Gas-phase measurements of the influence of stepwise solvation on the kinetics of S_N2 reactions of solvated F^- with CH_3Cl and CH_3Br and of solvated Cl^- with CH_3Br

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Received February 14, 1985

DIETHARD K. BOHME and ASIT B. RAKSIT. Can. J. Chem. **63**, 3007 (1985).

Flowing afterglow measurements are reported which reveal the influence of stepwise solvation on the nucleophilicity of F^- and Cl^- in the gas phase at room temperature. The specific rates of nucleophilic displacement reactions with CH_3Cl and CH_3Br are followed for additions of up to three molecules of solvent for F^- solvated with D_2O, CH_3OH, and C_2H_5OH and for Cl^- solvated with CH_3OH, C_2H_5OH, CH_3COCH_3, HCOOH, and CH_3COOH. The observed precipitous response of the specific rate to solvation is attributed to intermediate features of plausible reaction energy profiles.

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Les mesures des lueurs d'écoulement en phase gazeuse à la température ambiante révèlent l'influence de la solvatation graduelle sur le caractère nucléophile des ions F^- et Cl^-. On a étudié les vitesses spécifiques des réactions de déplacement nucléophile avec le CH_3Cl et le CH_3Br dans des additions impliquant jusqu'à trois molécules de solvant pour l'ion F^- solvaté avec D_2O, CH_3OH et C_2H_5OH et pour l'ion Cl^- solvaté avec CH_3OH, C_2H_5OH, CH_3COCH_3, HCOOH et CH_3COOH. On attribue la réponse en forme de pic observée pour la vitesse de solvatation, à des caractéristiques intermédiaires des profils d'énergie d'une réaction plausible.

[Traduit par le journal]

Introduction

The role of solvent in S_N2 reactions is exposed at its most fundamental level in reactions of type [1] which can now be executed and studied in the gas phase as a function of stepwise solvation of the nucleophile A^- (1, 2).

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

In reactions of this type available solvent is limited to that associated directly with the reacting ion and, when the reaction proceeds in a dilute inert gas, the transport of solvent to the products must occur within the reaction complex rather than through the surrounding medium as is possible in solution. Gas-phase measurements of such reactions therefore allow the role of solvation in S_N2 displacement to be isolated and investigated at a molecular level of solvation hitherto inaccessible.

Recently we have reported measurements for reactions of type [1] between solvated *homoconjugate* anions, $A^-\cdot(AH)_n$, and the methyl halides CH_3Cl and CH_3Br with AH = H_2O, D_2O, CH_3OH, C_2H_5OH, HCOOH, CH_3COOH, and CH_3COCH_3 (1). Their specific rates were followed as a function of stepwise solvation for additions of up to three molecules of solvent and found to respond precipitously, in some instances already with the addition of just one molecule of solvent. The response appeared not to be controlled directly by the overall exothermicity of the solvated reaction but instead could be attributed to intermediate features in the appropriate potential energy profile. In this study we explore the solvent response of the specific rates of similar reactions involving solvated *heteroconjugate* anions, $A^-\cdot(BH)_n$ by subjecting CH_3Cl and CH_3Br to displacement by the halide ions F^- solvated with up to three molecules of D_2O, CH_3OH, and C_2H_5OH and Cl^- solvated with up to three molecules of CH_3OH, C_2H_5OH, HCOOH, CH_3COOH, and CH_3COCH_3.

Experimental

The measurements were taken with a flowing plasma mass spectrometer (flowing afterglow) system. Details of the instrument together with methods of operation and data analysis have been reported earlier (3, 4). 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. Heteroconjugate anions were derived from solvent addition reactions of type [2].

$$[2] \quad A^-\cdot S_n + S + M = A^-\cdot S_{n+1} + M$$

The parent gas of A^- was added upstream of the electron gun while the vapour of S was added just downstream in amounts of about 2×10^{18} to 2×10^{19} molecules s^{-1}. Experiments were performed with A^- = F^- derived from C_2F_6 (at about 1×10^{20} molecules s^{-1}), and Cl^- derived from CCl_4 (at about 4×10^{19} molecules s^{-1}) or CH_3Cl (at about 5×10^{20} molecules s^{-1}). The solvated ions which could be produced in this fashion were $F^-\cdot(D_2O)_n$, $F^-\cdot(CH_3COCH_3)_n$, $Cl^-\cdot(CH_3OH)_n$, $Cl^-\cdot(C_2H_5OH)_n$, $Cl^-\cdot(CH_3COCH_3)_n$, $Cl^-\cdot(HCOOH)_n$, and $Cl^-\cdot(CH_3COOH)_n$. The production of $F^-\cdot(CH_3OH)_n$ is illustrated in Fig. 1. F^- is a relatively strong base and was observed to react with CH_3COCH_3, HCOOH, and CH_3COOH primarily by proton transfer under the adopted experimental conditions. The initial relative populations of $A^-\cdot S_n$ could be varied by adjusting the amount of added vapour. As discussed previously (1, 5, 6), a wide range in the initial relative populations is desirable for the determination of rate constants because of losses associated with the depletion of the source ion, $A^-\cdot S_{n-1}$. 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 step-wise solvation influences nucleophilicity are summarized in Table 1 *a* and *b*. The sources of uncertainty associated with the determination of rate constants have been described previously (3, 4). 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. The following section describes the results of the measurements in more detail.

$F^-\cdot(BH)_n$

F^- ions were readily solvated with up to three molecules of water and methanol and two molecules of ethanol. Figure 2 shows results of measurements taken with the addition of CH_3Cl into a $He/C_2F_6/D_2O$ plasma in which hydrated fluoride

TABLE 1

(*a*) Rate constants[a] measured for reactions of solvated fluoride ions, $F^- \cdot S_n$, with CH_3Cl at 296 ± 2 K

$F^- \cdot S_n$	Rate constant for n = 0	1	2	3
$F^- \cdot (D_2O)_n$	1.9 ± 0.4	0.015 ± 0.005	≤ 0.0003	≤ 0.003
$F^- \cdot (CH_3OH)_n$	1.9 ± 0.4	≤ 0.0006	≤ 0.0003	≤ 0.0003
$F^- \cdot (C_2H_5OH)_n$	1.9 ± 0.4	≤ 0.0003	≤ 0.0003	

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

(*b*) Rate constants[a] measured for reactions of solvated anions, $A^- \cdot S_n$, with CH_3Br at 296 ± 2 K

$A^- \cdot S_n$	Rate constant for n = 0	1	2	3
$F^- \cdot (D_2O)_n$	1.2 ± 0.2	0.16 ± 0.04	≤ 0.0005	
$F^- \cdot (CH_3OH)_n$	1.2 ± 0.2	0.12 ± 0.03	≤ 0.0002	≤ 0.0002
$F^- \cdot (C_2H_5OH)_n$	1.2 ± 0.2	0.085 ± 0.020	≤ 0.0002	
$Cl^- \cdot (CH_3OH)_n$	0.017 ± 0.004	≤ 0.0004	≤ 0.0004	≤ 0.0004
$Cl^- \cdot (C_2H_5OH)_n$	0.017 ± 0.004	≤ 0.0004	≤ 0.0004	
$Cl^- \cdot (CH_3COCH_3)_n$	0.017 ± 0.004	≤ 0.0008	≤ 0.0004	
$Cl^- \cdot (HCOOH)_n$	0.017 ± 0.004	≤ 0.0002	≤ 0.0002	
$Cl^- \cdot (CH_3COOH)_n$	0.017 ± 0.004	≤ 0.0002		

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

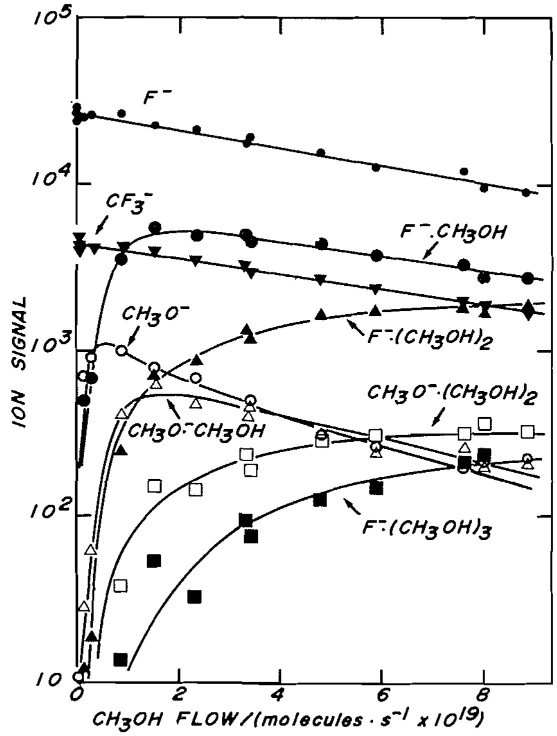

FIG. 1. The variation in dominant negative ions observed upon the addition of methanol as a 10% mixture in helium to a He/C_2F_6 plasma in which F^- and CF_3^- initially predominate. O^- and OH^- which are also present initially are not shown. T = 297 K, P = 0.320 Torr, $\bar{v}$ = 7.7 × 10^3 cm s^{-1}, L = 46 cm, flow of C_2F_6 = 2.4 × 10^{19} molecules s^{-1}.

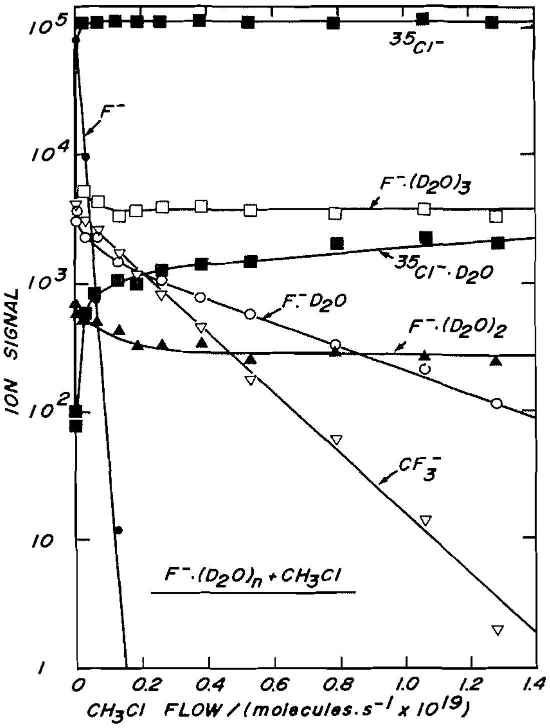

FIG. 2. Variations in ion signals recorded with the addition of CH_3Cl into a flowing $He/C_2F_6/D_2O$ plasma in which $F^- \cdot (D_2O)_n$ ions with n = 0 to 3 are initially predominant. T = 295 K, P = 0.347 Torr, $\bar{v}$ = 7.2 × 10^3 cm s^{-1}, and L = 46 cm.

ions have been established as dominant ions. Hydration is seen to reduce the reactivity of F^- already by a factor of about 100 with the addition of just one D_2O molecule. Further addition of D_2O molecules leads to immeasurably slow reactions. The slow reaction of $F^- \cdot D_2O$ with CH_3Cl appears to produce predominantly hydrated Cl^- product ions. With methanol and ethanol solvent the transition in reactivity was observed to be even more precipitous as solvation with just one solvent molecule resulted in immeasurably slow reactions.

More gradual transitions were observed with CH_3Br. The

TABLE 2. Support data and calculated values for methyl cation affinities of anions, A^-, in kcal mol^{-1}

A^-	EA(A)	Reference	$D^0(CH_3—A)^a$	Reference	$MCA(A^-)^b$
CF_3^-	42 ± 1.5	23	100	23, 24	285
F^-	78.4 ± 0.05	23	108.8	23	257
Cl^-	83.4 ± 0.07	23	82.4	23	226
Br^-	77.6 ± 0.07	23	69.1	23	218

[a] $D(CH_3—A)$ is calculated directly from the heats of formation of CH_3A, A, and CH_3.

[b] $MCA(A^-) = D(A—CH_3) - EA(A) + IP(CH_3)$ where $IP(CH_3) = 227$ kcal mol^{-1}, ref. 23.

singly solvated F^- ions were observed to react for all three solvents at a rate about 10 times less than that of the unsolvated F^- ion. There was evidence for substantial solvent retention only for the reaction of $F^- \cdot D_2O$. Figure 3 shows less than 10% solvent retention with $F^- \cdot CH_3OH$ which is similar to that observed with $F^- \cdot C_2H_5OH$. Further addition of solvent molecules resulted in a further drop in reactivity to levels which were not measurable. The reactivity of $F^- \cdot (D_2O)_3$ towards CH_3Br could not be explored because of overlap with $^{79}Br^-$ in the mass spectrum.

CF_3^-

With C_2F_6 as source gas significant amounts of CF_3^- were present initially in the flowing helium plasma. The CF_3^- was observed to react with both CH_3Cl (see Fig. 2) and CH_3Br (see Fig. 3) with rate constants of $(7 \pm 2) \times 10^{-11}$ and $(3 \pm 2) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. The reactions are believed to proceed by nucleophilic displacement and thus contribute to the appearance of Cl^- and Br^-, respectively, whose production is dominated by the reactions with F^- present under the same operating conditions.

$Cl^- \cdot (BH)_n$

Cl^- ions were readily solvated with up to three molecules of methanol, two molecules of ethanol, acetone and formic acid, and one molecule of acetic acid. Previous measurements in our laboratory had revealed only a very slow displacement reaction between unsolvated Cl^- and CH_3Br, $k = (2.1 \pm 0.4) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (7). This result was reproduced in the present study as k was measured to be $(1.7 \pm 0.4) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} and it was also observed that solvation with just one molecule reduced the rate of reaction by more than a factor of 20 for each of the five solvents to values corresponding to the lower limit accessible with the technique.

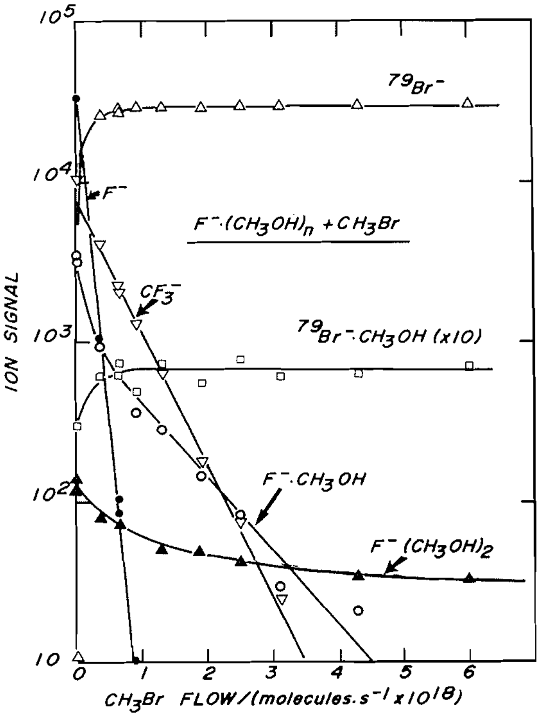

FIG. 3. Variations in ion signals recorded with the addition of CH_3Br into a flowing $He/C_2F_6/CH_3OH$ plasma in which $F^- \cdot (CH_3OH)_n$ ions with $n = 0$ to 2 are initially predominant. $T = 295$ K, $P = 0.306$ Torr, $\bar{v} = 7.7 \times 10^3$ cm s^{-1}, and $L = 46$ cm.

Discussion

Intrinsic energetics and kinetics

The reactions of F^- and CF_3^- with CH_3Cl and CH_3Br and the reaction of Cl^- with CH_3Br are all exothermic in the absence of solvent. The methyl cation affinities in Table 2 indicate a range in exothermicity for the S_N2 reactions investigated in this study from 8 to 67 kcal mol^{-1}. The reactions with CH_3Br are 8 kcal mol^{-1} more exothermic than those with CH_3Cl.

We have previously reported rate constants of (1.8 ± 0.4) and $(1.9 \pm 0.4) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} for the reaction of F^- with CH_3Cl (7, 8), $(1.2 \pm 0.2) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} for F^- with CH_3Br (7), and $(2.1 \pm 0.4) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for Cl^- with CH_3Br (7). These earlier flowing afterglow results agree with those obtained in the present study within experimental error. Pulsed ICR measurements have led to the lower values of (8.0 ± 0.9) and $(5.8 \pm 0.3) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} for F^- reacting with CH_3Cl (9, 10), $(6.0 \pm 0.6) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} for F^- reacting with CH_3Br (9), and 1.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for Cl^- reacting with CH_3Br (11) for which a value of $(8.0 \pm 1.0) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} had been reported earlier (9). The difference between the flowing afterglow and ICR results appears systematically to be about a factor of 2. Caldwell *et al.* have noted a similar difference for the reaction of Cl^- with CH_3Br for which they obtained a rate constant of 2.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at ca. 5 Torr (12) with a pulsed electron beam high pressure mass spectrometer. They have proposed that this difference can be expected as a result of the different pressures used in the different measurements. The expectation is based on a plausible "double-minimum" potential energy profile for reactions of this type. It is argued that when the energy of the central barrier in this profile lies below the initial energy of the system, as is the perception for the three reactions being considered here, collisional cooling of the excited adduct $A^- \cdot CH_3B$ will lead to an enhancement of formation of product as compared to decomposition back to reactants and so lead to an increase in the overall rate constant as the pressure is raised. Caldwell *et al.* also have provided crude model calculations which support the magnitude of the apparent pressure effect (12) but direct experimental verification has not yet been achieved so that systematic errors can not yet be ruled out to account for the disparity in

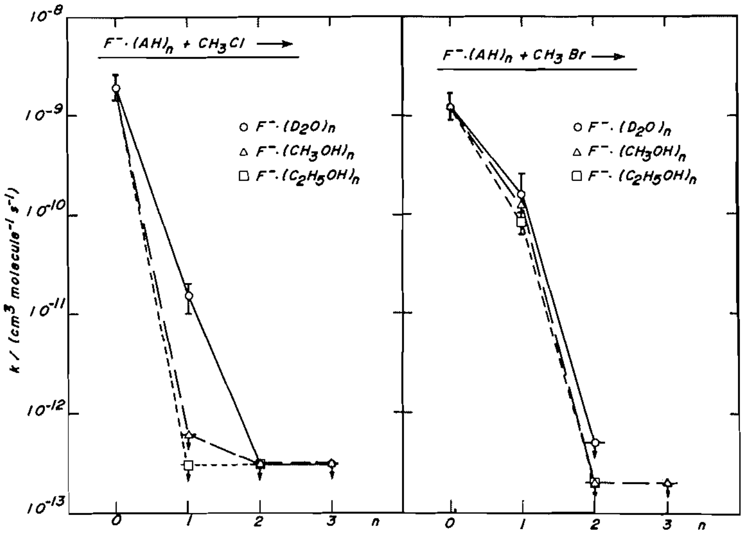

FIG. 4. Observed variations in the rate constant with the extent of solvation for gas-phase nucleophilic displacement reactions of solvated fluoride anions with methyl chloride and methyl bromide at room temperature.

results observed with the three techniques.

We have previously shown by experiment that the kinetic nucleophilicity of solvent-free S_N2 reactions in the gas phase, when expressed as a reaction probability per collision, has a dynamic range of more than 10^3. F^- exhibits nearly unit reactivity towards CH_3Cl and CH_3Br and so is among the most reactive nucleophiles in the gas phase. In comparison, the Cl^- reactivity towards CH_3Br is about 50 times smaller and puts Cl^- among anions of low nucleophilicity (7). The rate constants of $(7 \pm 2) \times 10^{-11}$ and $(3 \pm 2) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} for the reactions of CF_3^- with CH_3Cl and CH_3Br, respectively, correspond to reactivities of 0.03 and 0.2 so that this anion falls into the medium nucleophilicity range (7).

Kinetics of solvated S_N2 reactions

The results in Table 1 *a* and *b* indicate that the rate constants for the solvated reactions investigated become too small to measure with the addition of just two solvent molecules to the nucleophile or even, in some cases, just one. For the reactions of $F^- \cdot S_n$ this corresponds to a drop in the specific reaction rate in the gas phase of almost four orders of magnitude as is illustrated graphically in Fig. 4. In aqueous solution the specific rates of these S_N2 reactions are lower by another 15 to 16 orders of magnitude! The measured rate constants at 298 K for F^- reacting with CH_3Cl and CH_3Br in aqueous solution are 2.5×10^{-29} and 5.6×10^{-28} cm^3 $molecule^{-1}$ s^{-1}, respectively (13). Also Fig. 4 shows that the rate of change of the rate constant with solvation is sensitive to the nature of both the methyl halide and the solvent. The reactions with CH_3Br show a remarkably similar decrease in specific rate with solvation for the three solvents D_2O, CH_3OH, and C_2H_5OH, but with CH_3Cl the drop in specific rate appears earlier with less solvation and is more distinct for the three solvents. A similar behaviour was evident for several of the S_N2 reactions of solvated homoconjugate anions with CH_3Cl and CH_3Br reported earlier (1). The reaction of Cl^- with CH_3Br is intrinsically about 100 times less efficient than the corresponding F^- reaction but nevertheless addition of one solvent molecule to Cl^- was observed to decrease the specific reaction rate by another factor of more than 20 for methanol, ethanol, acetone, formic acid, and acetic acid. Since the rate constant became immeasurably small for all five of these solvents with the addition of one solvent molecule, no information was available in this case on the relative sensitivity of the rate constant to the nature of the solvent. For solutions of water, methanol, and acetone, rate constants of 8.2×10^{-27}, 1.1×10^{-26}, and 5.3×10^{-21} cm^3 $molecule^{-1}$ s^{-1}, respectively, have been reported for the S_N2 reaction of Cl^- at 298 K (13–15).

Overall energetics of solvated S_N2 reactions

The addition of solvent modifies the intrinsic exothermicity of the S_N2 reaction [1] by the solvation energies of the anions A^- and B^- entering and leaving the reaction and the neutral product D and "free" solvent S if these become solvated. A complete specification of the energetics of the solvated S_N2 reactions investigated in this study is not possible with the available data for solvation energies. Binding energies are available for additions of up to three molecules of water to F^-, Cl^-, and Br^- (16, 17). Also F^- and Cl^- affinities for single solvent molecules are available for some of the other solvents used in this study (18, 19). The available hydration energies for F^-, Cl^-, and Br^- allow the construction of the enthalpy diagrams in Fig. 5. These diagrams clearly show that hydration acts to decrease the overall exothermicities of the reactions of F^- with CH_3Cl and CH_3Br but that exothermic reaction channels remain available for additions of at least up to three water molecules, albeit, to preserve exothermicity, an increasing amount of retention of water by the product ion anion is required with increasing levels of hydration of the nucleophile. The observed kinetics for these two series of reactions therefore appear not to be controlled directly by the overall energetics, but must be attributed instead to intermediate features in the appropriate energy profiles.

Intermediate energy profiles

The intermediate features of the potential energy profiles of solvated S_N2 reactions are reasonably addressed in terms of double minima which evolve with step-wise solvation as the energy of the intermediate barrier increases relative to the initial energy of the reactants (11, 20). Morokuma has shown that several profiles are plausible at each level of solvation for the barrier itself depending on the mechanism of solvent transfer (21). For the singly solvated reactions the sequential solvate transfer and inversion mechanism indicated by reaction [3] will

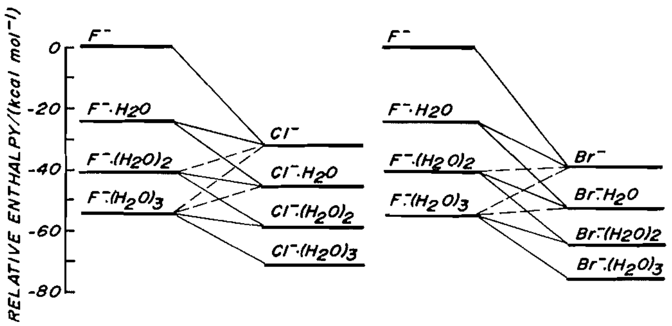

FIG. 5. Enthalpy diagrams for the gas-phase reactions of hydrated F^- with CH_3Cl and CH_3Br. The overall enthalpy changes ignore possible hydration of the neutral product CH_3F molecules. Solid diagonal lines correspond to exothermic channels while the dashed lines represent endothermic reaction channels.

be energetically unfavourable if the stability of $A^-\cdot CH_3B\cdot S$ is less than that of $A^-\cdot S + CH_3B$.

$$[3]\quad S\cdot A^-\cdot CH_3B \rightarrow A^-\cdot CH_3B\cdot S \rightarrow ACH_3\cdot B^-\cdot S$$

Because of the substantial magnitude of fluoride and chloride solvent affinities (18, 19) this is expected to be the case for all of the singly solvated reactions in Table 1. These should therefore prefer to proceed by sequential inversion and solvate transfer as illustrated in reaction [4].

$$[4]\quad S\cdot A^-\cdot CH_3B \rightarrow S\cdot ACH_3\cdot B^- \rightarrow ACH_3\cdot B^-\cdot S$$

Concerted solvate transfer and inversion is expected to be less favourable on entropic grounds (22). The excess energy in the product isomer $S\cdot ACH_3\cdot B^-$ formed in the inversion step in reaction [4] may be channeled directly into desolvation leaving unsolvated B^- as the principal product ion and so preempt the solvent transfer. Our observations are consistent with such a model. For the weakly exothermic reactions of $Cl^-\cdot S$ with CH_3Br the excess energy is insufficient to leave unsolvated Br^-. These reactions are therefore constrained to transfer solvent to the product anion but none do so with any measurably efficiency. The somewhat more exothermic reaction of $F^-\cdot D_2O$ with CH_3Cl appeared to produce $Cl^-\cdot D_2O$ exclusively but with low efficiency, while the most exothermic reactions of $F^-\cdot S$ with CH_3Br appeared to produce unsolvated Br^- preferentially.

Calculations (10, 12) suggest that the intermediate barriers for the solvent-free reactions of F^- with CH_3Cl and Cl^- with CH_3Br lie only about 1 or 2 kcal mol^{-1} below the corresponding energy of the reactants at room temperature. Consequently the intermediate barrier might be expected to emerge above the energy of the reactants already at very low levels of solvation. The results of the gas-phase measurements reported here suggest that this may indeed be the case already for the addition of one or two solvent molecules. Measurements in aqueous solution indicate that the energies of the intermediate barriers for these two reactions lie about 25 kcal mol^{-1} above the energies of the reactants (13). The observations in Fig. 4 for the reactions of $F^-\cdot S$ with CH_3Cl imply a relative enhancement of the energy of the intermediate barrier due to differential solvation by one solvent molecule which is less for D_2O than for CH_3OH and C_2H_5OH. The observations for the slightly more exothermic reactions of $F^-\cdot S$ with CH_3Br are consistent with an order of relative enhancement of $D_2O < CH_3OH < C_2H_5OH$ but the actual energies of the intermediate barriers still appear to lie below or close to the initial reactant energies since all three solvated reactions proceed with measurable efficiencies. This appears no longer to be the case at higher levels of solvation.

Acknowledgement

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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