Kinetic Studies of the Reactions of Oxide, Hydroxide, Alkoxide, Phenyl, and Benzylic Anions with Methyl Chloride in the Gas Phase at 22.5°

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Abstract: As part of a program directed toward an understanding of the intrinsic nature of anion–molecule reactions involving organic constituents, rate constants have been measured, reaction channels have been identified, and intrinsic reaction probabilities (the ratios of the experimentally determined rate constants to the theoretical collision rate constants) have been calculated for the reactions of oxide, hydroxide, alkoxide, phenyl, and benzylic anions with methyl chloride. All measurements were made in the gas phase at 22.5° under thermal equilibrium conditions using the flowing afterglow technique. The highly charge-localized anions were found to react rapidly with methyl chloride with rate constants larger than 8×10^{-10} cm^3 molecule^{-1} sec^{-1} whereas the charge-delocalized anions reacted only slowly with rate constants less than 3×10^{-11} cm^3 molecule^{-1} sec^{-1}. The formation of chloride ion was the dominant reaction channel observed in all cases. Calculated reaction probabilities were larger than 0.20 for the reactions involving highly charge-localized anions and less than 0.03 for the charge-delocalized anion reactions. These results obtained in a rarified medium provide evidence for a correlation well known from solution studies, namely, a correlation between the reactivity of an anion and the nature of the distribution of its charge. Solvated alkoxide ions could be established as the dominant negative ions in a low-pressure helium afterglow. This allowed an investigation of the effect of weak solvation on the rate of reaction of alkoxide ions with methyl chloride. Upon the association of one molecule of the conjugate acid to the alkoxide ion the specific rate for reaction decreased by at least a factor of three.

In our continuing studies of the intrinsic kinetics and energetics of anion–molecule reactions involving organic constituents, we have turned our attention to the intrinsic behavior of nucleophilic substitution reactions of the type

$$A^- + BX \longrightarrow X^- + AB \qquad (1)$$

where X is a halogen atom. It has been noted by organic chemists for many years that the rates of such reactions proceeding in solution can be influenced by the dielectric constant of the solvent and that a change in solvent may bring about alterations in the mechanism of these reactions. In order to rationalize completely such solvent effects in nucleophilic substitution reactions, it is desirable to obtain kinetic and mechanistic information for these reactions in the complete absence of solvent perturbations and, when possible, under conditions of very weak solvation. Such information can be obtained from investigations carried out in the gas phase at low pressures under thermal equilibrium conditions. An experimental technique which is suited for such studies, namely the flowing afterglow technique, has recently been described by the authors with reference to reactions of oxide radical ion and hydroxide ion with saturated and unsaturated hydrocarbons and of carbanions with molecular oxygen.[1] The availability in a flowing afterglow of a large number of both unsolvated and weakly solvated organic anions provides us with a unique opportunity to investigate the intrinsic nature of nucleophilic substitution, especially as regards the determination of an order of intrinsic nucleophilic reactivity, the intrinsic role played by the nature of both the nucleophile and the substrate, and the influence of weak solvation on the intrinsic kinetics of these reactions. This paper is concerned with the determination of kinetic and mechanistic information for nucleophilic substitution reactions involving organic anions in which the nature of the anion is altered while the substrate remains unaltered. In addition, direct investigations are made in several cases of the effect of weak solvation on the kinetics of the unsolvated reactions. Such investigations represent an important step in the "extrapolation" of intrinsic gas-phase results to condensed-phase chemistry.

Experimental Section

The present experiments were carried out in one of the flowing afterglow systems of the Environmental Science Services Administration Research Laboratories in Boulder, Colo. The details of the apparatus, its operation, and the related data analysis have been described in detail previously both with reference to studies of thermal energy ion–molecule reactions of interest in relation to the earth's ionosphere[2] and with reference to the novel application of this technique to negative ion organic chemistry in the gas phase.[1]

In the present investigations, helium was again used as the buffer gas. The steady-state pressures were in the range 0.22–0.25 Torr. The O^- ions were produced directly in the excitation region principally by the dissociative ionization reaction (eq 2) and, probably

$$e + O_2 \longrightarrow O^- + O^+ + e \qquad (2)$$

to a much lesser extent, the dissociative attachment reaction (eq 3). Hydroxide ions were produced indirectly downstream from

$$e + O_2 \longrightarrow O^- + O \qquad (3)$$

the excitation region but several milliseconds upstream from the reaction region by the rapid hydrogen atom abstraction reaction (eq 4) which has a measured rate constant of 2.6×10^{-9} cm^3 mole-

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[2] E. E. Ferguson, *Advan. Electron. Electron Phys.*, 24, 1 (1968); E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, *Advan. At. Mol. Phys.*, 5, 1 (1969).

$$O^- + NH_3 \longrightarrow OH^- + NH_2 \quad (4)$$

cule^{-1} sec^{-1} in the gas phase.[3] The alkoxide ions CH_3O^-, $CH_3CH_2O^-$, $(CH_3)_2CHO^-$, and $(CH_3)_3CO^-$ were generated by introducing the vapor of the corresponding alcohol into a flowing afterglow rich in either OH^-, O^-, or NH_2^-. The intrinsic basicity of OH^- has recently been shown to be higher than that of the simple alkoxide ions.[4,5] Thus, in the gas phase, OH^- will abstract a proton from a simple alcohol to form the corresponding conjugate base and water according to the reaction

$$OH^- + ROH \longrightarrow RO^- + H_2O \quad (5)$$

Transfer of only the hydroxylic proton has been demonstrated by several workers with appropriate deuterium-labeled compounds.[4,6] O^- ions will abstract both a hydrogen atom and a proton from simple alcohols according to the reaction

$$O^- + ROH \longrightarrow OH^- + RO \quad (6)$$

$$\longrightarrow RO^- + OH \quad (7)$$

Hydrogen atom transfer occurs almost exclusively from either the hydroxyl position or the terminal carbon atom whereas proton transfer again occurs exclusively from the hydroxyl position.[6] The NH_2^- ion was readily generated in the excitation region by electron impact on ammonia at partial pressures of ammonia less than 5 × 10^{-4} Torr. However, NH_2^- reacts rapidly with water impurities to yield OH^- *via* the proton transfer reaction

$$NH_2^- + H_2O \longrightarrow OH^- + NH_3 \quad (8)$$

The NH_2^- ion will also abstract a proton from the simple alcohols presumably from the hydroxyl position only.

In each of the present experiments, a sufficient amount of the vapor of the alcohol was added into the flowing afterglow to ensure maximum conversion of OH^-, O^-, or NH_2^- into the alkoxide ion upstream from the reaction region. A moderate addition of the alcohol vapors to the flowing afterglow yielded copious amounts of the solvated anions $CH_3O^-\cdot nCH_3OH$ (n = 1,2), $C_2H_5O^-\cdot nC_2H_5OH$ (n = 1–3), $(CH_3)_2CHO^-\cdot n(CH_3)_2CHOH$ (n = 1,2), and $(CH_3)_3CO^-\cdot n(CH_3)_3COH$ (n = 1–3) presumably *via* three-body ion–molecule association reactions of the type

$$RO^-\cdot nROH + ROH + He \longrightarrow RO^-\cdot(n+1)ROH + He \quad (9)$$

which are expected to have rate constants of at least 10^{-28} cm^6 molecule^{-2} sec^{-1}.[7]

The phenyl and benzylic carbanions are such strong bases in common hydroxylic solvents, such as water and alcohol, that they usually do not exist in appreciable concentrations in the condensed phase. In the gas phase, however, these ions can be readily generated and have been found to be stable in an excess of helium gas. In the present experiments the conjugate bases of benzene, methylbenzene, ethylbenzene, isopropylbenzene, and *tert*-butylbenzene were generated by proton transfer to NH_2^-. The NH_2^- ion was used since our intrinsic acidity studies have indicated that the hydroxyl ion is a weaker base than the phenyl anion, although it is sufficiently basic to abstract a proton from both methylbenzene and ethylbenzene in the gas phase.[8]

The various negative ions produced in the manner described above, either by direct electron impact or by secondary ion–molecule reactions, are allowed to thermalize for several milliseconds before they enter the reaction region into which the methyl chloride is added in measured amounts. The methyl chloride had a purity of 99.5 mol %. The helium buffer gas had a purity of 99.995 mol %, the oxygen a minimum purity of 99.95 mol %, and the anhydrous ammonia a purity of 99.99 mol %. The various alcohols and aromatic hydrocarbons were reagent grade. The accuracy of the absolute rate constants obtained using this technique has been conservatively estimated as ±30%, which is partly due to the complexities of the aerodynamic analysis of the system. The relative accuracy should be ±10% or less.

Results

Calculation of Intrinsic Reactivity. The intrinsic reactivities of the various anions toward methyl chloride were estimated in terms of a reaction efficiency or reaction probability, P, defined as the ratio of the experimentally determined rate constant, k_{exptl}, to the theoretical collision rate constant, k_c, *i.e.*, $P = k_{\text{exptl}}/k_c$. For a Maxwell–Boltzmann speed distribution of reactant ions and molecules, the maximum mean collision rate constant can be expressed as the sum of two terms according to eq 10,[9] where e is the electronic

$$k_c = k_L + k_D = 2\pi e\left(\frac{\alpha}{\mu}\right)^{1/2} + (2\pi e\mu_D/\mu)(2\mu/\pi kT)^{1/2} \quad (10)$$

charge, μ is the reduced mass of the reactants, T is the gas temperature, α is the polarizability, and μ_D the permanent dipole moment of the neutral substrate. The first term reflects the contribution of the ion–induced dipole interaction and the second term the contribution of the ion–permanent dipole interaction to the calculated collision rate constant. The ion–permanent dipole term is derived on the assumption that the dipole aligns itself or "locks-in" as the ion approaches. However, since the recent trajectory calculations of Dugan, *et al.*,[10] have indicated that the "locking-in" of the dipole does not necessarily occur, the permanent dipole term in eq 1 must be regarded as a measure of the maximum contribution of the ion–permanent dipole interaction to the calculated collision rate constant. The permanent dipole term, therefore, reflects the range of values of the mean collision rate constant, the actual value depending on the degree of alignment of the dipole with the electric field of the incoming ion. As a consequence of these considerations, calculations were made of both the reaction probability $P_c = k_{\text{exptl}}/k_c$ and the reaction probability $P_L = k_{\text{exptl}}/k_L$, where k_L is the value of k_c when the permanent dipole term is neglected. The true reaction probability is then likely to have a value intermediate between P_L and P_c when $P_L \leq 1$ and intermediate between 1 and P_c when $P_L > 1$. A reaction probability $P_c \approx 1$ suggests that the dipole indeed "locks-in" as the ion approaches.

Reactions of the Oxide Radical Ion, O^-, and the Hydroxide Ion, OH^-, with Methyl Chloride. The addition of methyl chloride to an afterglow rich in O^- ions indicated that these ions react rapidly with methyl chloride at 22.5° along the following three reaction channels (eq 11a–c). The decline of the primary O^- ion signal and the variation of the secondary Cl^-, OH^-, and $CHCl^-$ ion signals as a function of methyl chloride addition allow the determination of both the rate constant for the loss of the O^- ions and the branching ratios for the various product channels.[1]

$$O^- + CH_3Cl \xrightarrow{0.5} Cl^- + CH_3O \quad (11a)$$

$$\xrightarrow{0.4} OH^- + CH_2Cl \quad (11b)$$

$$\xrightarrow{0.1} CHCl^- + H_2O \quad (11c)$$

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[10] J. V. Dugan and J. L. Magee, NASA Report No. TN-D-3229, Feb 1966; J. V. Dugan, J. H. Rice, and J. L. Magee, *Bull. Amer. Phys. Soc.*, **12**, 702 (1967).

A rate constant of 2.4×10^{-9} cm^3 molecule^{-1} sec^{-1} was determined from the decline of the O^- signal. The branching ratios are indicated in eq 11a–c and the rate constants for the formation of the various products are summarized in Table I. The dominant product ion was observed to be Cl^-. The neutral products in reaction 11 were, of course, not identified. However, since the nucleophilic elimination reaction

$$O^- + CH_3Cl \longrightarrow Cl^- + CH_2 + OH \qquad (12a)$$

and the dissociative charge transfer reaction

$$O^- + CH_3Cl \longrightarrow Cl^- + CH_3 + O \qquad (12b)$$

are calculated to be at least 0.5 eV endothermic, the dominant reaction channel (eq 11a) is likely to proceed as written and thus correspond to a nucleophilic substitution. The exothermic channel leading to the direct formation of the neutral products formaldehyde and atomic hydrogen must be regarded as less favorable on mechanistic grounds. Any formation of formaldehyde and atomic hydrogen would probably result from the further decomposition of CH_3O radicals. The minor reaction channels correspond to hydrogen atom abstraction (20%) and H_2^+ transfer (10%). In comparison, hydrogen atom abstraction has recently been observed to be the only significant reaction channel in the reaction of O^- with CH_4.[11]

Table I. Measured Rate Constants for the Formation of Product Ions in the Reaction $O^- + CH_3Cl$

Product ions	$k \times 10^{10}$ cm^3 molecule^{-1} sec^{-1} 22.5° [a]	0.3 ± 0.3 eV[b]
Cl^-	12	0.7
OH^-	9	3.9
$CHCl^-$	3	2.7
$Cl^- + OH^- + CHCl^-$	24	7.3

[a] Present results obtained in a flowing afterglow. [b] Results obtained in the tandem mass spectrometer experiments of Hughes and Tiernan.[6]

Reactions of Alkoxide Ions with Various Degrees of Alkyl Substitution with Methyl Chloride. The measured rate constants and calculated reaction probabilities for the reactions of the alkoxide, as well as the oxide and hydroxide ions with methyl chloride, are listed in Table II. In calculating the reaction probabilities, the polarizability and the permanent dipole moment of methyl chloride were taken to be 4.44×10^{-24} cm^3 and 1.87 D, respectively. In each of these reactions, with the exception of the oxide ion reaction which was discussed in the previous section, the only ion observed in the product mass spectrum was Cl^-. No other product ions with an intensity of at least 1% of the primary ion signal were observed. The neutral product of the reactions of the alkoxide ions with methyl chloride, although it is not directly detected and identified in these experiments, is almost certainly the corresponding aliphatic ether (eq 13) since energetic

$$RO^- + CH_3Cl \longrightarrow Cl^- + ROCH_3 \qquad (13)$$

considerations indicate that the channel

$$RO^- + CH_3Cl \longrightarrow Cl^- + RO + CH_3 \qquad (14)$$

and the nucleophilic elimination channel

$$RO^- + CH_3Cl \longrightarrow Cl^- + CH_2 + ROH \qquad (15)$$

are both endothermic by more than 0.5 eV. We can conclude on the basis of these energy considerations that the reactions of the alkoxide ions with methyl chloride proceed principally by nucleophilic substitution in the gas phase at 22.5°. However, we must again regard the exothermic channel leading to the direct formation of formaldehyde and, in this case, hydrogen or saturated hydrocarbons to be mechanistically unfavorable.

Table II. Rate Constants and Reaction Probabilities for the Nucleophilic Substitution Reactions of Oxide, Hydroxide, and Alkoxide Ions[a]

Reaction	Rate constant, $k \times 10^9$ cm^3 molecule^{-1} sec^{-1} k_{exptl}	k_L	k_D	k_c	Reaction probability P_L	P_c
$O^- + CH_3Cl$	1.7[b]	1.41	4.94	6.35	1.2	0.27
$OH^- + CH_3Cl$	1.9	1.38	4.83	6.21	1.4	0.31
$CH_3O^- + CH_3Cl$	1.6	1.13	3.93	5.06	1.4	0.32
$CH_3CH_2O^- + CH_3Cl$	1.3	1.01	3.53	4.54	1.3	0.29
$(CH_3)_2CHO^- + CH_3Cl$	1.1	0.95	3.30	4.25	1.2	0.26
$(CH_3)_3CO^- + CH_3Cl$	0.8	0.90	3.15	4.05	1.0	0.20

[a] With methyl chloride in the gas phase at 22.5°. [b] Rate constant for the formation of Cl^-.

Reactions of Phenyl and Benzylic Anions with Methyl Chloride. The measured rate constants and calculated reaction probabilities for the reaction of the phenyl and benzylic anions with methyl chloride are listed in Table III. The only ion observed in the product mass spectrum with an intensity of at least 1% of the primary ion signal was Cl^-. Three reaction channels may again be written, since the neutral product is not identified.

$$B^- + CH_3Cl \longrightarrow Cl^- + BCH_3 \qquad (16a)$$

$$\longrightarrow Cl^- + B + CH_3 \qquad (16b)$$

$$\longrightarrow Cl^- + CH_2 + BH \qquad (16c)$$

where B^- represents the phenyl or benzylic anion. The reaction channel 16a is formally a nucleophilic substitution channel. Channel 16b represents a dissociative charge-transfer reaction. Channel 16c corresponds to nucleophilic elimination. Insufficient thermochemical data prevent a discrimination against channels 16b and 16c on energetic grounds. Thus it cannot be established unequivocally that this series of reactions proceeds by nucleophilic substitution, although this is likely to be the case.

Table III. Rate Constants and Reaction Probabilities for the Reactions of the Phenyl and Benzylic Carbanions[a]

Reaction	Rate constant, $k \times 10^{10}$ cm^3 molecule^{-1} sec^{-1} k_{exptl}	k_L	k_D	k_c	Reaction probability P_L	P_c
$C_6H_5^- + CH_3Cl$	8.7	8.93	31.2	40.1	0.97	0.22
$C_6H_5CH_2^- + CH_3Cl$	0.15	8.65	30.2	38.9	0.02	0.004
$C_6H_5\bar{C}HCH_3 + CH_3Cl$	0.24	8.45	29.5	38.0	0.03	0.006
$C_6H_5\bar{C}(CH_3)_2 + CH_3Cl$	0.26	8.28	28.9	37.2	0.03	0.007
tert-$BuC_6H_4^- + CH_3Cl$	8.0	8.15	28.5	36.7	0.98	0.22

[a] With methyl chloride to yield Cl^- ions in the gas phase at 22.5°.

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(11) D. K. Bohme and F. C. Fehsenfeld, *Can. J. Chem.*, 47, 2717 (1969).

The Effect of Solvation on the Kinetics of the Reactions of Alkoxide Ions with Methyl Chloride. It was stated in a previous section that the unsolvated alkoxide ions CH_3O^-, $CH_3CH_2O^-$, $(CH_3)_2CHO^-$, and $(CH_3)_3CO^-$ were all observed to react rapidly with methyl chloride probably *via* nucleophilic substitution. Upon the association of one molecule of the conjugate acid to these alkoxide ions a significant transition in the reaction kinetics was observed. The nature of this transition is demonstrated in Figure 1 for the reaction of both unsolvated and solvated isopropoxy anions with methyl chloride. The $(CH_3)_2CHO^-$ ion signal decreases rapidly upon the addition of methyl chloride to a helium afterglow rich in both unsolvated and solvated isopropoxy anions. This decrease corresponds to a rate constant of 1.1×10^{-9} cm^3 molecule^{-1} sec^{-1}. In comparison, the $(CH_3)_2CHO^- \cdot (CH_3)_2CHOH$ ion signal decreases only very gradually with a rate constant of about 3.0×10^{-10} cm^3 molecule^{-1} sec^{-1}. In fact, this rate constant must be regarded as an upper limit since at least a portion of this decline is due to a depletion of the source of $(CH_3)_2CHO^- \cdot (CH_3)_2CHOH$, namely $(CH_3)_2CHO^-$, in the reaction region. These results, therefore, clearly indicate that the rate constant for reaction decreases by at least a factor of 3 upon the association of one solvent molecule to the isopropoxy anion. As can be seen from Table IV, similar results were observed for the reactions of the unsolvated and solvated conjugate bases of methanol, ethanol, and *tert*-butyl alcohol. The determination of the rate constants for the reactions of the solvated alkoxide ions is facilitated in these experiments by what must certainly be a strong anion–solvent molecule bond. The data indicate that reaction 9 is far removed from equilibrium under the operating conditions of these experiments.

Table IV. Rate Constants for the Reactions of Unsolvated and Solvated Alkoxide Ions[a]

Alkoxide ion	$k_{\text{exptl}} \times 10^{10}$ cm^3 molecule^{-1} sec^{-1} RO^-	 $RO^- \cdot ROH$
CH_3O^-	16	≤ 5
$CH_3CH_2O^-$	13	≤ 4
$(CH_3)_2CHO^-$	11	≤ 3
$(CH_3)_3CO^-$	8	≤ 2

[a] With methyl chloride in the gas phase at 22.5°.

The reactions of the solvated alkoxide ions with methyl chloride may be considered in terms of the following reaction channels (17a–17e). The channels

$$\begin{aligned} RO^- \cdot ROH + CH_3Cl &\longrightarrow Cl^- + ROCH_3 + ROH &\quad (17a) \\ &\longrightarrow Cl^- + ROCH_3 \cdot ROH &\quad (17b) \\ &\longrightarrow Cl^- \cdot ROH + ROCH_3 &\quad (17c) \\ &\longrightarrow Cl^- \cdot ROCH_3 + ROH &\quad (17d) \\ &\longrightarrow RO^- \cdot CH_3Cl + ROH &\quad (17e) \end{aligned}$$

17b–17d represent nucleophilic substitution reactions with various modes of solvation whereas channel 17a represents a nucleophilic substitution unaccompanied by solvation of the products. Channel 17e represents a "switching" or competitive solvation reaction. In the present series of experiments the only ions observed in the product mass spectrum with an intensity of at least 1% of the primary ion signal were Cl^- and $Cl^- \cdot ROH$. However, an analysis of the data indicates that the major source for $Cl^- \cdot ROH$ is the three-body reaction

$$Cl^- + ROH + He \longrightarrow Cl^- \cdot ROH + He$$

It appears, therefore, that channels 17c–17e do not contribute significantly to the apparent declines of the $RO^- \cdot ROH$ ions with addition of methyl chloride to the reaction region. However, channels 17a and 17b cannot be precluded even though a principal source for Cl^- is the reaction of the unsolvated ion.

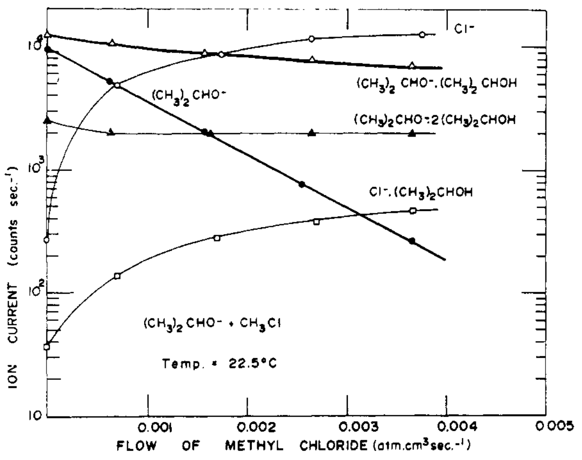

Figure 1. The variation of reactant and product ion signals with added neutral reactant for the reaction of unsolvated and solvated isopropoxy anions with methyl chloride in the gas phase at a pressure of 0.224 Torr and a temperature of 22.5°.

Discussion

The reaction of O^- with methyl chloride is unique in this series of measurements in that the nucleophilic substitution channel proceeds in competition with two additional channels. It would be most interesting to investigate this reaction as a function of the gas kinetic temperature or kinetic energy of the nucleophile and observe variations in the contribution of the various reaction channels to the overall reaction. The recent tandem mass spectrometer experiments of Hughes and Tiernan[6] already suggest that a significant alteration in the contribution of the various reaction channels occurs with increasing impacting ion energies. Hughes and Tiernan found the nucleophilic substitution channel to be the *minor* reaction channel at impacting ion energies of 0.3 ± 0.3 eV. The total rate constant for the formation of product ions was measured to be 7.3×10^{-10} cm^3 molecule^{-1} sec^{-1} with 10% of the reaction formally proceeding by nucleophilic substitution, 53% by hydrogen atom abstraction, and 37% by H_2^+ transfer. A comparison of the available flowing afterglow data and tandem mass spectrometer data is made in Table I. It can be noted from the data in Table I that the rate constants measured at 22.5° and at 0.3-eV ion kinetic energy for the formation of OH^- and $CHCl^-$ by H-atom abstraction and H_2^+ transfer, respectively, show no serious discrepancy since tandem mass spectrometer data and flowing afterglow data almost always agree to within a factor of 2 or 3 where comparisons can be made. In comparison, the rate constant observed in the two types of experimental systems for the nucleophilic substitution channel differs by a factor of about 20. Since this difference is likely to be real, the large decrease in the observed rate constant over such a relatively narrow energy range must be regarded as being quite unique in that fast exothermic ion–molecule channels often show a much milder decrease and at times an increase in their rate constants in this energy range. Certainly experimental results in the energy regime between 22.5° and 0.3 eV are desirable before any meaning can be attached to this apparent sharp drop in the rate constant for nucleophilic substitution with increasing ion kinetic energy.

Table II shows that the intrinsic reaction probability for the reaction of alkoxide ions with methyl chloride decreases with increasing aliphatic substitution on the nucleophile. The decrease in the reaction probability is, however, only very slight. This suggests that steric interference by the aliphatic substituent on the nucleophile is not very effective in this series of reactions but that, instead, the alkoxide ions probably orient themselves during their approach to the methyl chloride molecules so that the atomic oxygen, which bears most of the negative charge, faces the electrophilic carbon center and the aliphatic substituent "trails behind." Alternatively, the explanation for the slight lowering of the reaction probability for this series of reactions may be sought in the phenomenon of charge delocalization in the nucleophile. Recent measurements on the relative acidity of alcohols in the gas phase have suggested that increasing alkyl substitution is increasingly effective in stabilizing negative charge in the gaseous alkoxide anions.[4] This has been borne out by the recent molecular orbital calculations of Baird,[12] who indicates that a portion of the total stabilization occurs *via* hyperconjugative release of electron density from oxygen, since the oxygen atom net charge decreases from $-0.91e$ in CH_3O^-, to $-0.85e$ in $CH_3CH_2O^-$, and to $-0.81e$ in $(CH_3)_2CHO^-$. Therefore, in the absence of any steric effects, the lowering in the reaction probability with increasing alkyl substitution may simply result from increasing charge delocalization in the nucleophile. Such an effect may be demonstrated in a more striking manner in the series of reactions between methyl chloride and phenyl and benzylic carbanions which are discussed in the next section.

Table III shows that the measured rate constant and the calculated intrinsic reaction probability drop sharply by a factor of about 55 as the benzene ring of the aromatic hydrocarbon from which the carbanion is derived is substituted. However, the rate constant and the reaction probability recover sharply, by a factor of about 30, for the reaction of the carbanion derived from *tert*-butylbenzene with methyl chloride. One is again tempted to seek the explanation for these striking results in the phenomenon of charge delocalization in the nucleophile. The negative charge is localized on one carbon atom in the case of the phenyl anion and the anion derived from *tert*-butylbenzene and delocalized in other anions if the most acidic proton is removed from the corresponding conjugate acid. For example, in the case of the benzyl carbanion, calculations from the nuclear magnetic resonance spectrum of benzyllithium indicate that 62% of the charge is delocalized over the ring.[13] It therefore appears that the rate constant and efficiency of the reactions listed in Table III are proportional to the degree of localization of charge on the nucleophile, the rate constant and efficiency being large when the charge is localized and considerably smaller when the charge is significantly delocalized. Since the efficiencies of the ion–molecule reactions listed in Table III are a measure of the intrinsic reactivities (*i.e.*, the intrinsic stabilities toward reaction) of the corresponding carbanions, the results in Table III actually demonstrate a correlation well known from solution studies, namely, a correlation between the reactivity of a carbanion and the nature of the distribution of its charge.

The observed lowering of the rate constant for the reaction of alkoxide ions with methyl chloride upon the association of one molecule of the conjugate acid to the unsolvated ion needs to be rationalized in terms of the energetics and mechanism of the solvated ion reaction. There is insufficient information available at the present time on the energy of solvation of the solvated species in reaction 17 to allow the energetics of this reaction to be completely specified. However, it can be pointed out that if the energy of solvation of the alkoxide ions is sufficiently large, all channels in reaction 17 will be rendered endothermic. This being the case, the solvated alkoxide reactions would not be expected to occur rapidly at the thermal energies of these experiments. Alternatively, the observed lowering of the rate constant upon solvation may reflect the appearance of a steric requirement for nucleophilic substitution by solvated nucleophiles or result from charge delocalization in the solvated nucleophile or both. A conclusive statement, however, cannot be made at the present time. Efforts will be made to investigate further the effect of solvation on the intrinsic kinetics of anion reactions in the gas phase. Many solvated anions have now been generated in the flowing afterglow, some of which are being identified for the first time. For example, solvated ions such as $NO_2^- \cdot CHCl_3$, $\bar{C}H_2NO_2 \cdot CHCl_3$, and $Cl^- \cdot ROH$ (where $R = CH_3$, C_2H_5, $(CH_3)_2CH$, $(CH_3)_3C$) have been identified and found to be quite stable in the gas phase. It is expected that studies with these and similar solvated ions will yield additional information on the gap between intrinsic and solution kinetics.

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