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Gas-Phase Measurements of the Influence of Stepwise Solvation on the Kinetics of Nucleophilic Displacement Reactions with CH_3Cl and CH_3Br at Room Temperature

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Abstract: The absolute influence of stepwise solvation on nucleophilicity is explored with flowing afterglow measurements of rate constants in the gas phase at room temperature for nucleophilic displacement reactions of CH_3Cl and CH_3Br with the solvated homoconjugate anions $A^-\cdot(AH)_m$ with AH = H_2O, D_2O, CH_3OH, C_2H_5OH, CH_3COCH_3, HCOOH, and CH_3COOH. The specific rates are followed as a function of stepwise solvation for additions of up to three molecules of solvent (from n = 0–3). Comparisons are made with the kinetic behavior of the analogous reactions proceeding in solution. The observed trends in specific rate with solvation are discussed in terms of overall energetics and models for the intermediate potential energy profile.

Nucleophilic displacement (S_N2) reactions between anions and methyl halides are known to be extremely sensitive to the medium in which they proceed. For example, solution measurements have shown that nucleophilic displacement can be as much as a million times faster in dipolar aprotic than in protic solvents.[1] These same reactions have now also been executed in the gas phase where they have been found to proceed in the total absence of solvent with specific rates as much as *20 orders of magnitude* higher than those in solution.[2] The gas-phase experiments have provided, for the first time, a direct measure of the absolute influence of bulk solvent on the kinetics and efficiencies of these reactions.

In addition to the solvent-free reactions, solvated nulceophilic displacement reactions of the type in (1) can also be executed in the gas phase, and their kinetics can be followed as a function

$$A^-\cdot S_n + CH_3B \rightarrow B^-\cdot S_m + [(n-m)S + CH_3A] \quad (1)$$

of stepwise solvation of the nucleophilic as indicated in Figure 1. For example, reactions of the type in (2) were executed in the gas phase in our early gas-phase studies of solvated nucleophilic

$$RO^-\cdot(ROH)_n + CH_3Cl \rightarrow Cl^-\cdot(ROH)_m + [(n-m)ROH + ROCH_3] \quad (2)$$

displacement for R = CH_3, C_2H_5, $(CH_3)_2CH$, and $(CH_3)_3C$ and for values of n equal to 0 and 1.[3] A significant decrease in reactivity was observed for all alkyl groups with the addition of just the one molecule of solvent to the nucleophile. More recently we have reported in brief a quantitative study for reactions of the type in (3) between hydrated hydroxide ions and methyl bromide

$$OH^-\cdot(H_2O)_n + CH_3Br \rightarrow Br^-\cdot(H_2O)_m + [(n-m)H_2O + CH_3OH] \quad (3)$$

for additions of up to three molecules of water.[4] Here we report these results in more detail as part of an extended study of the influence of solvation on nucleophilic displacement in the gas phase.

With our previous measurements of intrinsic reactivities as a benchmark,[2] we have followed as a function of stepwise solvation the kinetics of reactions of homoconjugate anions $A^-\cdot(AH)_n$, with both CH_3Cl and CH_3Br. The measurements were carried out at room temperature with additions of up to three solvent molecules to the nucleophile. While such amounts of solvation scarcely correspond to the solvent environment found in solution, they do begin to bridge the gap between the totally unsolvated gas phase and solution. At the same time the role of solvent is expossed at its most fundamental level at these low degrees of solvation. In the experiments reported here the solvated reactions proceed in the absence of bulk solvent in an inert gaseous medium at low total pressures so that *available solvent is limited to that associated directly with the reacting ion.* As a consequence, solvation of the product ion can only arise by solvent transfer within the reaction complex rather than by transport from the surrounding medium. The measurements therefore promise to provide a new added dimension to the role of solvation in reactions of ions. Also, one can begin to probe the extent to which the properties of these solvated gas-phase reactions transform to those of the corresponding reactions in solution or, indeed, whether they do so at all.[5]

Experimental Section

The experiments were carried out in a flowing plasma mass spectrometer (flowing afterglow) system. Details of the instrument together with methods of operation and data analysis have been reported earlier.[6] Formation of solvated anions was initiated about 10-ms upstream of the reaction zone at total pressures of ca. 0.4 torr in either a flowing helium or hydrogen buffer gas.

Formation of homoconjugate anions was achieved with the addition from about 1×10^{19} to 1×10^{20} molecules s^{-1} of the pure vapor of AH upstream of the electron gun. Under these conditions A^- anions are produced by electron impact on AH (at 70 eV and 1.5 mA) and solvation proceeds subsequently through termolecular reactions of the type in (4) where M is a stabilizing moiety. Solvated anions were produced in this

$$A^-\cdot(AH)_n + AH + M = A^-\cdot(AH)_{n+1} + M \quad (4)$$

fashion from the vapors of distilled water: $OH^-\cdot(H_2O)_n$ and $OD^-\cdot(D_2O)_n$, methanol:$CH_3O^-(CH_3OH)_n$, ethanol:$C_2H_5O^-\cdot(C_2H_5OH)_n$, acetone: $CH_3COCH_2^-\cdot(CH_3COCH_3)_n$, formic acid:$HCOO^-\cdot(HCOOH)_n$, and acetic acid:$CH_3COOH)_n$.

In the special case of $CH_3O^-\cdot(CH_3OH)_n$ solvation could also be achieved through binary reactions with methyl formate of the type in (5).

$$CH_3O^-\cdot(CH_3OH)_n + HCOOCH_3 \rightarrow CH_3O^-\cdot(CH_3OH)_{n+1} + CO \quad (5a)$$

$$\rightarrow HCO_2^-\cdot(CH_3OH)_n + CH_3OCH_3 \quad (5b)$$

Figure 2 shows the rise of the products for a sequence of such reactions with values of n from 0 to 2 with the addition of only methyl formate upstream and downstream of the electron gun. Generally about 1×10^{19} molecules s^{-1} of methyl formate were added upstream with the filament at 70 eV and 1.5 mA.

The initial relative population of solvated $A^-\cdot S_n$ could be varied by adjusting the amount of added vapor. A wide range in the initial relative populations was desirable for the determination of rate constants because of losses associated with the depletion of the source ion, $A^-\cdot S_{n-1}$. The magnitude of this depletion could be assessed in those studies in which the daughter ion did not react with the added neutral reagent. Similar considerations applied in our earlier studies of solvated proton transfer reactions.[7]

The reacting mixture was sampled through a small orifice on the tip of a nose cone situated at the end of the reaction region and mass analyzed with a quadrupole mass spectrometer. The observed variations of

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Table I. Rate Constants[a] Measured for Reactions of Solvated Anions, $A^-\cdot S_n$, with CH_3Cl at 296 ± 2 K

$A^-\cdot S_n$	$n =$ 0	1	2	3
$OD^-\cdot(D_2O)_n$	1.5 ± 0.3	0.6 ± 0.3	≤0.002	≤0.001
$CH_3O^-\cdot(CH_3OH)_n$	1.4 ± 0.3	0.030 ± 0.012	≤0.0002	≤0.0002
$C_2H_5O^-\cdot(C_2H_5OH)_n$	1.3 ± 0.3	≤0.001	≤0.001	
$CH_3COCH_2^-\cdot(CH_3COCH_3)_n$	0.0015 ± 0.0006	≤0.0006		
$HCO_2^-\cdot(HCOOH)_n$	≤0.0001	≤0.0001	≤0.0001	
$CH_3CO_2^-\cdot(CH_3COOH)_n$	≤0.0006	≤0.0006		

[a] Rate constants and their estimated accuracies given in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}.

Table II. Rate Constants[a] Measured for Reactions of Solvated Anions, $A^-\cdot S_n$, with CH_3Br at 296 ± 2 K

$A^-\cdot S_n$	$n =$ 0	1	2	3
$OH^-\cdot(H_2O)_n$[b]	1.0 ± 0.2	0.63 ± 0.25	0.002 ± 0.001	≤0.0002
$OD^-\cdot(D_2O)_n$	1.2 ± 0.3	0.8 ± 0.3	0.008 ± 0.004	≤0.0004
$CH_3O^-\cdot(CH_3OH)_n$	1.1 ± 0.2	0.54 ± 0.11	≤0.002	≤0.0001
$C_2H_5O^-\cdot(C_2H_5OH)_n$	1.1 ± 0.3	0.39 ± 0.10	≤0.0002	
$CH_3COCH_2^-\cdot(CH_3COCH_3)_n$	0.16 ± 0.07	≤0.001		
$HCO_2^-\cdot(HCOOH)_n$	0.013 ± 0.003	≤0.001	≤0.001	
$CH_3CO_2^-\cdot(CH_3COOH)_n$	0.029 ± 0.009	≤0.01		

[a] Rate constants and their estimated accuracies are given in units of 10^{-9} cm_3 $molecule^{-1}$ s^{-1}. [b] From ref 4.

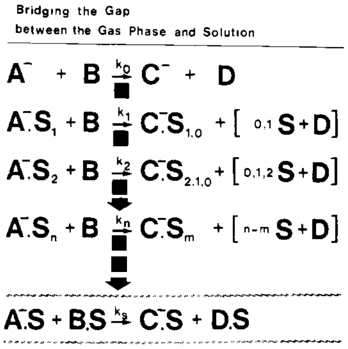

Figure 1. An illustration of the possible transition in the kinetics and product distributions of nucleophilic displacement reactions between the gas phase and solution. For the solvated reactions in the gas phase allowance has been made for the incomplete retention of solvent molecules by the product anion and for solvation of the product neutral. k represents the rate constant for reaction.

the reactant ion signals as a function of neutral reagent addition provided the raw data from which the rate constants were derived. The methyl chloride and methyl bromide used as reagents were of high purity (minimum 99.5 mol %).

Results

The results of the rate constant measurements which reveal the absolute degree to which stepwise solvation influences nucleophilicity are summarized in Tables I and II. The sources of uncertainty associated with the determination of rate constants have been described previously.[6] In deriving rate constants from the observed decays of solvated ions account was taken of the initial decay which can arise due to the depletion of the precursor ion in the reaction region. Product-ion distributions associated with specifically solvated nucleophiles could not be ascertained quantitatively due to complications which arise from the presence of some solvent vapor and various solvated reactant ions in the reaction region. Nevertheless, all product ions observed in the mass spectrum were monitored and their behavior did provide some useful qualitative insight. The following section describes the results of the measurements in more detail.

$OD^-\cdot(D_2O)_n$. We have reported previously in brief form our observations of the influence of hydration on the reactivity of the hydroxyl ion toward CH_3Br.[4] Here we report analogous measurements using heavy water which avoid the complication due to overlap in the mass spectrum of $Cl^-\cdot(H_2O)_n$ with $OH^-\cdot(H_2O)_{n+1}$. Also the measurements were extended to larger additions of CH_3Br as is shown in Figure 3. Clearly OD^- and $OD^-\cdot D_2O$ are reactive toward CH_3Br while the reactivity of $OD^-\cdot(D_2O)_2$ is much reduced and the reactivity of $OD^-\cdot(D_2O)_3$ immeasurably small. These results are in agreement with our earlier observations with $OH^-\cdot(H_2O)_n$.

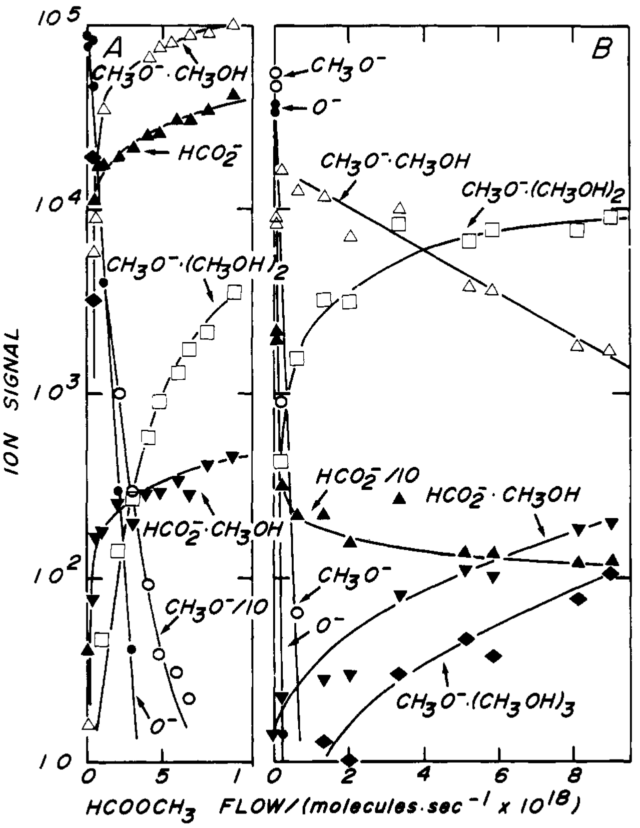

Figure 2. A split view of observations recorded for the addition of methyl formate into flowing helium gas (A) upstream of the electron gun as a 10% mixture in helium and (B) upstream of the electron gun as pure vapor at a fixed rate (about 1 × 10^{19} molecules s^{-1}) and downstream as a 10% mixture in helium. T = 294 K, P = 0.322 torr (A) and 0.327 torr (B), $\bar{v}$ = 7.7 × 10^3 cm s^{-1}, L = 46 cm (B), electron energy = 70 eV, and emission current = 1.4 mA. The distance from the electron gun to the nose cone is 75.9 cm.

Br^- was the dominant ion in the product spectrum, and small amounts of $Br^-\cdot D_2O$ were also produced. $Br^-\cdot(D_2O)_2$ was looked for at high sensitivity (low resolution) but there was no indication of its formation. Taken together, these observations indicate that the reactions of $OD^-\cdot D_2O$ and $OD^-\cdot(D_2O)_2$ primarily lead to unhydrated product ions. $OD^-\cdot D_2O$ appears to react to produce predominantly unhydrated Br^-. The hydrated ion $Br^-\cdot D_2O$ appears

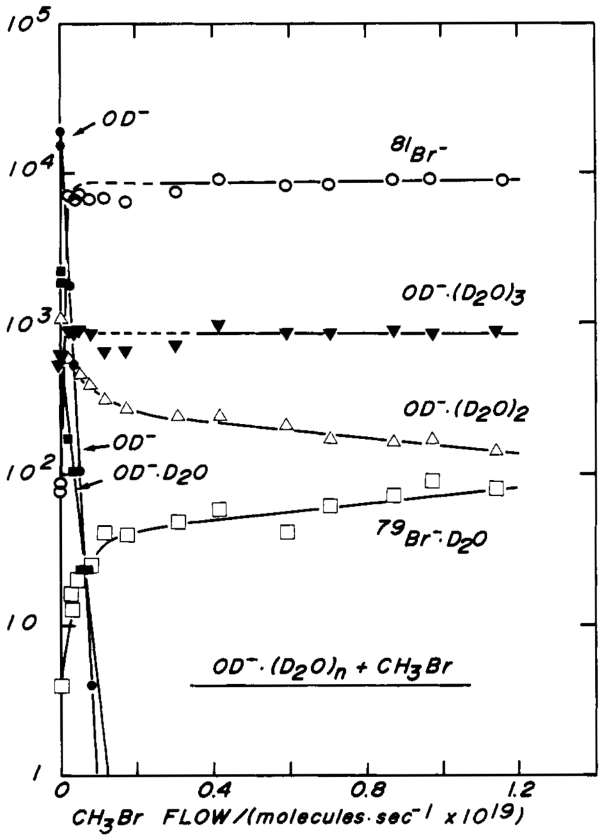

Figure 3. Variations in ion signals recorded with the addition of CH_3Br into a flowing He/D_2O plasma in which $OD^- \cdot (D_2O)_n$ ions with $n = 0$–3 are initially predominant. $T = 294$ K, $P = 0.332$ torr, $\bar{v} = 7.5 \times 10^3$ cm s^{-1}, and $L = 46$ cm.

to account for at most 10% of the total reaction. The upper limit arises due to the uncertainty associated with the possible production of $Br^- \cdot D_2O$ from the association reaction between Br^- and the source gas D_2O and from the reaction of $Br^- \cdot (D_2O)_2$ with CH_3Br, as well as the uncertainty arising from the initial depletion of $OD^- \cdot D_2O$ due to the depletion of the precursor ion OD^-. The slight rise in the $Br^- \cdot D_2O$ signal at large additions of CH_3Br suggests some production of this ion by the much slower reaction of $OD^- \cdot (D_2O)_2$ with CH_3Br. The initial decay in the $OD^- \cdot (D_2O)_2$ signal is due to the depletion of the precursor ion $OD^- \cdot D_2O$ in the reaction region.

Figure 4 shows results obtained from the "textbook" reaction of $OD^- \cdot (D_2O)_n$ with CH_3Cl. The changes in reactivity with hydration are similar to those observed with CH_3Br. In this case both the second and third hydrates exhibited no observable reactivity. The shape of the growth in the $Cl^- \cdot D_2O$ signal is consistent with its formation from $OD^- \cdot D_2O$. A sharper rise as that for Cl^- would have resulted if this ion were produced primarily by the association of Cl^- with D_2O source gas in the reaction region. Nevertheless, the observed production of $Cl^- \cdot D_2O$ does not appear to be sufficient to account for the total reaction of $OD^- \cdot D_2O$. Again some production by $OD^- \cdot D_2O$ of the unhydrated ion Cl^- seems to be indicated by the data although less than was the case for the production of Br^- from CH_3Br. There was no evidence in the product spectrum for the formation of $Cl^- \cdot CH_3OD$ that may be conceived for the reaction of $OD^- \cdot D_2O$ with CH_3Cl.

$OH^- \cdot (CO_2)_n(H_2O)_m$. Addition of CO_2 into a flowing plasma rich in hydrated hydroxide ions yields ions of the type $OH^- \cdot (CO_2)_n(H_2O)_m$ with $n = 1$ and $m = 0$ and 1. These ions are believed to correspond to unhydrated and singly hydrated bicarbonate ions, HCO_3^- and $HCO_3^- \cdot H_2O$, and are produced by termolecular addition and bimolecular ligand exchange reactions. Both of these ions were found to be unreactive toward CH_3Cl and CH_3Br with $k \leq 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

$RO^- \cdot (ROH)_n$. Both the unsolvated and singly solvated methoxide and ethoxide ions were observed to react with CH_3Br. Br^- was observed to be the major product in all cases. From the

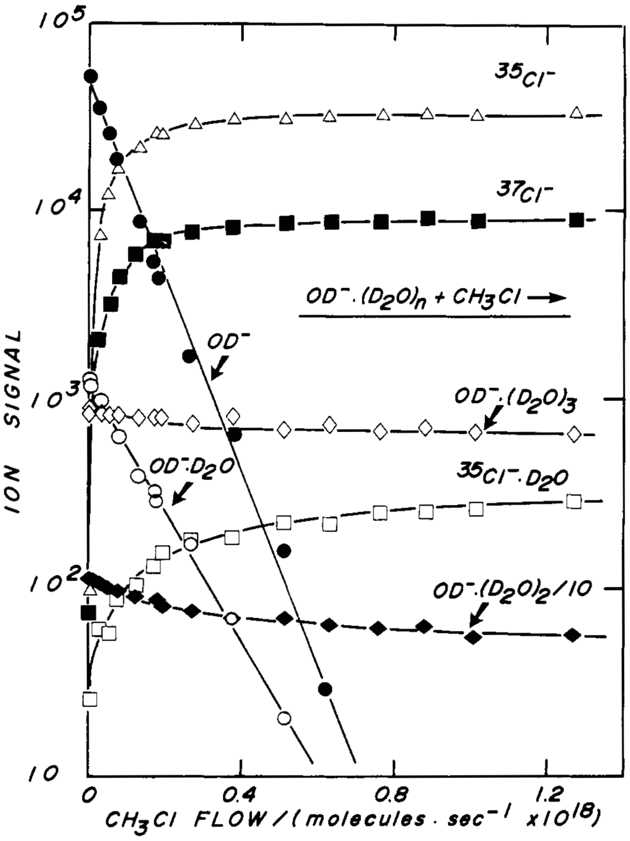

Figure 4. Variations in ion signals recorded with the addition of CH_3Cl into a flowing He/D_2O plasma in which $OD^- \cdot (D_2O)_n$ ions with $n = 0$–3 are initially predominant. $T = 297$ K, $P = 0.318$ torr, $\bar{v} = 7.7 \times 10^3$ cm s^{-1}, and $L = 46$ cm.

observed increases in the $Br^- \cdot ROH$ signals we estimate that less than 5% of the reactions of $CH_3O^- \cdot CH_3OH$ and $C_2H_5O^- \cdot C_2H_5OH$ lead to solvated Br^-. No measurable reactions were observed between $CH_3O^- \cdot (CH_3OH)_{2,3}$ or $C_2H_5O^- \cdot (C_2H_5OH)_2$ and CH_3Br.

With CH_3Cl the reactivity appeared to drop off with the addition of one less solvent molecule. $CH_3O^- \cdot CH_3OH$ reacts already about 50 times slower than the unsolvated methoxide ion while $C_2H_5O^- \cdot C_2H_5OH$ reacts at least 1000 times slower than $C_2H_5O^-$. The slow reaction of $CH_3O^- \cdot CH_3OH$ with CH_3Cl appeared to produce primarily $Cl^- \cdot CH_3OH$. Our earlier flowing afterglow study of the reactions of $CH_3O^- \cdot CH_3OH$ and $C_2H_5O^- \cdot C_2H_5OH$ with CH_3Cl had indicated reductions in the rate constant for the unsolvated ions by at least a factor of 3 in each case.[3]

$RCO_2^- \cdot (RCOOH)_n$. Formic and acetic acid were introduced in the flowing afterglow system to produce solvated ions of the type $RCO_2^- \cdot (RCOOH)_n$. These were found generally to be unreactive toward CH_3Br and CH_3Cl. Measurable reactions were observed only between CH_3Br and the unsolvated HCO_2^- and $CH_3CO_2^-$ ions. Our result for the latter reaction is in good agreement with the value of $(2.0 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} obtained very recently with a pulsed ion cyclotron resonance spectrometer equipped with a trapped ion cell.[8]

$CH_3COCH_2^- \cdot (CH_3COCH_3)_n$. The unsolvated $CH_3COCH_2^-$ was observed to react with CH_3Br quite rapidly and about 100 times faster than with CH_3Cl. The addition of one acetone molecule to $CH_3COCH_2^-$ led to an immediate drop in the rate to a level outside the detection limits of the technique.

Discussion

Nucleophilic displacement reactions between anions and methyl halides proceeding in the gas phase were first executed in the total absence of solvent.[3] Measurements of the rate constants of the unsolvated reactions established intrinsic reactivities and thus provided, for the first time, an absolute measure of the influence

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[8] (a) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 2672. (b) Pellerite, M. J.; Brauman, J. I. *ACS Symp. Ser.* **1982**, *81*, 198.

Table III. Support Data and Calculated Values for Methyl Cation Affinities of Anions, A^- (kcal mol^{-1})

A^-	EA(A)	ref	$D°$-(CH_3-A)[a]	ref	MCA-(A^-)[b]
OH^-	42.1 ± 0.05	*c*	91	*c*	276
$CH_3COCH_2^-$	41.3 ± 1.4	*d*	85	*c, h*	271
CH_3O^-	36.2 ± 0.5	*e*	77.5	*c, h*	268
$C_2H_5O^-$	39.8 ± 0.7	*f*	77.6	*c, h*	265
$CH_3CO_2^-$	78.2	*g*	88	*c, h, i*	237
HCO_2^-	81.4	*g*	86	*c, h, i*	232
Cl^-	83.4 ± 0.07	*c*	82.4	*c*	226
Br^-	77.6 ± 0.07	*c*	69.1	*c*	218

[a] $D°(CH_3\text{–}A)$ is calculated directly from the heats of formation of CH_3A, A, and CH_3. [b] $MCA(A^-) = D°(A\text{–}CH_3) - EA(A) + IP(CH_3)$, where $IP(CH_3) = 227$ kcal mol^{-1}, ref c. [c] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data Ser. Suppl. 1* **1977**, *6*, 106. [d] Zimmerman, A. H.; Reed, K. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 7203. [e] Engelking, P. C.; Ellison G. B.; Lineberger, W. C. *J. Chem. Phys.* **1978**, *69*, 1826. [f] Ellison, G. B.; Engelking, P. C.; Lineberger W. C. *J. Phys. Chem.* **1982**, *86*, 4873. [g] Yamdagni, R.; Kebarle, P., *J. Am. Chem. Soc.* **1973**, *95*, 4050. [h] Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1969**, *26*, 41. [i] Heat of formation of A derived with an assumed value for $D°(A\text{–}H) = 110$ kcal mol^{-1}.

of bulk solvent on kinetic nucleophilicity. Intrinsic reactivities of course also provide the benchmark for an assessment of the influence of solvation in the gas phase which was investigated in the present study and so need to be considered first.

Intrinsic Energetics and Kinetics. All of the reactions reported in Tables I and II are exothermic in the absence of solvent. The exothermicity of the solvent-free rections can be expressed simply in terms of the methyl cation affinities of the product and reactant anions for reaction 1 with $n = 0$ and is given by eq 6 where the

$$\Delta H°_{298} = MCA(B^-) - MCA(A^-) \qquad (6)$$

methyl cation affinity of say A^-, $MCA(A^-)$, is given by the standard enthalpy change for the loss of CH_3^+ by ACH_3 as expressed in eq 7.[8] Table III provides a listing of the methyl cation

$$MCA(A^-) = D°(A\text{–}CH_3) - EA(A) + IP(CH_3) \qquad (7)$$

affinities for the nucleophiles used in the present study. The nucleophile with the highest MCA is the strongest nucleophile in the thermodynamic sense. The methyl cation affinities in Table III indicate a range of exothermity for the reactions investigated here from 8 to 58 kcal mol^{-1}.

We have previously shown that a wide range of kinetic nucleophilicity (defined here in terms of the observed rate constant for nucleophilic substitution) is also associated with solvent-free S_N2 reactions in the gas phase.[2] The measured reaction rate constants were in the range from about 1×10^{-11} to 4×10^{-9} cm^3 $molecule^{-1}$, and several rate constants were less than 2×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. This represents a dynamic range in reaction probability of more than 10^3 with the fastest reactions proceeding at essentially unit efficiency.[2] The anions OH^- and CH_3O^- were found to exhibit a high kinetic nucleophilicity toward both CH_3Cl and CH_3Br. These results were reproduced in the present study, and several other nucleophiles were investigated. Of the new nucleophiles, $C_2H_5O^-$ falls into the former category while HCO_2^- and $CH_3CO_2^-$ fall into the latter. $CH_3COCH_2^-$ appears to behave in an intermediate fashion. It can also be noted that the latter three anions are consistently less reactive toward CH_3Cl than toward CH_3Br. Table III indicates that the reactions with CH_3Br are all 8 kcal mol^{-1} more exothermic.

We have reported earlier that the efficiency of solvent-free S_N2 reactions in the gas phase is generally observed to decrease with decreasing exothermicity, particularly within certain homologous series of exothermic reactions.[2] This empirical correlation appears to be maintained by the present results as shown, for example, by the higher reactivities of the anions toward CH_3Br than toward CH_3Cl. Variations in reaction efficiency have also been found to correlate with the degree of charge delocalization in the nucleophile.[2,9] Significantly reduced reactivities were observed in the present study for the delocalized anions HCO_2^-, $CH_3CO_2^-$, and $CH_3COCH_2^-$. The roles of both enthalpy change and charge delocalization in determining the reactivities of nucleophiles have been assessed in a number of recent theoretical treatments of gas-phase S_N2 reactions.[8-10] In particular, the Marcus rate-equilibrium formalism has been applied to the double-minimum potential energy surface for gas-phase S_N2 reactions.[8,10] With *this formalism the intrinsic nucleophilicity of an anion* A^- *toward* a methyl center can be defined by the height of the central barrier for its exchange reaction with CH_3A. Pellerite and Brauman[8] have shown that this barrier correlates with $MCA(A^-)$. Also there appears to be no significant difference in intrinsic nucleophilicity between the localized and the delocalized nucleophiles which they have considered including $CH_3CO_2^-$ and $CH_3COCH_2^-$. As a consequence it appears that the observed low reactivities of these latter two nucleophiles need to be rationalized within this formalism in the same manner as the reactivities of other anions, viz., in terms of a combination of the intrinsic barrier (the barrier the reaction would have it it were thermoneutral) which reflects the "kinetic" contribution and the exothermicity of the reaction which reflects the "thermodynamic" contribution to the reaction's energy barrier.[8] The exothermicity of the reaction acts to compensate for the height of the intrinsic barrier. For example, for the reaction of CH_3O^- with CH_3Cl, Pellerite and Brauman have suggested that a high intrinsic barrier is compensated by the high exothermicity of the reaction which lowers the reaction barrier to the point where the reaction proceeds rapidly.[8] For the nucleophilic displacement reactions reported here the higher reactivities observed at higher exothermicities and the trends with exothermicity observed within the series of reactions with CH_3Cl and CH_3Br also appear to be consistent with such an interpretation with only the reactions of $CH_3COCH_2^-$ with CH_3Cl and CH_3Br as apparent exceptions. But these latter two reactions can also be brought into line if methylation occurs (predominantly) at oxygen rather than carbon. To maintain the qualitative correlation with exothermicity the methyl cation affinity for the oxygen site would need to fall in the gap between $MCA(C_2H_5O^-)$ and $MCA(CH_3CO_2^-)$ which is not unreasonable.

Kinetics of Solvated S_N2 Reactions. It is clear from the results presented in Tables I and II that, for each of the 13 solvated nucleophilic displacement reactions investigated in this study, the rate constant in the gas phase becomes too small to measure ($k = 1 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) either with the addition of just one solvent molecule to the nucleophile or with the addition of two or three solvent molecules. Figure 5 shows graphically the results obtained for the reactions of $OD^-\cdot(D_2O)_n$, $CH_3O^-\cdot(CH_3OH)_n$, and $C_2H_5O^-\cdot(C_2H_5OH)_n$ with CH_3Cl and CH_3Br. In all cases solvation with three molecules of solvent or less leads to a decrease in the rate constant for reaction by at least three orders of magnitude. Also the results indicate trends in the rate of change of the rate constant with solvation which are sensitive to the nature of the neutral reactant. The drop in rate constant has an earlier onset for the reactions with CH_3Cl which are intrinsically less exothermic than the reactions with CH_3Br. Furthermore, of the reactions with CH_3Cl, those which are intrinsically less exothermic respond to solvation at lower levels of solvation. For example, the reaction of $C_2H_5O^-$ becomes immeasurably slow with the addition of just one molecule of C_2H_5OH while the reaction of OD^- which is intrinsically 11 kcal mol^{-1} more exothermic (see Table III) becomes immeasurably slow with the addition of two molecules of D_2O. Both of the reactions of $OH^-\cdot(H_2O)_n$ with CH_3Cl and CH_3Br have an energy barrier of more than 20 kcal mol^{-1} in aqueous solution.[11] The rate constants in aqueous solution at room temperature are 1.0×10^{-26} and 2.3×10^{-25} cm^3 $molecule^{-1}$ s^{-1}, respectively.[11] The ratio k_{CH_3Br}/k_{CH_3Cl} has a value of 23 in aqueous solution and may be approached by

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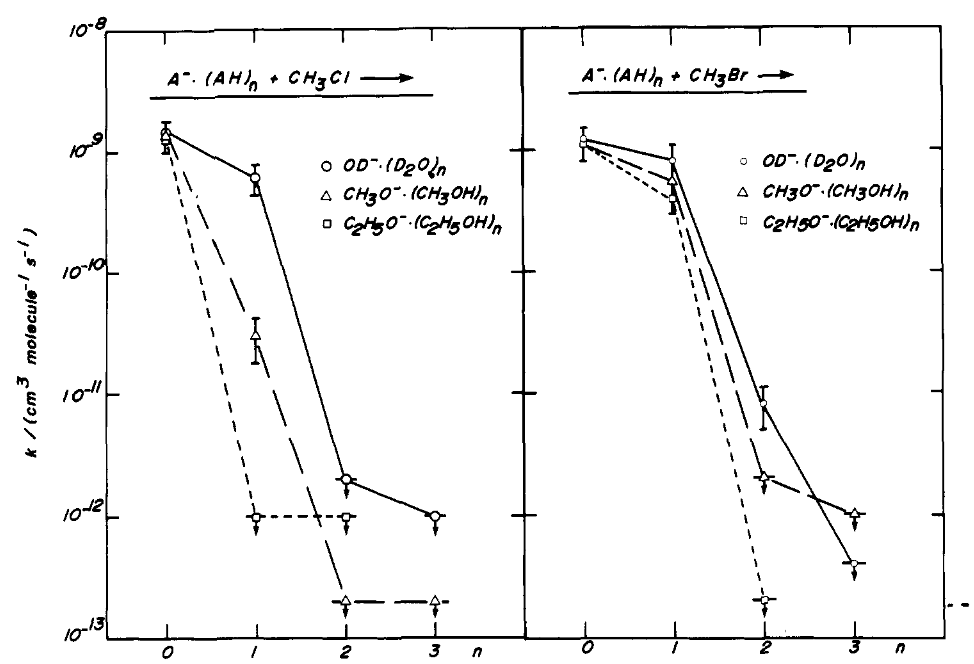

Figure 5. Observed variation in the rate constant with the extent of solvation for gas-phase nucleophilic displacement reactions of solvated homoconjugate anions with methyl chloride and methyl bromide at room temperature.

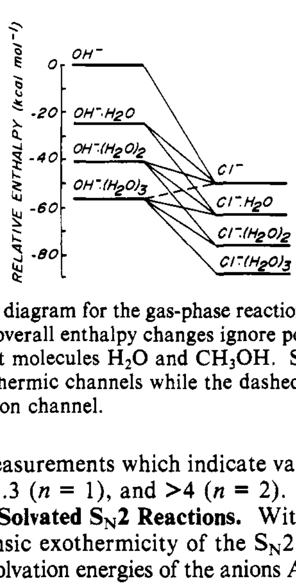

Figure 6. Enthalpy diagram for the gas-phase reactions of hydrated OH^- with CH_3Cl. The overall enthalpy changes ignore possible hydration of the neutral product molecules H_2O and CH_3OH. Solid diagonal lines correspond to exothermic channels while the dashed line represents an endothermic reaction channel.

the gas-phase measurements which indicate values for this ratio of 0.8 ($n = 0$), 1.3 ($n = 1$), and >4 ($n = 2$).

Energetics of Solvated S_N2 Reactions. With the addition of solvent the intrinsic exothermicity of the S_N2 reation (eq 1) is modified by the solvation energies of the anions A^- and B^- entering and leaving the reaction as well as the solvation energy associated with the possible solvation of the neutral product, D, and/or the "free" solvent, S. Unfortunately, available information on gas-phase solvation energies is not sufficient to allow a complete specification of the energetics of most of the solvated S_N2 reactions investigated in this study. Hydration energies of the anions OH^-, Cl^-, and Br^- for additions of up to three water molecules appear to be well established.[12,13] Also Cl^- affinities for single solvent molecules have recently become available for several of the solvents used in this study,[14,15] but beyond that little is known.

Figure 6 shows overall energetics for the reactions of hydrated OH^- with CH_3Cl. It emphasizes the multiplicity of product states which may arise with multiple solvation of the nucleophile in the gas phase. Product states must be considered which correspond to different degrees of solvation of the product anion. Possible solvation of the neutral products which in this case corresponds to hydration of CH_3OH would introduce additional states into the product manifold. These are not shown in Figure 6.

It is clear from Figure 6 that hydration acts to decrease overall exothermicity for the reaction of OH^- with CH_3Cl but also that this reaction retains exothermic channels for additions of up to three molecules of water. Many of these exothermic channels correspond to *incomplete* retention of water by the product anion. A similar situation also applies for the reaction of $OH^-\cdot(H_2O)_n$ with CH_3Br. Both of these series of hydrated reactions were shown in this study to exhibit a dramatic decrease in reactivity by a factor of more than 10^3 with the addition of three water molecules to the nucleophiles. These results establish, at least for these two series of reactions, that, to the extent the exothermic channels remain available to the reactants, the reaction kinetics are not controlled directly by the *overall* thermodynamics. Instead the drop in rate must be attributed to *intermediate* features in the appropriate potential energy surfaces.

Brauman and co-workers have discussed in detail the general applicability of double-minimum potential energy profiles to descriptions of the intermediate features of gas-phase nucleophilic displacement reactions.[8,9] With these discussions as a guide, we had sketched in our earlier communication a series of hypothetical potential energy profiles for the reactions of hydrated ions, $OH^-\cdot(H_2O)_n$, with CH_3Br for complete retention of water by the product Br^- ion.[4] The model profiles change with stepwise solvation, and the energy of the intermediate barrier increases with increasing solvation in response to the differential solvation of the reactants and the ionic transition state to values which can become greater than the energy of the reactants at very low levels of solvation. The energy barrier is associated with the isomerization of the intermediate complex which involves methyl cation transfer with inversion and the concomitant transfer of solvent molecules from the reactant nucleophile to the leaving group as indicated in eq 8 for the generalized reaction 1.

$$S_n\cdot A^-\cdot CH_3B \rightarrow ACH_3B^-\cdot S_n \qquad (8)$$

Morokuma has recently communicated a theoretical study which provides considerable insight into possible mechanisms of solvent transfer and the actual features of the intermediate potential energy profiles which are appropriate for the isomerization reaction 8.[16] In particular, Morokuma has pointed out that the transfer of solvent and methyl cation transfer need not proceed

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in a concerted fashion. His study of the isoergic reaction 9 indicates that the singly hydrated reaction may proceed only by

$$\mathrm{Cl^-{\cdot}(H_2O)_n + CH_3Cl \rightarrow ClCH_3 + Cl^-{\cdot}(H_2O)_n} \qquad (9)$$

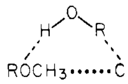
simultaneous migration of H_2O and CH_3 through a symmetric transition state but also *sequentially* by CH_3 transfer with subsequent migration of the H_2O molecule or vice versa. The doubly hydrated reaction involves two H_2O migrations and a CH_3 transfer which may take place one by one, two by one, or all three simultaneously. Each of these three paths results in a different shape of the intermediate potential energy profile. For the isoergic reaction 9 Morokuma has shown that the last of these options appears to be *least* favorable. In the most favorable path one molecule of H_2O is transferred first with little or no barrier. This is followed by CH_3 transfer and the transfer of a second water molecule.

Morokuma's calculations have not yet been extended to the unsymmetric exoergic reactions with CH_3Cl and CH_3Br of the type investigated here. However, Henchman et al. have recently applied Morokuma's insights to the unsymmetric reaction of $OH^-{\cdot}H_2O$ with CH_3Br to rationalize their own experimental observations.[5] These authors have argued on the basis of estimated energetics and entropic contributions that, for this particular reaction, sequential inversion and solvate transfer is the preferred route. The concerted process is likely to involve a greater "free energy" barrier resulting from the tight transition state required for solvate transfer and the sequential transfer, and inversion is inaccessible energetically at room temperature because of the higher energy of $OH^-{\cdot}CH_3Br{\cdot}H_2O$ compared to the energy of $OH^-{\cdot}H_2O + CH_3Br$. A similar situation is likely to apply for all of the singly solvated S_N2 reactions reported in Tables I and II. In each case the sequential solvate transfer and inversion route can be expected to be unfavorable if the stability of $A^-{\cdot}CH_3B{\cdot}S$ is less than that of $A^-{\cdot}S + CH_3B$. Also, the concerted route would remain less favorable on entropic grounds than the sequential inversion and solvate transfer represented in eq 10.

$$\mathrm{S{\cdot}A^-{\cdot}CH_3B \rightarrow S{\cdot}ACH_3{\cdot}B^- \rightarrow ACH_3{\cdot}B^-{\cdot}S} \qquad (10)$$

The product isomer $S{\cdot}ACH_3{\cdot}B^-$ formed in the inversion step in eq 10 can contain considerable excess energy. For the reaction of $OH^-{\cdot}H_2O$ with CH_3Br Henchman et al.[5] have argued that this excess energy is channeled directly into the desolvation of $H_2O{\cdot}HOCH_3{\cdot}Br^-$ leaving Br^- as the principal product ion with the additional consequence that the transfer of H_2O to form $HOCH_3{\cdot}Br^-{\cdot}H_2O$ and its subsequent desolvation to form $Br^-{\cdot}H_2O$ or Br^- are "pre-empted". The argument is based primarily on the product ion concentration ratio $Br^-{\cdot}H_2O/(Br^-{\cdot}H_2O + Br^-)$ which was observed to be nearly independent of relative translational energy between ≈0.03 and 1.0 eV. The divergence of this behavior from that observed by the same authors for the degree of retention of H_2O by CO_3^- in the exothermic reaction of $OH^-{\cdot}(H_2O)_2$ with CO_2 was taken as evidence for the notion that the observed Br^- does not result from the unimolecular decomposition of vibrationally excited $Br^-{\cdot}H_2O$ and, by inference, the excited $HOCH_3{\cdot}Br^-{\cdot}H_2O$ complex but rather from desolvation of the excited $H_2O{\cdot}HOCH_3{\cdot}Br^-$ complex formed initially in the inversion step. The tenacity of this argument and its general applicability remain to be tested. The beam data reported by Henchman et al. do allow for some drop (a factor of 2) in the $Br^-{\cdot}H_2O$ product ratio over the range in relative translational energy investigated. Also, $Br^-{\cdot}H_2O$ was in fact observed by these authors as a primary product ion although a plausible mechanism for its formation was not discussed by them. Nevertheless, it appears reasonable that solvent removal is preferred over solvent reorganization at the excess energy available to the complex formed in the inversion step when this energy is high but that solvent reorganization becomes competitive at lower excess energies.

Our observations which provide an upper limit of 10% retention of H_2O by Br^- in the reaction of $OH^-{\cdot}H_2O$ with CH_3Br are consistent with the yield of 5% $Br^-{\cdot}H_2O$ reported by Henchman et al.[5] CH_3OH was apparently not retained as a solvent molecule in either set of experiments. Retention of the solvent for the reactions of $CH_3O^-{\cdot}CH_3OH$ and $C_2H_5O^-{\cdot}C_2H_5OH$ with CH_3Br appeared in our experiments to be of the same order ($\lesssim 5\%$). These latter two reactions are intrinsically less exothermic by 8 and 11 kcal mol^{-1}, respectively, but also involve slightly lower solvent/nucleophile binding. Also it is interesting to note that our results are consistent with a much higher solvent retention for the reactions of $OD^-{\cdot}D_2O$ and $CH_3O^-{\cdot}CH_3OH$ with CH_3Cl which are 8 kcal mol^{-1} less exothermic than their CH_3Br counterparts. Figure 5 shows that the reactivity of the singly solvated ions toward CH_3Cl drops sharply as the intrinsic exothermicity decreases. The reaction of $C_2H_5O^-{\cdot}C_2H_5OH$ with CH_3Cl is still exothermic by 17 kcal mol^{-1} to produce unsolvated Cl^- but it is clear that an intermediate barrier has depressed the reactivity as the reaction was observed to be immeasurably slow. It is possible that the barrier associated with the solvate transfer in the sequential route (eq 10) has become rate determining in this case perhaps because of the weaker interaction of the asymmetric solvate molecule with the leaving group as shown for the following intermediate



Comparisons with Solution. Clearly reactions of solvated ions in the gas phase in which the solvent is transported into the intermediate complex by the nucleophile are not the exact duplicates of solvated ion reactions in solution and, of course, can never be so. It is equally clear that the connection with solution at levels of solvation involving one, two, or three solvate molecules may be extremely tenuous. At these levels of solvation in the gas phase the total energy of the system is shared intramolecularly within a reaction complex with relatively few degrees of freedom and not with a surrounding solvent medium. This can lead to reaction products in the gas phase dissimilar in degree of solvation to those associated with S_N2 reactions in solution. In the experiments reported here, the energy of the intermediate reaction complex may also be moderated by collisions with buffer gas molecules. Collisional cooling would presumably quench the unimolecular desolvation of the intermediate complex but no attempts have been made in this study to explore the influence of total pressure. The neutral products associated with the gas-phase reactions investigated in this study have also not been investigated, but it is clear that formation of dimers or polymers of solvent molecules may accompany the formation of the unsolvated or slightly solvated product ions and is in fact preferred on energetic grounds.

We believe that we have shown that measurements carried out in the gas phase, even at low levels of solvation and at relatively low pressures, can begin to provide new clues to solvate influence on chemical reactivity in nucleophilic displacement reactions. Higher levels of solvation at which solvated ions resemble more closely those found in solution can now also be generated in the gas phase. Morokuma has made the interesting observation that when the first solvation shell of the nucleophile is completed, the initial interaction between the reagents in the gas phase involves desolvation so that a new feature is expected to appear in the potential energy profile.[16] This feature may eventually transform to an energy profile in the gas phase not too dissimilar to that ascribed to S_N2 reactions in solution.[4] Unfortunately the experience reported here suggests that this transformation cannot be probed in the gas phase given the dynamic range in rate constant measurements available with current experimental techniques.

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Registry No. CH_3Cl, 74-87-3; CH_3Br, 74-83-9; H_2O, 7732-18-5; D_2O, 7789-20-0; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; CH_3COCH_3, 67-64-1; HCOOH, 64-18-6; CH_3COOH, 64-19-7; OD^-, 17393-79-7; CH_3O^-, 3315-60-4; $C_2H_5O^-$, 16331-64-9; $CH_3COCH_2^-$, 3122-07-4; HCO_2^-, 71-47-6; $CH_3CO_2^-$, 71-50-1; OH^-, 14280-30-9; Cl^-, 16887-00-6.