

High-Pressure Mass Spectrometric Investigations of the Potential Energy Surfaces of Gas-Phase S_N2 Reactions

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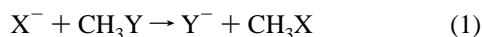
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Abstract: High-Pressure Mass Spectrometric (HPMS) experiments have been carried out to probe the details of the double minimum potential energy surface for gas-phase S_N2 reactions. The well depths and entropy changes associated with the formation of entrance and exit channel electrostatic complexes for the chloride and bromide adducts of methyl, ethyl, isopropyl, and *tert*-butyl chlorides and bromides have been determined from the temperature dependence of the equilibrium constants for adduct formation. In the cases of “symmetric” complexes associated with identity S_N2 reactions, there is an increase in well depth as the size and, therefore, polarizability of the alkyl group increases. Concomitant with this is an increase in the magnitude of the negative entropy change for complex formation which is the result of an increase in the frequency of the intermolecular mode(s) of the complex arising from the increased bond strength. The data for the unsymmetrical adducts for the non-identity S_N2 reactions show the same pattern of increasing well depth with increasing alkyl group size with the chloride adducts of alkyl bromides being more strongly bound than the bromide adducts of the corresponding alkyl chlorides. Enthalpies and entropies associated with transition state formation are determined from the temperature dependence of the rate constant for the net halide displacement reaction. These data show that the transition state for the reaction of chloride ion with alkyl bromides may lie below (CH₃Br), near (C₂H₅Br), or above (*i*-C₃H₇Br, *t*-C₄H₉Br) the energy of separated reactants. These three situations exhibit different changes in rate constant with increasing temperature. In addition, the lifetime of the transient, chemically activated intermediate formed between chloride ion and methyl chloride has been determined from the pressure dependence of the rate constant for formation of the observable, collisionally stabilized electrostatic adduct. The lifetime thus obtained is in excellent agreement with trajectory calculations performed by Hase and co-workers.

Introduction

Bimolecular nucleophilic displacement (S_N2)^{1,2} reactions have been examined by chemists for many years. These reactions have played a critical role in formulation of numerous interpretations of chemical reactions such as the role of steric effects, solvent effects, and structure reactivity correlations. In particular, the kinetics of reaction 1, where X and Y are halogens,



have been studied extensively in a variety of protic and dipolar aprotic solvents,³ and were initially recognized to be first order in both nucleophile and substrate by Ingold.⁴ This is thus distinct from the first-order S_N1 process, which involves dissociation of the substrate into a carbonium ion R⁺ and anion Y⁻ in the rate determining first step. Traditionally, S_N2 reactions had been envisioned as proceeding in one step, with formation of the new bond occurring synchronously with cleavage of the old bond. They proceeded very slowly in solution, and were characterized by activation energies approximately in the range of 15–30 kcal mol⁻¹, as typified by the qualitative reaction coordinate diagram shown in Figure 1.

The search for meaningful trends in chemical reactivity and their correlation with molecular parameters is one of the

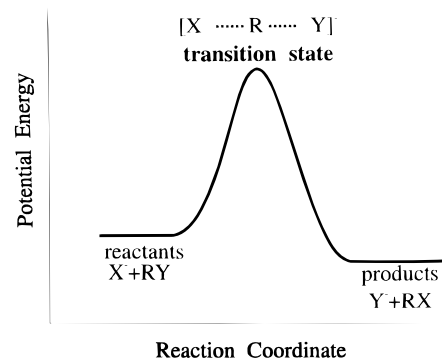


Figure 1. Hypothetical potential energy profile for a solution-phase S_N2 reaction.

fundamental goals of chemistry. It is known, however, that the rates and mechanisms of ion–molecule reactions in the gas phase and in solution differ dramatically, primarily because of solvent effects.^{5–7} Thus the concept of intrinsic reactivity should be best derived from chemical behavior in a solvent free environment which should, in principle, provide a more definitive separation of intrinsic structural effects from solvent and other environmental effects.

Gas-phase S_N2 reactions were first investigated experimentally by Bohme,^{8–10} using the flowing afterglow technique, and

[®] Abstract published in *Advance ACS Abstracts*, September 15, 1996.

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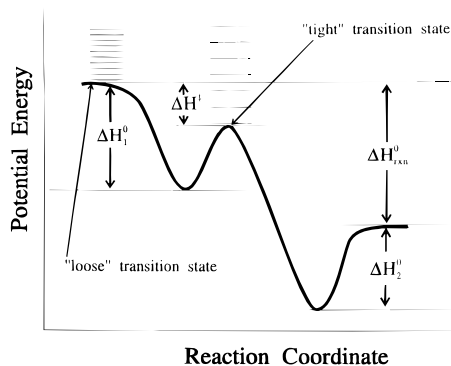


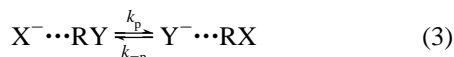
Figure 2. Hypothetical potential energy profile for a gas-phase S_N2 reaction.

by Brauman,^{11–13} using the trapped ion, pulsed ICR technique. These gas-phase measurements have shown that variation in the nucleophile, leaving group, and alkyl moiety lead to a wide variation of reaction rate constants, from almost collision controlled to too slow to be observed. On this basis, Brauman concluded that these reactions are best explained by a double-well potential with a secondary central barrier, as shown in Figure 2, and the variation of rates or reaction efficiencies is primarily due to the variation of the central barrier height.¹⁴ This potential energy surface also finds abundant theoretical support from *ab initio* calculations,^{15–19} which are currently one of the most useful tools for evaluating reaction potential energy profiles. For example, Truhlar *et al.*²⁰ have shown that *ab initio* calculations at the MP2/6-31G* level yield reasonable energy values, compared to the limited experimental data available, for the stationary points on the reaction profile.

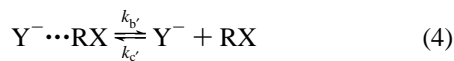
The exothermic gas-phase S_N2 reaction can then be represented by three elementary processes: (1) formation of the first loosely bound cluster or ion–dipole complex, eq 2;



(2) net S_N2 reaction forming the second-cluster, eq 3;

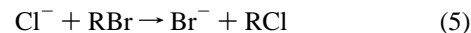


(3) decomposition of the second cluster, eq 4;



The first well depth in the potential energy surface corresponds to the stabilization energy of the first ion–molecule cluster X[−]⋯RY relative to the energy of the reactants while the second well depth corresponds to the stabilization energy of the second ion–molecule cluster Y[−]⋯RX relative to the energy of the products.

Kebarle and co-workers²¹ have investigated the temperature dependence of a series of reactions of chloride ion with selected alkyl bromides, eq 5, using high pressure mass spectrometry



(HPMS). Using a transition state theory formalism applied to the experimentally observed temperature dependence, they then inferred the barrier heights for a series of such reactions. These barriers were found to be below the energy of separated reactants in the case of methyl bromide, within 1 kcal mol^{−1} of this energy for ethyl and *n*-butyl bromides, and substantially above the energy of the reactants for isopropyl and isobutyl bromides. In these studies, the complexes Cl[−]⋯RBr were occasionally observed, but no measurements of the stabilization energy of the complex relative to the reactants were carried out.

Depuy and Bierbaum and co-workers²² have also investigated the rate constants at 298 K for a series of anionic nucleophiles with CH₃F, alkyl chlorides, and alkyl bromides to determine the important factors affecting the efficiency of these S_N2 reactions as well as those for the corresponding E2 reactions. One of these studies^{22a} showed that the central barrier for the Cl[−] + CH₃Cl reaction is of the order of 3 kcal mol^{−1}, accounting for the extremely slow rate constant observed for the symmetric nucleophilic displacement reaction.

Hase and co-workers²³ have carried out extensive trajectory studies of the Cl[−] + CH₃Cl reaction and find substantive evidence for non-statistical behavior arising from weak coupling between the intermolecular modes of the ion–molecule association complex and the intramolecular modes of the methyl chloride moiety. These studies have also predicted a room temperature lifetime for the nascent association complex on the order of 10 ps which has a significant bearing on the efficiency of central barrier crossing to give the S_N2 products.

Experimental support for this non-statistical behavior has been obtained by Viggiano *et al.*²⁴ in the temperature and kinetic energy dependence of the rate constant for the reaction of Cl[−] with CH₃Br as well as by Graul and Bowers²⁵ in the kinetic energy release measurements of metastable Cl[−][CH₃Br] association complexes. In addition, using collisional activation experiments, Johnson and co-workers²⁶ have shown that these entrance channel complexes are identifiably different from the corresponding exit channel complexes (Br[−][CH₃Cl]) for this reaction.

However, despite the many experimental studies carried out, quantitative details of the potential energy surfaces for S_N2 reactions still remain largely uninvestigated experimentally. Our interests in gas-phase S_N2 reactions are motivated by the thought that more detailed information about the stationary points on the potential energy surface would give us a better understanding of the intrinsic properties controlling the S_N2 reaction. HPMS techniques lend themselves ideally to the investigation of the energetics of adduct formation and to the temperature depen-

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dence of kinetics of reaction from which activation energies can be derived. In the present work such experiments have been exploited in an attempt provide as complete experimental detail as possible of the potential energy surfaces of S_N2 reactions involving chloride and bromide.

Experimental Section

All experiments were carried out on a high pressure mass spectrometer constructed at the University of Waterloo which has been described in detail elsewhere,²⁷ as have the principles and capabilities of HPMS in general.²⁸

Gas mixtures were prepared in a 5 L heated reservoir using CH_4 as the major bath gas at a pressure of 500–1000 Torr. The negative ion generation reagent, CCl_4 for Cl^- or CBr_4 for Br^- , was added in trace amounts to yield the desired negative reagent ion by dissociative electron capture. The neutral, alkyl halide, reagent was added to a pressure of between 0.1 and 10 Torr depending upon the temperature and nature of the experiment involved. This mixture was then flowed into the ion source to a total pressure of 3–7 Torr. Ionization occurred via 50 μs pulse of 2-keV electrons focused onto the 100 μm electron entrance aperture of the ion source. Mass selected ion temporal profiles were monitored using a PC based multichannel scaler data acquisition system typically configured with between 5 and 50 μs dwell time per channel. Equilibrium and/or rate constants were then monitored as a function of ion source temperature to determine the thermochemistry of termolecular association, bimolecular reaction, or activation enthalpies and entropies using methods and data treatment outlined below.

Results and Discussion

1. Symmetric Halide–Alkyl Halide Adduct Well Depths.

The first deduction that a double minimum potential energy surface was implicated in gas-phase S_N2 reactions arose from Brauman's investigation of the symmetric reaction, eq 6,



involving methyl chloride. In addition, the most extensive *ab initio* studies performed to date have been for this same reaction. The first objective of our experimental investigations was therefore to elucidate details of the potential energy profile for the series of symmetric chloride displacement reactions. Due to the unavailability of reasonably priced chlorine-labeled reagents for either chloride ion generation or alkyl chloride, the kinetics of the symmetric displacement reactions could not be investigated. However, the clustering equilibria, eq 7, were able



to be examined and this then provides the well depths for the two stable intermediates on the symmetric double minimum surface. Experimental data illustrating the temporal variation of ionic abundances with residence time in the ion source are shown in Figure 3 for methyl chloride. From the equilibrium ion intensity ratios and the known partial pressure of the alkyl chloride involved, equilibrium constants, K_{eq} , for the clustering equilibria may be derived and, from these, the free energy changes, ΔG°_c , obtained for that reaction. As illustrated in Figure 4 for *tert*-butyl chloride, the corresponding van't Hoff plots of $\ln K_{eq}$ vs T^{-1} then yield the enthalpy and entropy changes, ΔH°_c and ΔS°_c . The well depths for the association adducts for each of the chloride–alkyl chloride systems are summarized in Table 1. These data reveal several interesting trends and perhaps provide insight into the structure–reactivity relationships observed for solution-phase S_N2 reactions. The

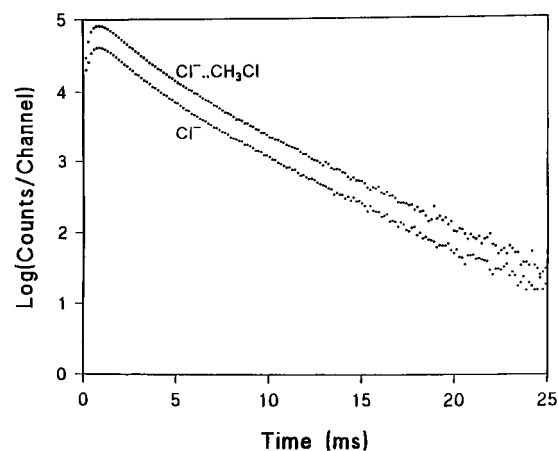


Figure 3. Variation of ion intensities with reaction time for Cl^- clustering onto CH_3Cl in a high pressure source at 296 K and 4 Torr of a 98% CH_4 , 2% CH_3Cl mixture.

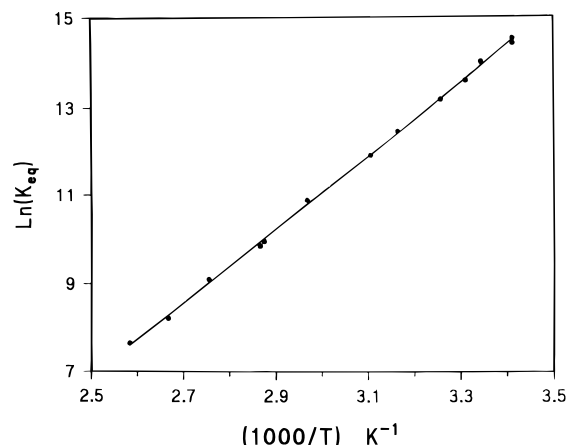


Figure 4. Van't Hoff plot ($\ln K$ vs T^{-1}) for the clustering reaction of Cl^- onto *t*- C_4H_9Cl , from which ΔH° and ΔS° are derived.

Table 1. Thermochemical Data for the Association of Halide Ions with Alkyl Halides

R	$Cl^- + R-Cl$		$Br^- + R-Br$	
	ΔH° ^a	ΔS° ^b	ΔH° ^a	ΔS° ^b
CH_3	-10.4	-15.3	-11.2	-22.0
C_2H_5	-12.4	-18.8	-12.0	-20.4
<i>i</i> - C_3H_7	-14.7	-23.3	-14.2	-26.6
<i>t</i> - C_4H_9	-16.6	-27.8	-15.6	-27.7

^a kcal mol⁻¹, ^b cal mol⁻¹ K⁻¹.

first clear trend is that as the alkyl group size increases from methyl to ethyl to isopropyl to *tert*-butyl the well depth increases. This can be readily understood from the point of view that these are predominantly electrostatically bound complexes and as the alkyl group size increases so too does the polarizability ($\sim 125\%$)²⁹ while the dipole moments increase only slightly (16%) from 1.87 D to 2.05 D to 2.17 D in going from methyl to ethyl to isopropyl chlorides and then remains almost constant at 2.13 D for *tert*-butyl chloride.³⁰ The strength and direction of the dipole moment cause the preferred direction of attack to be decidedly "backside" while the increasing polarizabilities result in the substantial increase (75%) in binding enthalpies. This general pattern of increasing well depth with increasing methyl for hydrogen substitution is also revealed in

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ab initio calculations for these same species where, at the 6-31G* MP2 level, agreement within $0.5 \text{ kcal mol}^{-1}$ is obtained in each case.³¹

However, perhaps just as revealing are the entropy changes which accompany these enthalpy changes. Normally, the entropy change associated with the clustering reaction of a monoatomic ion with a polyatomic neutral to give an electrostatic complex is minimal, i.e. $\sim 15 \text{ cal mol}^{-1} \text{ K}^{-1}$. In the series of chloride ion-alkyl chloride interactions, as the strength of interaction increases, so too does the decrease in entropy accompanying complex formation.

There are a number of possible factors which might give rise to this trend in the association entropy change values. One of these possibilities is that this is due to the increased loss in rotational entropy associated with the shorter chloride to carbon bond distance in the electrostatic complexes as the alkyl group size increases. However, simple estimation of the moments of inertia based on the *ab initio* geometries of these adducts indicates that this rotational entropy effect would constitute, at best, a minor contribution to the observed trend.

The increased loss in entropy is relatively constant with each methyl for hydrogen substitution, with a low value of $-15.3 \text{ cal mol}^{-1} \text{ K}^{-1}$ for the $\text{Cl}^- - \text{CH}_3\text{Cl}$ adduct to the high value in the case of the complex formed with *tert*-butyl chloride where the magnitude of the entropy decrease is $-28 \text{ cal mol}^{-1} \text{ K}^{-1}$. This then leads to the speculation that the number of methyl groups may be a determining factor and might imply that, as the Cl^- approaches the backside of the alkyl chloride neutral along the molecular dipole axis, methyl group rotations become restricted. In the cases of methyl chloride there is no such effect since the complex and methyl group axes are coincident and the internal and overall rotations are synonymous. However, for ethyl and other chlorides this is not the case and the chloride approach results in restriction of one, two, or three methyl group rotations. As the strength of interaction increases the degree of restriction of rotation in each methyl group also increases and hence the magnitude of the entropy change would then decrease in a nonlinear fashion. In order to test this possibility the energetics of association of Cl^- with *tert*-butyl chloride- d_9 were examined. Previous studies from this laboratory³² have shown that when association complexes are formed in which internal rotations are restricted there is a pronounced deuterium isotope effect in the entropy arising from a greater loss in entropy in restriction of, for example, CD_3 groups relative to CH_3 groups. However, when the $(\text{CD}_3)_3\text{CCl}$ system was examined an entropy of association virtually identical to that for $(\text{CH}_3)_3\text{CCl}$ was obtained. Thus the trend in entropy changes observed is most likely not due to restriction of methyl group rotations in the ion-dipole complexes.

Finally, an examination of the complexes for which vibrational frequencies were available from *ab initio* calculations led to the most probable source of the trend of increasingly negative entropies of association with increasing alkyl group size. Vibrational contributions to the entropy of a species are largest for low-frequency vibrations and at very low vibrational frequencies increase dramatically with decreasing frequency. Thus for the most weakly bound species, $\text{Cl}^-(\text{CH}_3\text{Cl})$, the "intermolecular" modes will have lower frequencies than those associated with the more strongly bound complexes of larger alkyl group size. The increasing bond strength evidently more

than counterbalances the increased reduced mass effect in determining the frequencies of the "intermolecular" modes.

These trends observed above for the symmetric chloride complexes are mimicked by the analogous bromide complexes. The data summarized for these species in Table 1 show the expected simultaneous increases in the magnitudes of ΔH° and ΔS° as the alkyl group size increases and proceeds from primary to tertiary. In addition, the binding energies in the bromide species are in general reduced slightly relative to the analogous chloride species reflecting the larger radius associated with the bromide ion. Accompanying this is an overall less favorable entropy change for the symmetric bromide adducts as well, which may be the result of a smaller change in rotational entropy of the bromide complexes relative to the corresponding neutral alkyl bromide as compared to the chloride systems.

Ab initio calculations at the 6-31G* MP2 level for the symmetric Cl^- -alkyl chloride adducts, as well as that between Br^- and CH_3Br , have been carried out which are also in good agreement with these experimental results with a maximum deviation of $0.6 \text{ kcal mol}^{-1}$ between experimental and theoretical values.

These experimental well depths for the symmetric halide-alkyl halide adducts provide a basis for understanding the well depths for the asymmetric systems where the shape of the potential energy profile can conceivably be modified by the exothermicity of the net nucleophilic displacement reaction.

2. Asymmetric Halide-Alkyl Halide Adduct Well Depths.

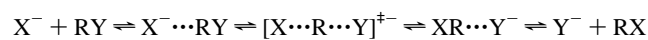
The position of the central barrier in the double minimum potential energy surface critically determines whether or not it is possible to observe asymmetric halide-alkyl halide adducts in the entrance channel of the potential energy surface. If the central barrier lies anywhere from ~ 1 to 2 kcal mol^{-1} below the energy of the separated reactants upwards then the adduct may be readily observed, provided that the lifetime of the initially formed chemically activated adduct is sufficiently long that it may be collisionally stabilized at the pressures used in the ion source. However, if the central barrier lies too far below the energy of the separated reactants then the lifetime of the initially formed adduct is too short, compared to the time between collisions, to be efficiently collisionally stabilized. In such cases the system passes nearly quantitatively over the central barrier to the exit channel adduct and, from there, dissociates to reaction products. As a result no information is obtainable for the well depth of the entrance channel complex for potential energy profiles of this type. In all cases the well depth for the exit channel complex, relative to separated products, is readily obtainable from experiments involving clustering of the product anion onto the product neutral. Data for the asymmetric cases studied are summarized in Table 2.

For the chloride-alkyl bromide series, the only case where an entrance channel well depth was undeterminable from the normal temperature-dependent equilibrium method was methyl bromide. This is consistent with *ab initio* calculations which place the central barrier $2.8 \text{ kcal mol}^{-1}$ below separated $\text{Cl}^- + \text{CH}_3\text{Br}$. The complex electronic energy of $-10.7 \text{ kcal mol}^{-1}$ relative to reactants obtained by Hase and co-workers²³ is consistent with the experimental well depth of $10.4 \text{ kcal mol}^{-1}$ for $\text{Cl}^- - \text{CH}_3\text{Cl}$ and the difference of $1.2 \text{ kcal mol}^{-1}$ obtained for the well depths of the $\text{Cl}^- - \text{C}_2\text{H}_5\text{Cl}$ and $\text{Cl}^- - \text{C}_2\text{H}_5\text{Br}$ complexes. Thermochemical data for the adduct of Cl^- with $\text{C}_2\text{H}_5\text{Br}$ were obtainable, although the equilibria observed exhibited a slight pressure dependence, possibly due to a lifetime of the initially formed adduct which is of the same order as the time required for collisional stabilization at the lowest pressures. This therefore introduces a somewhat larger than normal

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Table 2. Relative Energetics for Experimentally Determined Stationary Points on the S_N2 Potential Energy Surface^a

X ⁻	RY	well 1		transition state		well 2	
		ΔH ^o ₁	ΔS ^o ₁	ΔH [‡]	ΔS [‡]	ΔH ^o ₂	ΔS ^o ₂
Cl ⁻	CH ₃ Br	-12.5	(-19.0) ^b	-1.8	-24.1	-10.9	-20.3
Cl ⁻	CH ₃ Br			1.9 ^c	-24.3 ^c		
Cl ⁻	CH ₃ Br			-2.8 ^d	-26.1 ^d		
Cl ⁻	CH ₃ Br			-3.3 ^e	-29.7 ^e		
Cl ⁻	CH ₃ Br			-1.8 ^f	-25.1 ^f		
Cl ⁻	CH ₃ Br	-12.4 ^g	-19.0 ^g	-1.8 ^g	-24.5 ^g		
Cl ⁻	C ₂ H ₅ Br	-13.6	-22.4	-0.7	-22.7	-11.2	-19.6
Cl ⁻	C ₂ H ₅ Br			0.1 ^e	-21.1 ^e		
Cl ⁻	C ₂ H ₅ Br			-0.5 ^c	-22.2 ^c		
Cl ⁻	C ₂ H ₅ Br			-0.5 ^d	-22.4 ^d		
Cl ⁻	<i>n</i> -C ₃ H ₇ Br	-14.2	-20.0	-1.3	-24.0	-12.1	-20.6
Cl ⁻	<i>i</i> -C ₃ H ₇ Br	-15.2	-22.4	2.9	-20.0	-12.4	-20.6
Cl ⁻	<i>i</i> -C ₃ H ₇ Br			4.5 ^e	-15.9 ^e		
Cl ⁻	<i>n</i> -C ₄ H ₉ Br			-1.6 ^e	-24.3 ^e		
Cl ⁻	<i>n</i> -C ₄ H ₉ Br			-1.4 ^c	-23.5 ^c		
Cl ⁻	<i>t</i> -C ₄ H ₉ Br	-17.7	-29.5			-13.9	-24.5
CN ⁻	CH ₃ Cl	-10.2	-17.8			-15.8	-18.7
CN ⁻	<i>t</i> -C ₄ H ₉ Cl	-15.9	-28.0			-18.5	-25.0
CN ⁻	CH ₃ Br					-14.3	-18.7

^a Unless otherwise noted all values reported are from the present work. ^b A value of -19 cal mol⁻¹ K⁻¹, based on *ab initio* calculations (ref 23e), has been used to convert the single temperature clustering ΔG^o measurement to a ΔH^o value. ^c HPMS measurements at 3 Torr from ref 33. ^d Ion mobility MS measurements at atmospheric pressure from ref 33. ^e HPMS measurements from ref 21. ^f Flowing afterglow measurements from ref 24. ^g *Ab initio* calculations from ref 23f.

uncertainty in these values. The slightly greater stabilization of alkyl bromide relative to alkyl chloride adducts is repeated in the difference of 0.5 kcal mol⁻¹ for the isopropyl case and 1.1 kcal mol⁻¹ for the *tert*-butyl case. This is likely a consequence of the greater polarizability of the bromides relative to the chlorides since the dipole moments of the pairs of alkyl chlorides and bromides are nearly equal.

The well depths associated with the corresponding exit channel complexes are also summarized in Table 2. As expected, these values are less than those of the entrance channel complexes due to the lower nucleophilicity of bromide relative to chloride and the lower polarizability of the alkyl chlorides relative to the corresponding alkyl bromides. What is clear from the energetics, however, is that there are indeed two different complexes of the same elemental composition with the exit channel complex being lower in energy than the entrance channel complex by an amount somewhat less than the exothermicity of the net S_N2 reaction. Johnson and co-workers have also previously demonstrated this for the Cl⁻-CH₃Br system based on collision-induced dissociation experiments.²⁶

The difference in the stabilization energies of the exit and entrance channel complexes relative to their separated components increases with increasing alkyl group size. This is likely a consequence of the larger atomic radius of the bromide relative to the chloride ion and the 1/*r*⁴ dependence of the ion-induced dipole potential which diminishes this part of the intermolecular potential significantly as the bulkier alkyl group leads to a greater distance between the charge and center of polarizability.

In several cases experiments have also been carried out using CN⁻ interacting with alkyl chlorides and for chloride and bromide ions interacting with alkyl cyanides. This was motivated by our previous observation that when Cl⁻ and CN⁻ interactions with Bronsted acids are compared they are usually very similar.³⁴ This can be rationalized on the basis of the very similar effective radii of these two anions and the assumption

that the interactions are largely electrostatic. On this basis it is then logical to expect that the S_N2 adducts of Cl⁻ and CN⁻ might have comparable energetics and this is borne out in the similar well depths (within 0.2 kcal mol⁻¹) for these two anions with methyl chloride. A slightly enhanced well depth (0.7 kcal mol⁻¹) for Cl⁻ relative to CN⁻ is seen, however, for *tert*-butyl chloride. The interaction between Cl⁻ and CH₃CN is substantially greater (5.6 kcal mol⁻¹) than that between CN⁻ and CH₃-Cl because of the substantially greater dipole moment on the alkyl cyanide and also because of its significantly greater gas-phase acidity. Because of this latter factor the interaction between an anion and acetonitrile might then be more correctly regarded as a hydrogen-bonded adduct. This is also reflected in the smaller difference observed (2.6 kcal mol⁻¹) between Cl⁻ and *t*-C₄H₉CN compared to CN⁻ and *t*-C₄H₉Cl where the enhanced dipole interaction remains but no significant hydrogen bond interaction exists due to the absence of an acidic hydrogen α to the cyano group.

3. Intermediate Barrier Heights. As noted above, it is the height of the intermediate barrier on the potential energy surface which determines the overall rate of conversion of the entrance channel complex to exit channel complex and thence to products. Kebarle and co-workers²¹ have previously demonstrated for these S_N2 systems that the temperature dependence of the rate constant for the S_N2 reaction provides a measure of the Arrhenius "activation energy", eq 8, which can then be related to the enthalpy of activation, ΔH^{o‡}, via a transition state theory analysis, eq 9.

$$\frac{d \ln k}{d(1/T)} = \frac{-E_a}{R} \quad (8)$$

$$k = \frac{kT}{h} e^{\Delta S^\ddagger/R} e^{\Delta H^\ddagger/RT} \quad (9)$$

For a gas-phase reaction at constant volume, the conditions of the HPMS experiment, and assuming ideal gas behavior, the experimentally determined Arrhenius activation energy, E_a, can be related to ΔH^{o‡} by eq 10, where n_R[‡] is the molecularity of

$$E_a = \Delta H^{o\ddagger} + RT \sum n_R^\ddagger \quad (10)$$

the reaction and is equal to 2 in this case. Interestingly, for the double minimum potential energy surface where the central barrier lies close to the energy of separated reactants, either a positive or negative temperature dependence can be observed for the bimolecular rate constant.

The bimolecular rate constants and associated temperature dependencies were determined in two ways. The first follows the example of Caldwell, Magnera, and Kebarle²¹ in determining the first-order disappearance rate of the Cl⁻ ion as a function of alkyl bromide partial pressure, as, for example, in Figure 5. A slope of the plot of this rate as a function of RBr pressure, for example Figure 6, then gives the second-order rate constant for the bimolecular S_N2 reaction.

The second method is based on the approach to equilibrium for a reversible S_N2 process. For example, as shown in Figure 7, the forward and reverse rate constants for the reversible reaction between ethyl bromide and ethyl chloride can be obtained by fitting the Cl⁻ and Br⁻ intensities to a reversible pseudo-first-order set of kinetic equations. The temperature dependence of this behavior then gives the activation energy for reaction in each direction as described above. An added benefit of this method is that the overall bimolecular equilibrium

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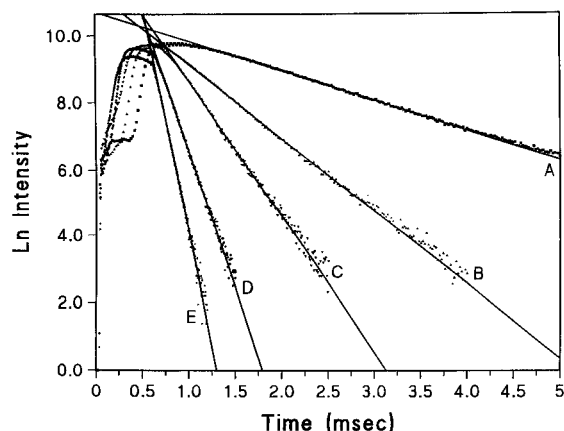


Figure 5. Variation of intensities of Cl^- at a constant ion source temperature of 264 °C and constant ion source pressure of 5.0 Torr. The concentration of the neutral substrate, $i\text{-C}_3\text{H}_7\text{Br}$, increases from zero to 5.8×10^{15} molecule cm^{-3} in going from A to trace E. The rate constant for disappearance of Cl^- is obtained from the slope of the linear portions of each trace after a suitable initial source residence time.

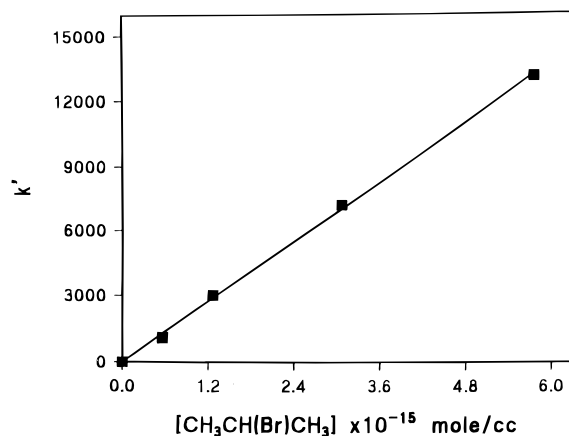


Figure 6. Plot of the pseudo-first-order rate constant for disappearance of Cl^- vs the concentration of neutral $i\text{-C}_3\text{H}_7\text{Br}$ at a temperature of 264 °C. The second-order rate constant of 2.3×10^{-12} cm^3 molecule $^{-1}$ s^{-1} is obtained from the slope. The non-zero intercept represents the first-order rate constant for loss of Cl^- to the ion source walls at 5.0 Torr of CH_4 pressure.

constant for the S_N2 reaction may also be obtained and, from the temperature dependence of this equilibrium constant, the ΔH° and ΔS° for the reaction can be obtained. In principle, these quantities are well-known in advance from tabulated thermochemical data for ions and neutrals and the degree to which the experimentally derived data agree with the anticipated values is an excellent calibration of the validity of the thermochemical data obtained from these HPMS experiments. In all cases this agreement was within ± 0.4 kcal mol^{-1} for ΔH° and ± 2 cal mol^{-1} K^{-1} for ΔS° . Data for the intermediate barrier heights which could be determined in either of the above two ways are also summarized in Table 2. In the case of CH_3Br clustering, equilibrium was observable only at the lowest temperature attainable and an experimental value of ΔH° given is based on the ΔG° value derived and the *ab initio* value of ΔS° obtained by Hase.^{23e}

An important specific case to consider is that of $\text{Cl}^- + \text{CH}_3\text{Br}$, whose temperature dependence has been examined experimentally by several groups as well as in considerable theoretical detail by Hase. The suggestion has been made that the lifetime of the complex initially formed between Cl^- and CH_3Br is too short to permit randomization of the internal energy and the dissociation of such complexes will therefore be decidedly non-

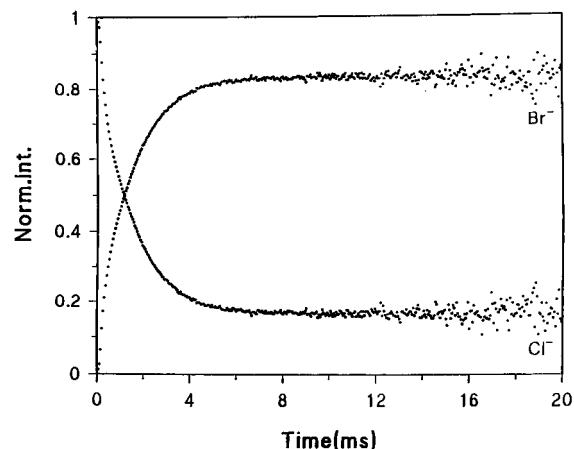


Figure 7. Variation of relative abundances of Cl^- and Br^- at 516 K in a high-pressure ion source containing 5.1 Torr of CH_4 , 0.83 Torr of $\text{C}_2\text{H}_5\text{Cl}$, and 2.1 mTorr of $\text{C}_2\text{H}_5\text{Br}$. From the intensity variation on approach to equilibrium and the equilibrium constant of 2050 obtained, forward and reverse rate constants of 1.5×10^{-11} and 7.5×10^{-15} cm^3 molecule $^{-1}$ s^{-1} , respectively, are obtained.

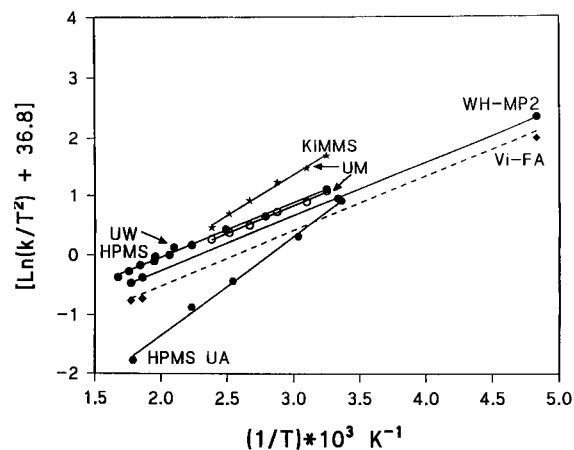


Figure 8. Plot of $\ln(k/T^2)$ vs $1/T$ from which ΔH^\ddagger and ΔS^\ddagger data are derived. HPMS indicates data either at 3 Torr (UM) from Grimsrud (ref 33), from Kebarle (UA, ref 21), or from the present work (UW); KIMMS signifies ion mobility data at atmospheric pressure (ref 33); Vi-FA is flowing afterglow data by Viggiano and co-workers (ref 24); and WH-MP2 (ref 23f) indicates a calculated plot based on *ab initio* derived values for the transition state thermochemistry.

statistical. This non-statistical behavior is exacerbated by the poor coupling between the intermolecular and intramolecular modes of the complex such that the probability of intermediate barrier crossing is inefficient. As a result the reaction cannot, with confidence, be treated using standard statistical rate theory models, such as RRKM theory. One consequence of this non-statistical behavior has been suggested to be the observation of a rate constant for the S_N2 reaction that is a function of the pressure of a third body in the system. Grimsrud and co-workers³³ reported substantial differences in the temperature dependence of the rate constant between 3 Torr in a HPMS apparatus and 640 Torr in an ion mobility device. Viggiano et al.²⁴ find rate data as a function of temperature that are in good agreement with those from Grimsrud's HPMS experiment. Our current data are almost exactly coincident with those of Grimsrud. We have carried out our experiments over a pressure regime from 2 to 10 Torr and find the rate data invariant. In addition we have extended the temperature range examined. All of these rate data, together with that predicted by Hase's calculations are shown together in Figure 8 in a modified Arrhenius type plot in a form appropriate to extract the activation enthalpy and entropy. The excellent agreement obtained

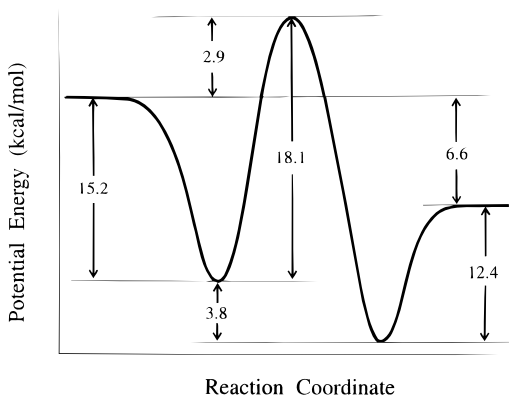


Figure 9. Complete potential energy profile derived from experimental determination of each of the stationary points on the surface for the S_N2 reaction of Cl^- with $i-C_3H_7Br$.

between Grimsrud's and the current HPMS data at 3–10 Torr, the flowing afterglow data at 0.5 Torr, and the *ab initio* calculations of Hase thus indicate that the initially formed intermediate complex between Cl^- and CH_3Br is much shorter lived than the time between collisions in the flowing afterglow or HPMS experiments. In contrast, in the ion mobility experiment, where the pressure is sufficiently high that the time between collisions becomes comparable to the transient lifetime, an increased rate constant is observed. This is a result of the fact that as a larger fraction of the activated intermediates are intercepted and collisionally stabilized the system more closely resembles one of thermal dissociation of the S_N2 complex, for which the Br^- dissociation channel is the more energetically favored.

From these equilibrium and kinetic data a clear, experimental validation of the double minimum potential energy surface for S_N2 reactions emerges which, in the few cases where comparison can be made, quantitatively supports *ab initio* calculations for these same systems.^{23,35–37} Many of the clustering equilibria for entrance and exit channel complexes establish the ion–dipole complex well depths and clearly show that two energetically distinct species of the same molecular formula do exist, which requires that a significant central barrier separate these two minima. In the case of the more complex alkyl species the determination of the energetics from the overall S_N2 equilibrium reaction confirms, by comparison with literature thermochemistry, that nucleophilic displacement rather than elimination is indeed occurring. Finally, the temperature dependence of the reaction rate constants establishes the position of the central barrier relative to the separated reactants. In favorable cases all of these data can be obtained for a single reaction system and a clear experimental determination of all of the stationary points on the potential energy surface can be obtained. One such example is that shown in Figure 9 for the reaction of chloride with isopropyl bromide. This and the similar examples in Table 2 are the first completely experimental determinations of the relative energetics of all five of the important stationary points on a double minimum potential energy surface.

The trend of increasing activation enthalpy with increasing methyl group substitution at the site of nucleophilic attack is of interest viewed in the context of analogous solution-phase behavior. In solution the S_N2 mechanism is normally operative at primary and, occasionally, secondary carbon centers. However, reaction of nucleophiles with tertiary carbon centers

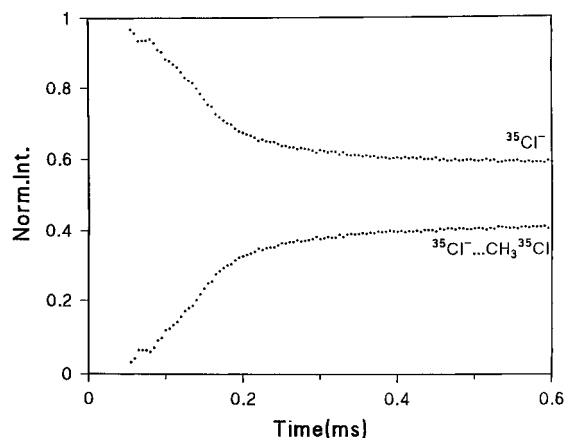
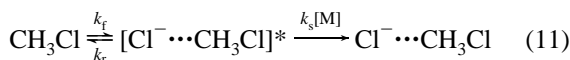


Figure 10. Variation of relative ionic abundances with reaction time for Cl^- clustering onto CH_3Cl in a high pressure source at 296 K and 4 Torr of a 98% CH_4 , 2% CH_3Cl mixture. From the intensity variation at short reaction times the rate constant for the formation of the $Cl^-(CH_3Cl)$, entrance channel, adduct may be obtained.

normally proceeds *via* a S_N1 mechanism. Similarly, in the gas-phase reactions of Cl^- with methyl, ethyl, *n*-propyl, isopropyl, and *tert*-butyl bromides, the reactions of the methyl, the two primary, and the secondary alkyl halide are observable while reaction with the tertiary system is too slow to be seen on the HPMS time scale at all temperatures. The primary species each have negative activation enthalpies, the secondary system has a significant positive activation enthalpy, and the tertiary system has an activation enthalpy sufficiently high that no reaction can proceed even at the highest temperatures attainable in the HPMS system. Such an increase in activation enthalpy can be envisioned to arise from an increasing difficulty to effect inversion at the substituted center with increasing alkyl group substitution.

4. Lifetime of a Transient S_N2 Intermediate. The deduction of the double minimum nature of the S_N2 potential energy surface by Brauman¹¹ arose from his attempt to explain the slow rate for the thermoneutral reaction of Cl^- with CH_3Cl . The intermediate barrier height of 2–3 kcal/mol above the energy of reactants then causes the rate constant to be several orders of magnitude lower than the collision rate constant. Hase's trajectory calculations²³ also show that intermediate barrier crossing is extremely inefficient and this inefficiency is proposed to be due, at least in part, to an extremely short lifetime of the intermediate ion–dipole complex between chloride and methyl chloride. The lifetime suggested by the calculations of ~10 ps is insufficient for energy randomization among the internal degrees of freedom of the complex and thus energy flow to the reaction coordinate leading to barrier crossing cannot readily occur. Despite this apparently extremely short lifetime, the HPMS experiments described above are capable of detecting the Cl^-/CH_3Cl adduct and observing the clustering equilibrium from which the energetics for the complex are obtained. At 298 K and 5 Torr in the high-pressure source the mean time between ion–molecule collisions is on the order of 5 ns. The three orders of magnitude difference between the proposed lifetime of the transient intermediate and the time between collisions suggests that the formation of the collisionally stabilized adduct should be slow and, from an examination of the kinetics of the formation of the adduct, a lifetime of the initially formed transient might be obtained. This can be readily seen from the kinetic scheme for eq 11 outlined below and the experimental data shown in Figure 10.



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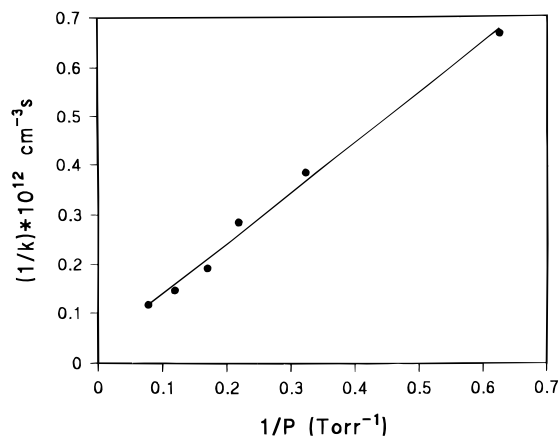


Figure 11. Plot of the reciprocal bimolecular rate constant for the formation of the collisionally stabilized $\text{Cl}^-(\text{CH}_3\text{Cl})$ adduct *vs* the reciprocal ion source pressure from which the lifetime of the transient, chemically activated, S_N2 intermediate may be derived.

Applying the steady state approximation to the initially formed, chemically activated complex yields the rate equation for disappearance of the bare chloride ion and formation of the collisionally stabilized S_N2 intermediate, eq 12.

$$-\frac{d[\text{Cl}^-]}{dt} = \frac{k_f[\text{Cl}^-]P_{\text{CH}_3\text{Cl}}}{k_r + k_s[\text{M}]} \quad (12)$$

The apparent bimolecular rate constant for the formation of the stabilized complex is then given by the combination of bimolecular and unimolecular rate constants and bath gas pressure in eq 13.

$$k_{\text{app}} = \frac{k_f k_s [\text{M}]}{k_r + k_s [\text{M}]} \quad (13)$$

From this, it is evident that a plot of $(k_{\text{app}})^{-1}$ *vs* $[\text{M}]^{-1}$ should yield a straight line whose slope is $k_r/(k_f k_s)$ and whose intercept is k_f^{-1} . The values for k_{app} can be obtained from fitting of experimental data, such as that shown in Figure 10, to a reversible first-order reaction system during the approach to equilibrium ion intensities. The resulting reciprocal plot is shown in Figure 11, which exhibits the anticipated linear behavior with a slope of $3.5 \times 10^{28} \text{ s cm}^{-6}$. Both k_f and k_s can be approximated from either the Su-Chesnavich trajectory algorithm³⁸ for collisions of ions with polar molecules ($k_f = 2.28 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) or the simple Langevin relation for the interaction of ions with non-polar neutrals ($k_s = 1.03 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$), in this case for CH_4 which is being used as the bath gas in the HPMS experiment. Combination of these values with the experimentally determined slope then gives a value for the unimolecular dissociation rate constant of the initially formed S_N2 intermediate of $8.2 \times 10^{10} \text{ s}^{-1}$ corresponding to a lifetime of 12 ps. Alternatively, Hase's trajectory value for the association rate constant, k_f , of $1.04 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ may be used in conjunction with the above Langevin value of the collisional stabilization rate constant to yield a unimolecular dissociation rate constant of $3.75 \times 10^{10} \text{ s}^{-1}$ and a lifetime of 27 ps. Within the limits of accuracy of these assumed rate constants it is anticipated that where the reciprocal plot is linear over the pressure range studied and a significant fraction of the intermediates are collisionally stabilized then the derived lifetime should be accurate to within a factor of 2. In each case, these values are in excellent agreement with the order of magnitude

of lifetimes predicted by Hase's calculations for $\text{Cl}^-/\text{CH}_3\text{Cl}$ collisions at relative translational energies of 1 kcal mol^{-1} , rotational temperatures of 300 K, and vibrational energies equal to the zero-point energy of the system.

Conclusion

The data presented herein provide a number of valuable insights into the nature of the potential energy surfaces and the dynamics of a number of simple, but important, gas-phase S_N2 reactions. For thermoneutral, symmetric reactions between chloride ion and alkyl chlorides and bromide ion and alkyl bromides the well depths associated with the electrostatic complexes are readily obtainable. These species are the identical entrance and exit channel intermediates on the potential energy surface. The data show that as the alkyl group size increases so does the well depth, which is a consequence of the increased polarizability of the alkyl halide with increased alkyl group size. In addition, the magnitude of the negative entropy change associated with complex formation also increases with increasing alkyl group size and this has been shown likely to be attributable to the increasing frequency of the intermolecular vibrational modes of the complexes accompanying the increased binding energy.

In the case of unsymmetrical S_N2 reactions of chloride ion with alkyl bromides four different important pieces of information concerning the potential energy surface are, in principle, obtainable. These are the following: (i) the overall energetics (ΔH° , ΔS°) of the net S_N2 reaction, determined from observation of the reaction at equilibrium in alkyl chloride, alkyl bromide mixtures; (ii) the energetics of the entrance channel, $\text{Cl}^-(\text{RBr})$, complex relative to separated reactants; (iii) the energetics of the exit channel, $\text{Br}^-(\text{RCl})$, complex relative to separated products; and (iv) the energetics of the transition state associated with the intermediate barrier on the double well potential energy profile. In the favorable cases where all such data are obtained an exceptionally complete picture of the potential energy surface is provided. The data for the transition states reveal that as the alkyl group size increases the height of the barrier relative to separated reactants increases from several kcal mol^{-1} below the reactants for CH_3Br to significantly above the reactants for *t*- $\text{C}_4\text{H}_9\text{Br}$. These thermochemical data for the gas-phase S_N2 potential energy profile provide the first completely experimental direct verification and characterization of the double well nature of the potential energy surface. In addition, the entropy data provide some insight into the structural and vibrational character of the intermediates and transition states.

Finally, an examination of the pressure dependence of the formation of the stabilized adduct between chloride ion and methyl chloride provides an experimental route to the determination of the lifetime of the chemically activated transient adduct formed immediately upon collision of these two reaction partners. The excellent agreement between the experimental lifetime and that determined from Hase's trajectory calculations gives further graphic evidence of the beneficial interplay between theory and experiment when applied to the intricacies of mechanism, dynamics, and potential energy surfaces for gas-phase ion-molecule reactions.

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