Gas-Phase S_N2 and E2 Reactions of Alkyl Halides

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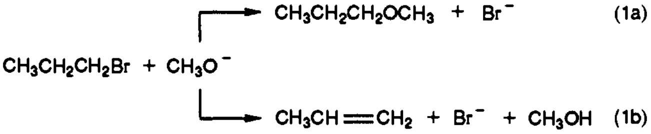
Abstract: Rate coefficients have been measured for the gas-phase reactions of methyl, ethyl, *n*-propyl, isopropyl, *tert*-butyl, and neopentyl chlorides and bromides with the following set of nucleophiles, listed in order of decreasing basicity: HO^-, CH_3O^-, F^-, HO^- (H_2O), $CF_3CH_2O^-$, H_2NS^-, $C_2F_5CH_2O^-$, HS^-, and Cl^-. For methyl chloride the reaction efficiency first falls significantly below unity with HO^- (H_2O) as the nucleophile and for methyl bromide with HS^- as the nucleophile; in both cases the overall reaction exothermicity is about 30 kcal mol^{-1}. Earlier conclusions that these halides react slowly with stronger bases are shown to be in error. In the region where the rates are slow oxygen anions react with the alkyl chlorides and bromides by elimination while sulfur anions of the same basicity react by substitution. This difference is due to a slowing down of elimination with the sulfur bases; sulfur anions show no increased nucleophilicity as compared to oxy anions of the same basicity. Rate coefficients have also been measured for reaction of methyl fluoride with HO^- and CH_3O^- and ethylene oxide with HO^-, CH_3O^-, and F^-. All of these rates are slow but measurable; combining the results of these experiments with those of the alkyl chlorides and bromides suggests that the gas-phase barrier to the symmetrical S_N2 reaction of F^- with methyl fluoride is lower than previous estimates. We have also measured rates for reaction of allyl chloride with F^-, H_2NS^-, and HS^-, chloromethyl ether with H_2NS^- and HS^-, chloroacetonitrile with F^-, H_2NS^-, HS^-, and $^{37}Cl^-$, bromoacetonitrile with Cl^- and $^{81}Br^-$, and α-chloroacetone with H_2NS^-, HS^-, and $^{37}Cl^-$. Our results also imply that the gas-phase S_N2 barrier for Br^- reacting with methyl bromide is nearly equal to the ion–dipole attraction energy of the reactants, in agreement with previous estimates.

No gas-phase ion–molecule reaction has been more thoroughly studied from a theoretical point of view than simple bimolecular nucleophilic substitution (S_N2) and yet, paradoxically, experiments lag far behind. With a few notable exceptions systematic kinetic measurements of gas-phase S_N2 processes have been carried out only with methyl halides as substrates and with a limited number of anions as nucleophiles.[1,2] As a consequence, such fundamental comparisons as the effect of alkyl structure on reactivity remain largely unexplored. Indeed when an alkyl halide is allowed to react with a nucleophile in the gas phase it is not even generally known whether substitution (S_N2) or elimination (E2) is the preferred pathway, except in those few cases where the E2 reaction is structurally or thermodynamically forbidden. In this paper we report results of an extensive study of the rates of reaction of a characteristic group of alkyl halides with a carefully chosen set of nucleophiles using our flowing afterglow (FA) and flowing afterglow-selected ion flow tube (FA-SIFT). Our goal was to make a more detailed comparison of gas-phase S_N2 reactions with those in solution and lay the groundwork for more accurate calculations of gas-phase activation barriers in so far as it is possible to do so.

Mechanistic investigations of gas-phase S_N2 reactions are complicated by several factors that account, at least in part, for the absence of extensive previous experimental data. First among these is the fact that in most gas-phase experiments only the ionic products of reaction are monitored. So, for example, when *n*-propyl bromide is allowed to react with methoxide ion in the gas phase, the bromide ion produced can arise either by substitution (eq 1a) or by elimination (eq 1b), and the two pathways cannot be distinguished from the ions alone. In this particular case the very difficult method of collection and identification of the neutral product of the reaction was employed, and it was found that elimination is the major or exclusive product.[3] In contrast, substitution has been found to compete with elimination in the reaction of amide ions with sulfites.[4] Before any general conclusions can be drawn about the effect of alkyl structure on S_N2 reactivity, a way must be found to distinguish between substitution and elimination.



$$CH_3CH_2CH_2Br + CH_3O^- \longrightarrow CH_3CH_2CH_2OCH_3 + Br^- \qquad (1a)$$

$$CH_3CH_2CH_2Br + CH_3O^- \longrightarrow CH_3CH{=}CH_2 + Br^- + CH_3OH \qquad (1b)$$

In addition to this mechanistic ambiguity there are experimental limitations on the range of rates that can be studied in the gas phase. At one extreme alkyl chlorides, bromides, and iodides react with strongly basic nucleophiles at essentially every encounter. For these reactions there is no observed effect of structure on reactivity except for the minor and uninteresting one by which it may change the collision rate of the halide and the nucleophile. As a consequence the kinetics of very fast S_N2 reactions yield little mechanistic information. On the other hand, present experimental techniques do not allow the measurement of very slow rates, a practical lower limit of measurement, except in very special cases, being of a rate coefficient corresponding to about one reaction in every 10^4 collisions between the substrate and the nucleophile. Thus the very large variations in rate commonly encountered in solution cannot be measured in the gas phase. In addition, until recently the number of different anions that could be cleanly generated and used as nucleophiles for kinetic investigations in the gas phase was severely limited.

These experimental problems are compounded by the fact that the interpretation of the kinetic results once obtained is complicated by the unique energetics of gas-phase ion–molecule reactions. In the usual gas-phase experiment an ion and a molecule, both initially at room temperature, are attracted to one another by ion–dipole and ion–induced-dipole forces which typically amount

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[1] For a recent review of gas-phase nucleophilic displacement reactions see: Riveros, J. M.; Jose, S. M.; Takashima, I. *Adv. Phys. Org. Chem.* **1985**, *21*, 197.

[2] For earlier experimental studies of gas-phase S_N2 rates see especially: (a) Bohme, D. K.; Young, L. B. *J. Am. Chem. Soc.* **1970**, *92*, 7354. (b) Young, L. B.; Lee-Ruff, E.; Bohme, D. K. *J. Chem. Soc., Chem. Commun.* **1973**, 35. (c) Tanaka, K.; MacKay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643. (d) Bohme, D. K.; MacKay, G. I. *J. Am. Chem. Soc.* **1981**, *103*, 978. (e) Bohme, D. K.; Raksit, A. B. *Can. J. Chem.* **1985**, *63*, 3007. (f) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219. (g) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 2672. (h) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 4123. (i) Brauman, J. I.; Dodd, J. A.; Han, C.-C. In *Nucleophilicity*; Harris, J. M., McManus, S. P., Eds.; American Chemical Society: Washington D. C., 1987. (j) Caldwell, G.; Magnera, T. F.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 959. (k) Damrauer, R.; DePuy, C. H.; Bierbaum, V. M. *Organometallics* **1982**, *1*, 1553. (l) Barlow, S. E.; Van Doren, J. M.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1988**, *110*, 7240.

[3] Jones, M. E.; Ellison, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 1645.

[4] Lum, R. C.; Grabowski, J. J. *J. Am. Chem. Soc.* **1988**, *110*, 8568.

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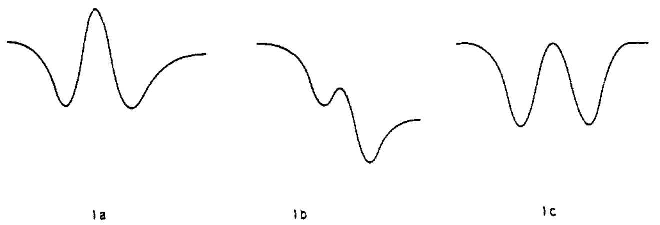

Figure 1. Schematic reaction coordinate diagrams for gas-phase S_N2 reactions. See text for discussion.

to 10–15 kcal/mol by the time they reach reaction distances and enter into a relatively long-lived ion–dipole complex.[5] This complex will eventually dissociate with loss of its attractive energy, but during its lifetime a reaction may occur. If an S_N2 process has an activation barrier significantly *greater* than the total energy of the complex, i.e. greater than the sum of the ion–dipole forces and the thermal energy, then no reaction will be observed (Figure 1a). If the barrier is significantly *lower* than this energy (Figure 1b), reaction will occur at every encounter. Only in those cases in which the energy at the top of the barrier (i.e. the S_N2 transition-state energy) and the energy of the reactants are similar (e.g. Figure 1c) will one be able to measure accurately a rate smaller than the encounter rate. Heating or cooling the reactants will have only a minor effect on the rate since most of the energy for surmounting the barrier comes from the attractive potential. In the gas phase, then, instead of manipulating the energy of the reactants in order to allow them to surmount a barrier of fixed height, one must manipulate the height of the barrier until it matches the (relatively fixed) energy of the reactants or vary the attractive potential while keeping the barrier unchanged.

According to Marcus theory[6] an S_N2 activation energy may be thought of as consisting of an *intrinsic* barrier, i.e., a barrier the reaction would have if the reaction were thermoneutral, modified by a barrier-lowering effect due to any *exothermicity* of the reaction. For example in Figure 1c the barrier is an intrinsic one because the reaction is thermoneutral. Unfortunately, thermoneutral S_N2 reactions are extremely slow in the gas phase and the rate coefficient for only one reaction of this type, that between $^{37}Cl^-$ and $CH_3{}^{35}Cl$, has ever been accurately determined.[2l] Its reaction rate is at the extreme edge of measurability, with S_N2 reaction occurring once in every 50 000 collisions. Even in this case the exact height of the barrier is difficult to determine precisely. By analyzing the effect of ion kinetic energy on the reaction rate Bierbaum and co-workers[2l] inferred a barrier height of 13.2 ± 2 kcal/mol, about 1 kcal/mol greater than the ion–dipole attraction energy. Tucker and Truhlar,[7] using transition-state theory and the thermal energy rate constant, placed the barrier 2 kcal/mol higher, at 15 kcal/mol.

Increasing the basicity of the nucleophile has the effect of lowering the energy of the right-hand side of the potential energy diagram by making the reaction exothermic. Lowering the energy of the products also lowers the energy of the transition state (Figure 1b), but as one changes the nucleophile the intrinsic barrier also changes, and it is difficult to separate the two effects. For highly exothermic reactions the transition state may be too far below the barrier to have an effect on the reaction rate. Indeed, it might be supposed that the barrier can have no effect on the rate until it is at least equal in energy to that of the reactants. However, as Brauman has so clearly pointed out,[2g] this is not necessarily the case and a gas-phase S_N2 reaction can be slowed down appreciably by a barrier that is significantly below this energy. Potential energy diagrams like those in Figure 1 neglect the effects of entropy; the S_N2 transition state is a highly structured one compared to the transition state for dissociation back to reactants, and a favorable activation energy may be offset by an unfavorable activation entropy. Thus the effect of the barrier will be felt over a range of energies from a few kcal/mol above the energy of the reactants to an experimentally unknown number of kcal/mol below this energy.

In previous work from other laboratories a number of rate coefficients for reactions of alkyl chlorides, bromides, and fluorides have been measured with use of ion cyclotron resonance (ICR) spectrometry, flowing afterglow (FA), and high-pressure mass spectrometric techniques.[2] Rates measured by ICR are sometimes found to be too slow,[1] possibly because the ions are not at room temperature. Previous FA studies used only methyl halides as substrates, and the nucleophiles chosen were not ideal for our present purposes. The mass spectrometric measurements were limited to chloride ion as a nucleophile.[2j] It seemed to us that a thorough study of a range of substrates and nucleophiles from a single laboratory might resolve some of the previous experimental ambiguities and allow us to draw some firmer conclusions about the mechanisms of gas-phase substitution and elimination reactions.

Experimental Section

These experiments were carried out in our flowing afterglow (FA)[8] and flowing afterglow–selected ion flow tube (FA-SIFT)[9] instruments, both of which have been described previously. Hydroxide, halide, and amide ions are generated by electron impact on appropriate precursors in a stream of helium. Other ions are prepared from one of these ions by gas-phase ion–molecule reactions. Reaction rate coefficients were measured by adding a known flow of the neutral substrate at varying distances along the flow tube, either through a moveable inlet (in the FA) or through a series of fixed inlets (in the FA-SIFT). Flow rates of the neutral were determined by monitoring the pressure increase with time in a calibrated volume. Rate measurements were carried out at a helium pressure of 0.4–0.5 Torr. The experimental precision of each rate constant is better than ±10% except for extremely slow rates where the precision is ±20%.

All neutral reagents were obtained from commercial sources and purified by distillation before use. The helium buffer gas (99.997%) was passed through a molecular sieve trap immersed in liquid nitrogen before entering the flow tubes.

Results

In Table I are listed the rate coefficients and, in parentheses, reaction efficiencies we have measured in this study. In the gas phase the collision frequencies of ions with neutral molecules vary somewhat with the masses, dipole moments, and polarizabilities of the reactants,[5] so that in making comparisons among different reactants it is usual to use reaction efficiencies, i.e. the ratio of the reaction rate coefficient to the collision rate coefficient, rather than reaction rate coefficients themselves. For example, a reaction efficiency of 0.18 means that 18% of collisions result in product, the other 82% dissociating to reactants. For the reactions studied here the collision rates, calculated by the method of Su and Bowers,[10] vary by less than a factor of 2, and while we will couch our subsequent discussions in terms of reaction efficiencies, no conclusion in this paper would be changed if comparisons among absolute rates were made instead.

The alkyl chlorides and bromides were chosen so as to explore the standard effects of changes of structure on reactivity in S_N2 reactions. Methyl halides are the simplest substrates for which no competing E2 pathway is possible. Ethyl, *n*-propyl, isopropyl, and *tert*-butyl halides serve to explore the usual effects of carbon branching, i.e., primary, secondary, and tertiary, on reactivity. Neopentyl halides, while primary, are known to react slowly because of steric interactions between the nucleophile and the bulky *tert*-butyl group and, because they have no β-hydrogens, cannot eliminate.[11] In those cases in which the same nucleophile

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(6) For a discussion of Marcus theory as applied to gas-phase S_N2 reactions see ref 2g.

(7) (a) Tucker, S. C.; Truhlar, D. G. *J. Am. Chem. Soc.* **1990**, *112*, 3338. (b) Tucker, S. C.; Truhlar, D. G. *J. Phys. Chem.* **1989**, *93*, 8138.

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(11) See, for example: Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; p 377.

Table I. Rate Coefficients and Reaction Efficiencies of Gas-Phase S_N2 Reactions

	nucleophile ($\Delta H^\circ{}_{acid}{}^c$)								
	HO^- (391)	CH_3O^- (381)	F^- (371)	$HO^-(H_2O)^h$ (366)	$CF_3CH_2O^-$ (362)	H_2NS^- (362)	$C_2F_5CH_2O^-$ (357)	HS^- (351)	Cl^- (333)
CH_3F	0.12^a (0.0052)^b	0.017 (0.001)							
CH_3Cl	20 (0.84)	13 (0.65)	13 (0.56)	3.6 (0.20)	2.2 (0.15)	1.5 (0.085)	1.0 (0.080)	0.12 (0.006)	0.00035^d
C_2H_5Cl	25 (0.93)	19 (0.88)	23 (0.91)	8.1 (0.41)	2.5 (0.16)	0.38 (0.021)	0.59 (0.041)	<0.001	<0.001
n-C_3H_7Cl	33 (1.1)	21 (0.93)	26 (0.93)	10 (0.48)	3.2 (0.19)	0.85 (0.043)	1.1 (0.073)	<0.001	<0.001
i-C_3H_7Cl	26 (0.92)	20 (0.89)	27 (1.0)	13 (0.60)	4.3 (0.27)	<0.001	0.85 (0.06)	<0.001	<0.001
t-C_4H_9Cl	28 (0.92)	21 (0.85)	23 (0.79)	13 (0.59)	6.1 (0.36)	<0.001	1.7 (0.11)	<0.001	<0.001
neo-$C_5H_{11}Cl$	31 (1.0)	7.9 (0.33)	17 (0.56)	0.49 (0.023)	<0.36 (<0.022)^e	<0.047 (<0.0023)^e	<0.19 (<0.013)^e	<0.001	<0.001
CH_3Br	22 (0.95)	17 (0.93)	20 (0.88)	17 (0.96)	8.9 (0.70)	7.0 (0.35)	8.5 (0.73)	3.2 (0.17)	0.27 (0.015)
C_2H_5Br	26 (0.98)	20 (0.97)	27 (1.1)	17 (0.88)	12 (0.85)	9.1 (0.49)	9.9 (0.78)	2.0 (0.10)	0.05 (0.0025)
n-C_3H_7Br	32 (1.1)	21 (0.99)	23 (0.88)	21 (1.0)	12 (0.82)	11.1 (0.61)	11 (0.83)	2.8 (0.13)	0.15 (0.007)
i-C_3H_7Br	29 (1.0)	20 (0.90)	31 (1.1)	19 (0.91)	14 (0.94)	3.5 (0.17)	11 (0.82)	0.020 (0.0008)	<0.001
t-C_4H_9Br	31 (1.1)	24 (1.1)	24 (0.86)	15 (0.71)	13 (0.87)	1.3 (0.068)	12 (0.90)	<0.001	<0.001
neo-$C_5H_{11}Br$	27 (0.86)	21 (0.86)	23 (0.77)	0.50 (0.022)	<0.7 (<0.044)^e	<0.5 (<0.02)^e	<0.3 (<0.020)^e	<0.05 (<0.002)^e	<0.001
CH_2CHCH_2Cl			22 (0.86)			7.1 (0.38)		0.15 (0.0072)	
CH_3OCH_2Cl						8.5 (0.63)		3.2 (0.21)	
CH_3COCH_2Cl						18 (0.88)		14 (0.60)	2.7 (0.12)
$NCCH_2Cl$			30 (0.86)			24 (0.96)		17 (0.60)	3.2 (0.12)
$NCCH_2Br$									13 (0.49)^f
c-CH_2OCH_2	2.5 (0.1)^g	0.74 (0.035)^g	0.025 (0.001)						

[a] Bimolecular rate coefficient in units of 10^{-10} cm^3/(molecule·s). [b] The ratio of the experimental rate coefficient to the collision rate coefficient (k_{exp}/k_{col}) where k_{col} is calculated from the average dipole orientation (ADO) theory of Su and Bowers, ref 10. [c] The experimental gas-phase acidity of the corresponding conjugate acid in kcal/mol. Values, except for that of H_2NS^- and $CF_3CF_2CH_2O^-$, taken from ref 13. [d] This value is from ref 21. The reaction efficiency is 0.00002. [e] These rates represent loss of nucleophile signal mainly due to formation of cluster ions. S_N2 rates are considerably smaller. [f] The rate for reaction of this substrate with Br^- is 4.0×10^{-10} (0.20). [g] See ref 12. [h] For the reactions with alkyl chlorides, DO^- (D_2O) was used.

was studied our rate data for methyl chloride and bromide are in substantial agreement with those of Bohme,[2c] who also carried out measurements in a FA apparatus, but are generally significantly larger than those determined by Brauman[2f] using an ICR spectrometer.

In Table I we have also listed rate coefficients and reaction efficiencies for S_N2 reactions of methyl fluoride with HO^- and CH_3O^-. Our rates are significantly slower than those of Bohme;[2c] the difference may be due to the presence of impurities of methyl chloride in his sample of methyl fluoride. Also included in the table are rates of reaction with nucleophiles of a number of substituted halides which are known to react relatively rapidly by S_N2 processes in solution (e.g. α-halo ketones and nitriles, allylic halides, alkoxymethyl halides). We have also included reactions of ethylene oxide with some of these nucleophiles because, as we have shown previously,[12] it reacts relatively slowly and allows us to compare the relative reactivity of strongly basic nucleophiles. Our present values are in good agreement with those reported earlier based on experiments in the FA.

The basicities of the nucleophiles listed in Table I are taken from ref 13 with the exception of those for H_2NS^- and $CF_3CF_2CH_2O^-$ which were measured in this study. The ion H_2NS^- was prepared by allowing NH_2^- to react with COS in the flowing afterglow source of the FA-SIFT and then injecting this ion into the second flow tube where its proton transfer reactions were determined. H_2NS^- will abstract a proton from pyrrole ($\Delta G^\circ{}_{acid}$ = 351 kcal mol^{-1}) and from $((CH_3)_3Si)_2NH$ ($\Delta G^\circ{}_{acid}$ = 353 kcal mol^{-1}), but it undergoes proton transfer only sluggishly with CF_3CH_2OH ($\Delta G^\circ{}_{acid}$ = 354 kcal mol^{-1}) and not at all with methyl vinyl ketone ($\Delta G^\circ{}_{acid}$ = 356 kcal mol^{-1}). We therefore assign $\Delta G^\circ{}_{acid}(H_2NSH) = 354 \pm 3$ kcal mol^{-1} and $\Delta H^\circ{}_{acid}(H_2NSH) = 362 \pm 3$ kcal mol^{-1}. This latter value may be compared with our previous estimate[14] of the basicity of H_2NS^- of 360 ± 3 kcal mol^{-1}. The acidity value of $CF_3CF_2CH_2OH$ was refined by bracketing it between those of pyrrole and crotonaldehyde ($\Delta G^\circ{}_{acid}$ = 348 kcal mol^{-1}) and assigning to it a value of $\Delta G^\circ{}_{acid} = 349 \pm 3$ kcal mol^{-1} or $\Delta H^\circ{}_{acid} = 357 \pm 3$ kcal mol^{-1}. Previous measurements[13] of this latter value gave 355 ± 7 kcal mol^{-1}.

Discussion

Our first objective in carrying out the work reported in this paper was to determine which nucleophiles react with methyl halides at rates that are clearly below the collision rate. The collision rate is a theoretical value and depends somewhat upon the model used for its calculation. For calculating the reaction efficiencies given in Table I we have used the method of Su and Bowers,[10] the most commonly employed model. Note in Table I that for the most rapidly reacting substrates the reaction efficiencies using the Su and Bowers method lie in the range 0.9–1.1, as expected for reactions that occur at every collision. It therefore appears that this method of calculating collision rates is appropriate.

Let us now examine the data in Table I more closely. We can see from the table that hydroxide ion reacts slowly with methyl fluoride, with only one collision in 200 leading to the formation of F^-. Obviously there is some activation barrier whose influence is being felt in this reaction. In contrast, all the alkyl chlorides and bromides react very close to the collision rate with this strongly basic nucleophile. Methoxide ion is a weaker gas-phase base, and methyl fluoride reacts more slowly still with it, but the alkyl chlorides and bromides, with the exceptions of methyl chloride (reaction efficiency 0.65) and neopentyl chloride (0.33), react at essentially every collision. The still weaker base F^- is also a highly efficient nucleophile, reacting faster than methoxide with neopentyl chloride, and nearly as fast with methyl chloride. Only when we reach HO^- (H_2O) do we find a nucleophile whose reactions with the alkyl chlorides are consistently smaller than the collision rates, and for the alkyl bromides this is true only for HS^- and Cl^- among the nucleophiles studied here. Thus we can feel confident we are studying reactions whose rates are being influenced by a central barrier when we use these weak bases as nucleophiles.

We note, however, that methyl chloride also reacts at somewhat less than unit efficiency with HO^-, CH_3O^-, and F^-. One could argue that in these reactions the influence of a central barrier is also being felt, and this is certainly a possible interpretation of our data. However, the efficiencies of these reactions are sufficiently close to unity that we do not find this explanation convincing, especially since neopentyl chloride, for which one would expect an even higher barrier, reacts as rapidly as methyl chloride with both HO^- and F^-, and nearly as rapidly with CH_3O^-. We believe, rather, that these lower efficiencies reflect the formation of some short-lived complexes that dissociate without ever sampling that part of the reaction surface which is associated with the S_N2

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Table II. Reaction Efficiencies and Exothermicities for Methyl and Neopentyl Chloride with Various Nucleophiles

	nucleophile (ΔH°_{acid}, (kcal/mol)					
	HO^- (391)	CH_3O^- (381)	F^- (371)	$HO^-(H_2O)$ (366)	HS^- (351)	Cl^- (333)
CH_3Cl	0.84	0.65	0.56	0.20	0.006	0.00002
ΔH°_{Rx}	−50	−44	−31	−25	−23	0
$(CH_3)_3CCH_2Cl$	1.0	0.33	0.56	0.023	<0.0001	<0.0001
ΔH°_{Rx}	−54	−45	−30	−29	−20	0

Table III. Reaction Efficiencies and Exothermicities for Methyl and Neopentyl Bromides with Various Nucleophiles

	nucleophile (ΔH°_{acid}, kcal/mol)					
	HO^- (391)	CH_3O^- (381)	F^- (371)	$HO^-(H_2O)$ (366)	HS^- (351)	Cl^- (333)
CH_3Br	0.95	0.93	0.88	0.96	0.17	0.015
ΔH°_{Rx}	−57	−51	−38	−32	−30	−7
$(CH_3)_3CCH_2Br$	0.86	0.86	0.77	0.022	<0.002	<0.0001
ΔH°_{Rx}	−61	−52	−37	−36	−27	−7

Table IV. The Reaction Efficiencies for Alkyl Chlorides with Various Nucleophiles

	nucleophile (ΔH°_{acid}, kcal/mol)				
	HO^- (H_2O)[a] (366)	$CF_3CH_2O^-$ (362)	H_2NS^- (362)	$C_2F_5CH_2O^-$ (357)	HS^- (351)
CH_3Cl	0.20	0.15	0.085	0.080	0.0063
C_2H_5Cl	0.41	0.16	0.021	0.041	<0.0001
n-C_3H_7Cl	0.48	0.19	0.043	0.073	<0.0001
i-C_3H_7Cl	0.60	0.27	<0.0001	0.060	<0.0001
t-C_4H_9Cl	0.59	0.36	<0.0001	0.11	<0.0001

[a] DO^- (D_2O) was used in these experiments to avoid overlapping masses.

Table V. Reaction Efficiencies for Alkyl Bromides with Various Nucleophiles

	nucleophile (ΔH°_{acid}, kcal/mol)			
	H_2NS^- (362)	$C_2F_5CH_2O^-$ (357)	HS^- (351)	Cl^- (333)
CH_3Br	0.35	0.73	0.17	0.015
C_2H_5Br	0.49	0.78	0.10	0.0025
n-C_3H_7Br	0.61	0.83	0.13	0.007
i-C_3H_7Br	0.17	0.82	0.0008	<0.0001
t-C_4H_9Br	0.068	0.90	<0.0001	<0.0001

process. Such collisions have been discussed recently by Su, Morris, Viggiano, and Paulson in their study of the rates of S_N2 reactions as a function of ion kinetic energy.[15] They point out the necessity for the proper orientation in the ion–molecule trajectory; for example, the nucleophile might collide with the side of the alkyl halide containing the leaving group and be deflected without ever encountering the reactive part of the molecule. In any event, we believe that in seeking to interpret such things as the effect of structure and basicity of the nucleophile on gas-phase S_N2 rates it is safest to confine oneself to nucleophiles for which the reaction efficiency with the methyl halide is ≤0.2 and, simultaneously, its reaction efficiency with the corresponding neopentyl halide is significantly lower still.

In Table II we have extracted the data for the reaction efficiencies and exothermicities of the six S_N2 reactions of methyl and neopentyl chloride for which thermodynamic data are available. Note first from these data and also from the remaining data in Table I that there is a good general correlation between the basicity of the attacking nucleophile and the reaction efficiency, regardless of the atom attacking the carbon. We have reported a similar relationship earlier for gas-phase S_N2 reactions of methyl iodide.[2k] If we accept that the influence of the central barrier is first felt with the nucleophile HO^- (H_2O), we see from the table that this corresponds to an overall reaction exothermicity in the range of 25–30 kcal/mol. In Table III we make a similar comparison for the reactions of methyl and neopentyl bromide. For HS^-, where the barrier is clearly felt, the reaction exothermicity is also in the 25–30-kcal/mol range.

We next wished to explore the reactivity of other nucleophiles in the region where the central barrier influences the rate. However, the number of appropriate nucleophiles is limited, especially since we wished to confine ourselves to the study of localized anions, since delocalized anions appear to react abnormally slowly in S_N2 reactions.[2f] Two obvious choices for localized anions with basicities in the region between HO^- (H_2O) and HS^- are the fluorinated alkoxides $CF_3CH_2O^-$ (ΔH°_{acid}(CF_3CH_2OH) = 362 kcal/mol) and $C_2F_5CH_2O^-$ (ΔH°_{acid}($C_2F_5CH_2OH$) = 357 kcal/mol). These anions could not be used in kinetic studies in our conventional FA because they rapidly cluster with their alcohol precursor. In the FA–SIFT, however, the anions can be injected into the second flow tube in the absence of the alcohol so that clustering cannot occur, and accurate and reproducible rates can easily be obtained. In addition to these two oxy anions we wished to include in our study a second sulfur anion with a basicity in this range. In earlier work[14] we had used our FA to prepare the unusual ion H_2NS^- by the reaction shown in eq 2. At that time we were only able to make a rough estimate of its basicity because of problems associated with making the ion and studying its reactions in the same flow tube. In the FA–SIFT we can prepare H_2NS^- in the first flow tube and study its reactions in the second. We have therefore been able to examine its proton abstraction reactions with several reagents and obtain an accurate gas-phase acidity for the corresponding neutral.

$$NH_2^- + S{=}C{=}O \rightarrow H_2NS^- + CO \qquad (2)$$

In Table IV we have summarized the efficiencies with which five nucleophiles react with methyl, ethyl, *n*-propyl, isopropyl, and *tert*-butyl chloride. Three of the bases are oxy anions, namely HO^- (H_2O), $CF_3CH_2O^-$, and $C_2F_5CH_2O^-$, while two are sulfur anions (H_2NS^- and HS^-). The gas-phase basicities vary along the series by 15 kcal/mol, and the reaction efficiencies span a range of more than 10^4, from near unit efficiency for the reaction of isopropyl chloride (0.6) with HO^- (H_2O) to reactions of HS^- which occur less often than once in every 10^4 collisions.

Note first that for methyl chloride, where only an S_N2 reaction is possible, there is a good correlation between the basicity of the attacking nucleophile and the reaction efficiency. There is no enhanced nucleophilicity associated with the reaction when the nucleophile is a sulfur atom rather than an oxygen. Indeed if there is any slight trend to be discerned, the sulfur nucleophiles react slightly *less* rapidly than might be predicted from their basicity compared to the oxygen nucleophiles. These results confirm and extend earlier conclusions that the extraordinary nucleophilicity of sulfur nucleophiles in solution is not observed in the gas phase and is most likely a solvent effect.[2f]

Next consider the effect of alkyl branching on the reaction efficiencies. *When HO^- (H_2O) or $CF_3CH_2O^-$ is the nucleophile, increased α-branching leads to an increase in rate.* Ethyl, *n*-propyl, isopropyl, and *tert*-butyl chloride all react *faster* than methyl chloride with both of these bases, and for the latter base there is a gradual, monotonic increase in rate as branching increases along the series. Even with the much weaker base $C_2F_5CH_2O^-$ there is no large falloff in rate as branching increases, and indeed *tert*-butyl chloride reacts more rapidly than does methyl chloride even with this base. In sharp contrast, *when H_2NS^- or HS^- is the nucleophile, increased α-branching leads to a dramatic decrease in rate*, and there is no detectable reaction of either nucleophile with the secondary and tertiary chlorides. These results clearly suggest that isopropyl and *tert*-butyl chloride react with the three oxy anions exclusively by E2 elimination and that even ethyl and *n*-propyl chloride have a major E2 component competing with and, indeed, overwhelming the S_N2 reaction. However, these same alkyl chlorides react with the sulfur anions exclusively by an S_N2 process.

In Table V we have summarized the reaction efficiencies of the corresponding alkyl bromides with nucleophiles in the crucial basicity region where *their* reactions are most affected by the S_N2 barrier. The same trends are observable in this series as were found

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(15) Su, T.; Morris, R. A.; Viggiano, A. A.; Paulson, J. F. *J. Phys. Chem.* In press.

for the alkyl chlorides. Note, for example, that with H_2NS^- the secondary bromide, isopropyl bromide, reacts more slowly (0.17) than does methyl bromide (0.35) and the tertiary bromide, *tert*-butyl bromide, more slowly still (0.068). Both the secondary and tertiary halides also react far slower than does methyl bromide with HS^- and Cl^-, an order expected for S_N2 processes. In sharp contrast there is no such dropoff in rate when $C_2F_5CH_2O^-$ is the base; isopropyl and *tert*-butyl bromide react as fast as, or faster than, methyl bromide. Admittedly all of the rates in Table V with this latter base are closer to unit efficiency. However, note (Table I) that $C_2F_5CH_2O^-$ reacts only very slowly with neopentyl bromide (<0.02) so that the top of the barrier is close in energy to that of the reactants and would be expected to exert an effect on the rate of S_N2 reactions at a hindered center like that of a tertiary halide. No such effect is detected. We therefore conclude that all of the bromides, with the exception, of course, of methyl and neopentyl bromide, react mainly or exclusively by E2 reactions with the oxy anion and mainly or exclusively by S_N2 with the other three nucleophiles. Indeed alkyl bromides must react with Cl^- by an S_N2 pathway since E2 reactions are endothermic by approximately 10 kcal/mol. However, they are exothermic with HS^- by approximately the same amount.

As noted above, for both methyl chloride and methyl bromide S_N2 rates decrease as the basicity of the attacking nucleophile decreases when one is truly sampling the effect of the reaction barrier. We wondered whether this same trend would be observed with stronger bases like HO^-, CH_3O^-, and F^-. Bohme[2c] measured S_N2 rates of methyl fluoride with a number of nucleophiles and found it to react rather slowly with HO^- but nearly as fast with CH_3O^-. However, he noted that his sample of methyl fluoride has a chlorine-containing impurity and we wondered if his rate data could have been affected by the presence of this impurity. We therefore reinvestigated the reactions of CH_3F with HO^- and CH_3O^- and indeed found the rates to be significantly slower than he reported (Table I). There is nearly a 10-fold decrease in rate between these two nucleophiles, which are 10 kcal/mol apart in basicity. We also knew that ethylene oxide reacts rather slowly with strong bases in the gas phase so that it can be used as a probe for the variation of S_N2 rate with basicity. Again the rate falls off regularly along the series HO^-, CH_3O^-, F^-. We have also found that S_N2 rates are speeded up in the gas phase, as they are in solution, by substitution on the reaction carbon by a double bond, a methoxy group, or electron-withdrawing groups like carbonyl and cyano (Table I).

The results reported in this paper show that many of the conclusions previously drawn in the literature about gas-phase S_N2 reactions are based on questionable assumptions about when the central barrier begins to influence the reaction rate. We believe that it does not have an effect on the reactions of methyl chloride and bromide with HO^-, CH_3O^-, or F^-. If this is the case, many current estimates of barrier heights given in the literature are incorrect. To take a specific example, consider the question of the height of the (intrinsic) barrier in the symmetrical reaction between F^- and CH_3F (eq 3). This rate constant cannot be

$$F^- + CH_3F \rightleftharpoons FCH_3 + F^- \qquad (3)$$

investigated experimentally because of the lack of an isotope of fluorine. However, it is an important one as a calculational target because fluorine has sufficiently few electrons that large basis sets can be used in high-level ab initio calculations. On the basis of extrapolations from presumed low reactivities of the corresponding methyl chloride and bromide with strong bases, previous estimates of the barrier height for this reaction placed the top of the barrier well above the energy of the reactants and predict that the reaction could not be observed.[2g,16] The measured barrier height for the analogous chloride–methyl chloride exchange reaction[21] is much lower. Thus F^- would appear to be quite different from the other halogens as either a nucleophile or a leaving group or both. Our present results indicate that these barrier calculations are not correct. It does not appear fruitful at the present time to attempt RRKM calculations with HO^- (H_2O) or H_2NS^- as the nucleophiles, since appropriate transition-state frequencies are not available.

It is tempting, however, to make an estimate of the barrier height for eq 3 on the basis of some very simple analogies among rates reported in Table I. For example, we have noted that S_N2 rates decrease in a regular fashion as the basicity of the attacking nucleophile decreases. This is true not only for reactions of the alkyl chlorides and bromides with weak bases but also for reactions of ethylene oxide with the strong bases HO^-, CH_3O^-, and F^-. If we assume that the same trend applies to reactions of methyl fluoride, we could extrapolate along the series from HO^- (0.005) to CH_3O^- (0.001) to F^- and estimate an efficiency for the F^- + CH_3F reaction that is similar to that for Cl^- + CH_3Cl (10^{-4}–10^{-5}). This would suggest that the intrinsic barrier in the fluoride–methyl fluoride reaction is not very different from that for chloride–methyl chloride and that there is nothing unique about fluorine among the halogens. Indeed from our data we see nothing unique about F^- as a nucleophile, since its reactivity with the substrates studied is just what one would anticipate on the basis of the gas-phase acidity of HF.[17] This conclusion agrees well with ab initio calculations.[18l,dd]

What can be said about the barrier for the analogous symmetrical S_N2 reaction between Br^- and CH_3Br? Brauman has argued,[21] quite reasonably, that it too should be close in height to that for Cl^- with CH_3Cl, but the rate of the reaction has not been measured experimentally. In our FA-SIFT we can inject $^{81}Br^-$ and allow it to react with methyl bromide. Unfortunately the reaction is sufficiently slow that minute traces of HBr present in the methyl bromide interfere with the measurement, since HBr reacts extremely rapidly with Br^-. We have, therefore, adopted another strategy, namely to measure the exchange rate for both a chloride and a bromide in compounds that react sufficiently rapidly that traces of hydrogen halide will not affect the rate significantly. Having found that α-halo acetonitriles react much faster than methyl halides in the gas phase, as they do in solution,[19]

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(16) Shaik, S. S.; Pross, A. *J. Am. Chem. Soc.* **1982**, *104*, 2708.

(17) The reactivity of fluoride as a leaving group also appears approximately normal for a halogen if our measured rates for reactions of methyl fluoride are correct. There is always the chance, however, that a trace of some fast-reacting impurity in the methyl fluoride could be giving rise to the observed reaction. A referee has commented that SiF_4 is a common impurity in methyl fluoride and might account for our observed rate. However, reaction of SiF_4 with HO^- in our FA-SIFT forms SiF_3O^- whereas F^- is the only ionic product from reaction of HO^- with our sample of CH_3F. An impurity of HF cannot be invoked to account for the reaction rate of CH_3F with HO^- since CH_3O^- should react equally fast with this impurity.

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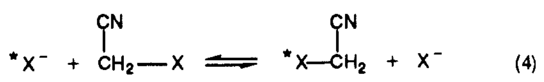
we chose these compounds as substrates (eq 4). α-Chloro-



$$^{*}X^- + CH_2(CN)\!-\!X \rightleftharpoons {}^{*}X\!-\!CH_2(CN) + X^- \qquad (4)$$

acetonitrile reacts with $^{37}Cl^-$ with an efficiency of 0.12, which is significantly below the collision limit. This corresponds to an increase in efficiency of a factor of 6000 compared to methyl chloride and a larger increase compared to *n*-propyl chloride. With reaction efficiencies of this magnitude trace impurities will not have a significant effect on rate measurements. We next studied α-bromoacetonitrile and found that it reacts, as expected, somewhat faster with Cl^- (efficiency 0.49). It also reacts quite readily with $^{81}Br^-$ (efficiency 0.20). Since α-chloro- and α-bromoacetonitrile undergo symmetrical, thermoneutral substitution reactions with nearly the same efficiency, it seems reasonable to predict that methyl chloride and bromide will also do so, and that for all the halogens the top of the barrier is quite similar in energy to that of the reactants.

The most unusual results of this study pertain not so much to the gas-phase S_N2 reaction but rather to the E2. It has often been assumed that E2 reactions are favored over S_N2 reactions in the gas phase when both processes are structurally and thermodynamically accessible, possibly because the E2 transition state is a looser one and so favored entropically. However, as the data in Tables IV and V show, this is only true for oxy anions; sulfur anions do not appear to induce gas-phase E2 reactions even if they are sufficiently basic to do so. This is not because of an increase in rate for the S_N2 process but rather because of a decrease in the E2 rate. Since the exothermicity of an E2 reaction is the same for any two anions of the same basicity, this result must have a kinetic rather than a thermodynamic explanation. RS^- attacks a β-proton to induce elimination much less readily than does RO^- even when the two anions have identical basicities. We will not propose an explanation for this phenomenon, but it is in line with our previous observations[20] that proton transfers to and from second-row elements (e.g. in SiH_4, PH_3, H_2S) are slow in the gas phase compared to proton transfers to and from the oxygen atom in H_2O or alcohols.

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(20) Damrauer, R.; Kass, S. R.; DePuy, C. H. *Organometallics* **1988**, *7*, 637.

The Isomerization of Oxirane. Stable $^{\bullet}CH_2OCH_2^{\bullet}$, $^{\bullet}CH_2CH_2O^{\bullet}$, and $:CHOCH_3$ and Their Counterpart Ions

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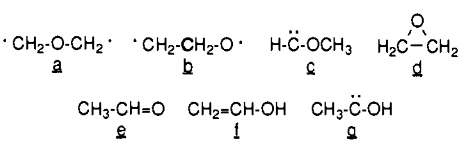
Abstract: Unimolecular C–C bond rupture in oxirane leading to $^{\bullet}CH_2OCH_2^{\bullet}$ is favored over C–O rupture to $^{\bullet}CH_2CH_2O^{\bullet}$, but the latter is the first-step in the lowest energy dissociation pathway through excited $CH_3CH{=}O$ to $CH_3^{\bullet} + {}^{\bullet}CHO$. With collisional activation, $^{\bullet}CH_2OCH_2^{\bullet}$ isomerizes mainly to oxirane, not methoxycarbene, $:C(H)OCH_3$, while $^{\bullet}CH_2CH_2O^{\bullet}$ isomerizes mainly to CH_3CHO. All of these neutral isomers were prepared in the gas-phase via neutralization of the corresponding radical cations. Their structures, and those of their precursor cations, were established by collisionally activated dissociation (CAD), neutralization–anionization, and CAD of the mass-selected recovered molecular ions (MS/MS/MS) from neutralization–cationization. All of the neutrals and cationic isomers are found to represent stable bound structures, clarifying in particular previous contrary evidence concerning $^{\bullet}CH_2CH_2O^{\bullet}$, $^{+}CH_2CH_2O^{\bullet}$, and the oxirane cation. Anionization showed the isomers $^{\bullet}CH_2CH_2O^-$, $^{-\bullet}C(H)OCH_3$, and $^{-\bullet}C(OH)CH_3$ to be stable.

The unusual reactivity of diradicals (in polymerization, stereoisomerization, synthesis)[1] and of carbenes (insertion into C–H bonds, addition to multiple bonds, skeletal rearrangements)[2] also makes difficult their study by usual experimental methods. Recently, neutralization–reionization mass spectrometry (NRMS)[3,4] has provided new information on the stabilities and reactivities of hydroxycarbene, $:C(H)OH$,[4a] and hydroxymethylcarbene, $:C(OH)CH_3$ (**g**).[4b] In NRMS such species are formed in the gas phase by neutralization[5] of the corresponding molecular cations, and their unimolecular isomerization and dissociation products characterized by reionization. In this paper NRMS is used to provide the first experimental characterization of the diradicals $^{\bullet}CH_2OCH_2^{\bullet}$ (**a**) and $^{\bullet}CH_2CH_2O^{\bullet}$ (**b**), of methoxycarbene, $:C(H)OCH_3$ (**c**), and of their tendencies to isomerize to the stable C_2H_4O isomers oxirane (**d**) and acetaldehyde (**e**). Similar studies of the C_2H_4O isomers **e**–**g**[4b] and the ylide $^-CH_2{}^+OH_2$[4c] (**a** is a carbonyl ylide, $^-CH_2{}^+O{=}CH_2$) have been reported recently.



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