement. It is clear from the one-dimensional picture of the potential energy surface in Figure 1 that the complexation energy referred to in the Marcus theory picture is that for the  $S_N2$  "backside" structure. It is conceivable in many cases, however, that other ion-molecule structures of comparable or lower energy could exist on the potential energy hypersurface. The experimental thermodynamic measurement will only reflect the stability of the most stable structure, not necessarily the  $S_N 2$ "backside" structure. The experimentally determined complexation energy should, therefore, be thought of as an upper bound to the " $S_N$ 2 backside" complexation energy.

Determination of  $\Delta E^{i}$ . For many years, statistical theories have been used to interpret kinetic data from both unimolecular

and bimolecular reactions in the gas phase. In particular, Rice-Ramsperger-Kassel-Marcus (RRKM) theory,63-71 including both variational and nonvariational analogs, have been used extensively to estimate activation energies for many ion-molecule reactions. including S<sub>N</sub>2 reactions.<sup>29-31,72,73</sup> A variety of other statistical treatments have also found use, including simple transition state theory (TST),<sup>74</sup> phase-space theory (PST),<sup>75-77</sup> and the statistical adiabatic channel model (SACM).78-81 Statistical modeling of ion-molecule reactions is especially difficult, in that part of the analysis involves the modeling of a unimolecular dissociation through a "loose" transition state. Both the number and position of the dynamical transition states depend strongly on both the total energy and the total angular momentum of the system. The actual reaction pathway can also become difficult to define. Finally, problems in the modeling of such transition states can also arise due to the effects of the uncoupling of modes as the fragments come apart, a problem of current interest. Recently, we addressed these issues in a study of the potential surface for the identity exchange reaction of Cl<sup>-</sup> + ClCH<sub>2</sub>CN, reaction d of Table I.<sup>42</sup> Among other things, RRKM- $\mu$ VTS modeling of the experimental kinetic data produced a value for the activation energy consistent (within 1 kcal mol<sup>-1</sup>) with that predicted from high-level ab initio quantum calculations. Also, we found that the final estimate of the activation energy was relatively insensitive to the model used (variational or nonvariational). These results lend support to the notion that quantitative energetics can be obtained for such systems (at least in the determination of activation energies relative to separated reactants,  $\Delta E^{d}$ ).

Although RRKM theory seems to work quite well for reaction d, recent theoretical<sup>82-86</sup> and experimental<sup>60,87</sup> work suggests that such theories may not be applicable to every S<sub>N</sub>2 system. In a series of theoretical trajectory studies on the  $Cl^- + CH_3Cl$  reaction, Vande Linde and Hase<sup>82-86</sup> found nonstatistical behavior in both the association and substitution dynamics. Similarly, both Viggiano and co-workers<sup>87</sup> as well as Graul and Bowers<sup>60</sup> found experimental evidence for nonstatistical behavior in the exothermic  $S_N^2$  reaction,  $Cl^- + CH_3Br$ . Given these results, it is likely that other  $S_N 2$  systems would exhibit similar behavior. It may be possible, however, that the nonstatistical contribution to the activation barrier is modest in most cases or it may be specific to certain reactions. Moreover, it is unclear to what extent these effects influence the practical use of transition state theories. For example, Tucker and Truhlar<sup>74</sup> have used semiclassical variational TST to calculate the rate coefficient for the Cl-+ CH<sub>3</sub>Cl reaction based on a complete multidimensional potential surface based on ab initio calculations. Although they found a significant tunneling effect, their final statistical analysis reproduced the experimental rate coefficient quite well.

In order to determine  $\Delta E^d$  from the kinetic data using RRKM theory, it is obvious that the reaction rate must fall in a useful range and still be accurately measurable. This means that the reaction rate must be slow enough that it is not collision controlled yet fast enough that it can be observed. The height of the activation barrier is the dominant factor which influences the overall rate. In general, ion-molecule reactions that contain energetic barriers higher than approximately 2 kcal mol<sup>-1</sup> above reactants will be too slow to measure at room temperature using ICR spectrometry. For most reactions with a sizable thermodynamic driving force this is not a problem. Measurement of identity exchange reaction rates can pose a problem, however, simply because they lack the necessary thermodynamic driving force to lower the activation barrier sufficiently. Because a test of the additivity postulate is most conveniently accomplished using measurements of identity exchange rates, systems must be found that contain low intrinsic activation energies. Based on the arguments concerning intrinsic nucleophilicity developed by Pellerite, Dodd, and Brauman<sup>28,29,31</sup> for reaction at methyl centers, Cl- and Br- appear to have the lowest intrinsic activation energies of all nucleophiles studied and thus are the most likely candidates

to have measurable identity exchange rates. Fortunately, both Cl-and Br-satisfy another important criterion necessary for their identity exchange rates to be conveniently measurable; both nucleophiles contain more than one stable and naturally abundant isotope. Multiple isotopes are required to distinguish between reactant and product ions for the identity kinetic measurements.

Actual examples of identity exchange of Cl<sup>-</sup> and Br<sup>-</sup> ions at alkyl centers in the gas phase are rare.<sup>42,58,88,89</sup> Bierbaum, DePuy, and co-workers<sup>88,89</sup> have recently measured the exchange rate between Cl<sup>-</sup> and CH<sub>3</sub>Cl in the gas phase at 300 K using a FA apparatus. The corresponding identity reaction with Br<sup>-</sup> has yet to be measured accurately due to problems associated with impurities.<sup>90</sup> Fortunately, certain  $\alpha$ -substituted methyl halides undergo identity exchange much faster than their methyl analogs. Using such substrates, the necessary kinetic measurement can be made to test the Marcus additivity postulate.

Details of the RRKM- $\mu$ VTS modeling along with the actual data used to interpret the kinetic results and obtain the values of  $\Delta E^d$  given in Tables I and II are not presented here. The reader is referred to the recent studies mentioned above.<sup>42,57</sup> As is the case with other S<sub>N</sub>2 systems, the estimation of the  $\Delta E^d$  values was found to be relatively insensitive to the theoretical model and the choice of the molecular parameters.

# Discussion

The application of Marcus theory to gas-phase doubleminimum potential surfaces has previously been considered by Dodd and Brauman.<sup>30</sup> To account for the problems associated with experimental measurements of complexation energies and interpretation of the results, Dodd and Brauman redefined the Marcus expression in terms of separated reactants and products, where the ion-molecule complexes are not considered explicitly, eq 7.

$$\Delta E^{\mathbf{d}} = \Delta E_0^{\mathbf{d}} + \frac{\Delta E^{\mathbf{o}}}{2} + \frac{(\Delta E^{\mathbf{o}})^2}{16(\Delta E_0^{\mathbf{d}} - \Delta E^{\mathbf{w}})}$$
(7)

This new expression is very similar to the original Marcus equation and can be obtained directly from eq 2 by assuming  $\Delta E^{\circ} = \Delta E$ (i.e., the reactant and product ion-molecule complexation energies are equal). There is no real mathematical advantage in using this new expression, but there are conceptual ones. Unlike  $\Delta E^{\dagger}$ , the activation energy in this new expression,  $\Delta E^{d}$ , is that obtained directly from the RRKM analysis. Second, the thermodynamic term is redefined in terms of the overall reaction exothermicity which can be obtained from tabulated thermodynamic data, requiring no approximation about the similarity of reactant and product complexation energies. Most important, it is easy to see from eq 7 that  $\Delta E^{w}$  contributes only to second order in the overall expression, and the second-order term contributes less for systems with large complexation energies. Thus, eq 7 helps to clarify the way uncertainties in the complexation energy measurements enter into the determination of the intrinsic activation energy. We analyze our data using this modified expression to make use of these conceptual advantages.

Table I shows the kinetic results (observed reaction rates and efficiencies) for the two  $S_N 2$  systems studied. The kinetic results for the nitrile-substituted substrates presented here are in reasonable agreement ( $\pm 30\%$ ) with those obtained by Bierbaum, DePuy, and co-workers using a flowing afterglow (FA) apparatus.<sup>58</sup> The observed activation energies,  $\Delta E^d$ , and intrinsic components to the activation energy,  $\Delta E_0^d$  as determined from eq 7, for each reaction are also given in Table I. For the benzyl substrate, identity exchange of chloride ion (reaction a, Table I) is slower than the identity exchange of bromide ion (reaction b, Table I) by a factor of 20. Conversely, for the nitrile substrates, the identity exchange rates for both ions are nearly equal (reactions d and e, Table I). In both cases the corresponding cross reactions

(reactions c and f, Table I) are faster than either of their respective identity exchange reactions. Moreover, reactions involving the nitrile substrates are faster than the corresponding reactions involving the benzyl substrates for all cases. These findings are a qualitative indication that the substitution transition state lies closer to the reaction threshold for the benzyl substrates compared with the nitrile substrate counterparts. This is confirmed quantitatively from the RRKM analysis.

Values for the intrinsic activation energies,  $\Delta E_0^d$ , were obtained using eq 7; the reaction enthalpy,  $\Delta E^{\circ} = -8.6 \pm 2$  kcal mol<sup>-1</sup>, is the same for both systems.<sup>91</sup> If Marcus theory, eqs 3 and 7, and the additivity postulate, eq 4, are internally consistent with one another for such  $S_N 2$  systems, then the intrinsic activation energy for each cross reaction should fall halfway between the activation energies of the identity reactions. For the benzyl substrate ( $R = C_6H_5$ ) almost perfect agreement is found. The value, -0.8, is within 0.2 kcal mol<sup>-1</sup> of the mean. For the nitrile substrate (R = CN) the value for the intrinsic component of the activation energy of the cross reaction also falls between those of the two corresponding identity exchange reactions. In this case the value of -6.1 kcal mol<sup>-1</sup> is within 0.5 kcal mol<sup>-1</sup> of the mean. We view these results as an encouraging indication of the internal consistency between Marcus theory and the additivity postulate for gas-phase S<sub>N</sub>2 reactions involving halide ions.

The results presented here are significant, but they are restricted to a relatively limited energetic range. It is easy to see why this problem is such a difficult one to address for gas-phase ionmolecule reactions. If we neglect the quadratic term in eqs 3 and 7, the observed activation energy for some cross reaction should be lowered by one-half of the overall reaction exothermicity. Therefore, in order to maximize the sensitivity of the additivity postulate comparison, one would like to use a cross reaction that is highly exothermic but still contains a large intrinsic activation energy component. Due to the narrow dynamic range for our kinetic experiments (about 10<sup>4</sup>) this is not a viable option, and unlike solution-phase reactions we cannot easily use temperatures as a variable to expand the apparent range. The energetic scale that can be accurately measured for  $\Delta E^d$  corresponds to about 10 kcal mol<sup>-1</sup>, ranging from about -8 to about +2 kcal mol<sup>-1</sup>. As a result, both the substrate and nucleophile must be carefully chosen such that activation energies fall within this range. Given these restrictions,<sup>92</sup> it is unlikely that a test of Marcus theory and the additivity postulate can be made for many other  $S_N 2$  systems using the same approach described here, at least using experimental methods. It may be possible, however, to show internal consistency between the two expressions by looking at a series of related cross reactions and using only one identity exchange reaction to reference the results. This approach will be discussed further subsequently.

Theoretical techniques, however, are not limited to such energetic and dynamic constraints93 and therefore represent an interesting alternative approach to this problem. Energetic data which cannot be obtained experimentally can be obtained computationally. Wolfe et al.35 used ab initio quantum methods to obtain the needed energetic data for a variety of S<sub>N</sub>2 systems, including those with activation energies far above the reaction threshold. The level of theory used in these studies is not adequate for a quantitative description of the absolute geometries and energetics involved, as is evident from recent theoretical studies of other  $S_N 2$  systems. Wolfe *et al.* argued, however, that errors in the absolute results would cancel when considering the relative changes. Given the level of agreement found, this argument appears justified. Thus, the internal consistency between the Marcus equation and the additivity postulate has been well demonstrated, with the theoretical and now experimental evidence presenting a strong case.

Rate-equilibrium relationships like Marcus theory can be used to predict the behavior of a variety of other gas-phase  $S_N 2$  systems by estimating the activation energy using available kinetic data. All that is required is a knowledge of two of three related activation energy parameters; the third can then be easily calculated using eqs 3 and 4.

$$X^- + CH_3 X \to XCH_3 + X^-$$
 (8a)

$$Y^- + CH_3Y \rightarrow YCH_3 + Y^-$$
(8b)

net: 
$$X^- + CH_3Y \rightarrow XCH_3 + Y^-$$
 (8c)

Reactions that have rates of substitution too slow to be measured at room temperature (usually reaction 8a or 8b) are of particular interest. Kinetic and energetic information for several related  $S_N^2$  reactions is given in Table II, along with the information predicted using Marcus theory and the additivity postulate. Using the activation energies from reactions g and h, the activation energy and corresponding rate of substitution for reaction i can be estimated. As noted previously, the identity exchange rate of Br with CH<sub>3</sub>Br (reaction i) has not been measured in the gas phase. According to the analysis in Table II, however, the reaction rate should be measurable. The activation energy is predicted to lie above the reaction threshold, but only by approximately 1.3 kcal mol<sup>-1</sup>. This is consistent with the notion that the difficulty in measuring the rate for reaction i arises from impurities and not because of any energetic considerations.<sup>90</sup> Also given in Table II is a prediction for the activation energy of a non-halide identity exchange reaction,  $CN^- + CH_2(CN)_2$ , malonitrile (reaction k). Consistent with the earlier proposal by Pellerite,<sup>31</sup> the intrinsic activation for CN-identity exchange at an alkyl center is predicted to be very large and the corresponding rate of substitution immeasurable at room temperature. In this case the activation energy is predicted to be  $\approx$ 40 kcal mol<sup>-1</sup>, which is in remarkable agreement with predictions for the activation energy of the methyl analog reaction (CN- + CH<sub>3</sub>CN).<sup>31,35</sup>

Application to Other Systems. Although there is encouraging theoretical and now experimental evidence which suggests that the Marcus formalism along with the additivity postulate can be used as a predictive tool, one should be cautious when applying it quantitatively to every  $S_N 2$  system in the gas phase. The identity exchange reaction

$$F^- + CH_3F \rightarrow FCH_3 + F^-$$
 (9)

is an excellent example. Since fluorine has only one stable and naturally abundant isotope, the reactant and product ions for this reaction cannot be distinguished from one another easily.<sup>94</sup> As a consequence, neither the rate of substitution nor the activation energy for the reaction can be measured directly using experimental methods. Use of the Marcus formalism and the additivity postulate represents an alternative approach to obtaining this information. The reaction rate and corresponding activation barrier for related cross reactions (i.e.,  $F^- + CH_3X$  or  $Y^- + CH_3F$ ) can be determined experimentally. Analogous to the examples giving in Table II, the reaction exothermicities along with the activation barriers of the related identity reaction (i.e.,  $X^-$  +  $CH_3X$  or  $Y^- + CH_3Y$ ) can be used to estimate the activation barrier in eq 9. Problems can arise, however, when the chosen cross reaction is too fast or too slow relative to the collision rate such that determination of the activation energy is difficult.

Pellerite and Brauman<sup>31</sup> used this approach to determine the intrinsic activation energy for eq 9 utilizing the kinetic and thermodynamic results from the cross reaction of fluoride ion with methyl chloride,  $F^- + CH_3Cl$ , and the identity exchange reaction,  $Cl^- + CH_3Cl$ . The activation energy for the  $Cl^- + CH_3Cl$  identity exchange reaction has been well characterized both experimentally and theoretically and represents an excellent reference. Using this information, the activation energy for eq 9 was predicted to be quite high ( $\Delta E_0^{\dagger} = 26.2$  kcal mol<sup>-1</sup>), and the reaction rate was expected to be immeasurably slow at room temperature. Most importantly, the activation energy was

predicted to be anomalously high relative to the intrinsic  $S_N 2$  activation energies of the other halides, which have intrinsic activation energies predicted to be much lower. This is consistent with solution-phase results which suggest an order of intrinsic reactivity  $I^- > Br^- > CI^- \gg F^-$ .

In a recent publication, however, Bierbaum, DePuy, and coworkers<sup>58</sup> reported kinetic results for two related S<sub>N</sub>2 cross reactions, OH- + CH<sub>3</sub>F and CH<sub>3</sub>O- + CH<sub>3</sub>F. They found that both reaction rates are slow relative to the conclusion rates but measurable at room temperature (0.52% and 0.1% efficient, respectively). These data along with the reaction thermodynamics and identity exchange activation barriers for the reactions OH-+ CH<sub>3</sub>OH and CH<sub>3</sub>O<sup>-</sup> + CH<sub>3</sub>OCH<sub>3</sub> can also be used to predict the activation energy for eq 9 using the procedure outlined above. Unlike the Pellerite and Brauman example using the Cl- + CH<sub>3</sub>-Cl identity reaction, neither of these two identity exchange activation barriers can be measured directly from experiment since their exchange rates are too slow. Estimates for these values can be made, however, by referencing them to the Cl<sup>-</sup> + CH<sub>3</sub>Cl system using the cross reactions  $OH^- + CH_3Cl$  and  $CH_3O^- +$ CH<sub>3</sub>Cl. As long as we know the intrinsic activation energy for two out of the three related reactions, the remaining one can be determined. Using this new information, the predicted activation energy for eq 9 obtained from the Marcus analysis is much lower  $(E_0^{\dagger} \approx 10 \text{ kcal mol}^{-1})$  and more in line with the other halide exchange reactions. In principle, the results from Pellerite and Brauman for the  $F^-$  + CH<sub>3</sub>Cl reaction and the results from DePuy et al. for the  $OH^- + CH_3F$  and  $CH_3O^- + CH_3F$  reactions should ultimately lead to the same activation energy for eq 9 if the Marcus formalism holds for all sets of S<sub>N</sub>2 cross reactions. In fact, this method could also be used to show internal consistency of the Marcus analysis. The activation energies for a series of related cross reactions can be referenced back to a single identity reaction. The two sets of results, however, are clearly in conflict with one another. It remains to be seen whether this is due to some breakdown in the Marcus formalism and additivity postulate or whether it is related to problems in the experimental measurements or to problems with the estimates of the activation barriers.

In their study, DePuy et al.58 pointed out that intrinsic activation energies will be overestimated using the Marcus formalism if the energetics for the corresponding cross reaction are overestimated. As an example, DePuy et al. argued that the cross reactions of F- with other methyl halides may in fact be collision controlled. and therefore, only an upper limit to the activation energy can be determined from a statistical analysis. An overestimation of the activation barrier for the cross reactions could lead to the anomalously high estimate of the activation barrier for eq 9.95 On the other hand, the reaction rates reported by DePuy et al. for  $OH^- + CH_3F$  and  $CH_3O^- + CH_3F$  are sufficiently slow that a small amount of an impurity (e.g., 0.1% HF) could affect the rate measurement significantly; this is unlikely however (see ref 57 and references therein). If this were the case, the prediction of the intrinsic activation energy for eq 9 would be anomalously low. Due to the nature of the experimental measurement, there is reason to prefer the prediction based on the measurement of Bierbaum, and co-workers. It is clear that caution is indicated when interpreting results for systems whose rates fall outside a given dynamic range. It appears that the dynamics of the key reactions in both sets of data  $(F^- + CH_3C)$  and  $OH^-$  or  $CH_3O^-$ + CH<sub>3</sub>F) lie near the extremes of this dynamic range. As a result, the utility of Marcus theory to determine the intrinsic activation energy for the reaction in eq 9 is questionable.

Theoretical results on the  $S_N 2$  system in eq 9 are still of little utility in resolving this important issue. Over the past 20 years several researchers have reported theoretical results for the activation energy and complexation energy using *ab initio* quantum methods.<sup>35,96-99</sup> Of note, Wolfe and co-workers<sup>35</sup> reported a value for the activation energy,  $E_0^{\dagger} = 11.7$  kcal mol<sup>-1</sup>. In more recent work, Vetter and Zulicke<sup>98</sup> reported a value as high as 20 kcal mol<sup>-1</sup>. A clear systematic study to address the details of the effects of both basis set and electron correlation on the energetics of this system has yet to be presented.

# Conclusion

The Marcus theory additivity postulate has been tested for S<sub>N</sub>2 reactions in the gas phase. Experimental determination of the potential surface energetics have been obtained for  $X^-$  +  $YCH_2R \rightarrow XCH_2R + Y^-$ , where X and Y = Cl and/or Br and  $R = C_6H_5$ , CN. When cast in the Marcus formalism, the results satisfy the additivity postulate within experimental uncertainty. Problems associated with the kinetic measurement of identity exchange reactions are highlighted as well as experimental and conceptual problems associated with formation of intermediate ion-molecule complexes and their relationship to the  $S_N 2$ activation energy.

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- (93) Although the use of theoretical techniques is not restricted in this way, there does exist a practical limit to the size of the system which can be studied due to issues related to computational time constraints.
- (94) It may be possible to use a radioactive isotope of fluorine to distinguish between reactant and product ions. However, the most stable radioactive isotope,  ${}^{18}F$ , has a half-life of only 109.7 min.
- (95) Fast thermoneutral proton-transfer reactions like CH<sub>3</sub>OH + CH<sub>3</sub>Orepresent an excellent example of a system where such problems can occur. Even though the potential surface has little or no barrier to proton transfer, the reaction rate is slower than expected due to problems related to dynamical constraints. (96) Keil, F.; Ahlrichs, R. J. Am. Chem. Soc. 1976, 98, 4789.
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