Solvation of Negative Ions by Protic and Aprotic Solvents. Gas-Phase Solvation of Halide Ions by Acetonitrile and Water Molecules

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Abstract: The temperature dependence of the equilibria $(n,n-1)$, $X^-(CH_3CN)_n = X^-(CH_3CN)_{n-1} + CH_3CN$, was studied for $n = 1$–4 or 5 in a high-pressure mass spectrometer. van't Hoff plots of the equilibrium constants $K_{n,n-1}$ led to the determination of $\Delta H_{n,n-1}$ and $\Delta S°_{n,n-1}$. These data are compared with the corresponding thermochemical quantities for X^- and water determined earlier. It is found that the acetonitrile $\Delta H_{n,n-1}$ values decrease as the size of the ion is increased (*i.e.*, from F^- to I^-). Solvation by acetonitrile becomes more favorable relative to water as the size of the ion is increased. The change of $\Delta H_{n,n-1}$ with n for acetonitrile shows that this solvent leads to very weak interactions at higher n. Thus for Cl^- the $\Delta H_{1,0}$ values for water and acetonitrile are almost the same, but the $\Delta H_{4,3}$ for acetonitrile is much smaller. Some peculiar solvation shell structure is indicated by the $\Delta H_{n,n-1}$ and $\Delta S°_{n,n-1}$ values for acetonitrile. Comparison of the acetonitrile $\Delta H_{1,0}$ values for Cl^- and K^+ (potassium) shows that the positive ion interaction with acetonitrile is much stronger. Most of the above observations can be rationalized by consideration of the size of acetonitrile and the charge location of the dipole: $CH_3C^+{\equiv}N^-$.

Significant differences between the solvent effects of protic solvents (HOH, CH_3OH, etc.) and dipolar aprotic solvents like dimethylformamide, dimethyl sulfoxide, acetonitrile, and others have been observed in heterolytic organic reactions. Parker[1,2] has prepared summaries of such observations. Many of the effects can be explained by the assumption that aprotic solvents, in spite of their high dipole moment, solvate negative ions relatively poorly. The energetics of negative and positive ion solvation by aprotic solvents have been examined also by various classical methods. Choux and Benoit[3] have determined enthalpies of transfer of salts from aqueous solution to aprotic solvents, while Coetzee and Campion[4] have studied relative activities of reference cations and anions in acetonitrile and water.

The studies of the energetics and activity coefficients of solvated ions suffer from the difficulty of separating the effects on positive and negative ions. Thus a separation of the enthalpies of transfer to contributions of positive and negative ions can be made only by some extrathermodynamic assumption.[3]

Considering the interest on protic and aprotic solvent systems, we thought that the application of the gas-phase ion equilibria method might prove useful. For this purpose a program was initiated which aimed at the study of the gas-phase solvation of the halide negative ions and the alkali positive ions by acetonitrile. The study of the negative ions is complete and subject to the present publication. The alkali ion study is not complete, but some results are available which allow a comparison between positive and negative ions to be made. The data on solvation of the halide[5] and alkali[6] ions by water used in the present publication were obtained earlier.

The gas-phase method of ion equilibria studies has been described earlier,[5,7,8] so that only a brief outline need be given here.

The ions, say Cl^-, are created in the gas phase by ionizing radiation in the presence of the solvent vapor, which is at pressures in the Torr range. Rapid clustering reactions occur under these conditions which lead to equilibrium. The scheme involving acetonitrile is shown below.

(0,1) $Cl^- + CH_3CN = Cl^-{\cdot}CH_3CN$

(1,2) $Cl^-{\cdot}CH_3CN + CH_3CN = Cl^-(CH_3CN)_2$

$(n-1,n)$ $Cl^-(CH_3CN)_{n-1} + CH_3CN = Cl^-(CH_3CN)_n$

A particular equilibrium $(n-1,n)$ can be observed by proper choice of reaction temperature, the (0,1) equilibrium occurring at the highest temperature. van't Hoff plots of the equilibrium constants $K_{n-1,n}$ lead to the evaluation of the corresponding $\Delta H_{n-1,n}$ and $\Delta S°_{n-1,n}$. The equilibrium constants are defined by

$$K_{n-1,n} = P_n/P_{n-1}P_A \qquad (1)$$

where P_A is the pressure of the acetonitrile vapor and P_n and P_{n-1} are the pressures of the ions $Cl^-(CH_3CN)_n$ and $Cl^-(CH_3CN)_{n-1}$. The ratio of the ionic partial pressures is determined by a mass spectrometric technique described in the Experimental Section.

Comparison of the $\Delta H_{n-1,n}$ values for acetonitrile with the corresponding values for water can reveal specific differences regarding initial interactions and changes with increased number of solvent molecules. Furthermore, comparative measurements with the solvents can also be executed on positive ions and thus reveal difference of solvation of positive and negative ions.

Experimental Section

The experiments were done with a "high-pressure" pulsed electron beam mass spectrometer with multiscaler time-resolved ion

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(1) A. J. Parker, *Quart. Rev., Chem. Soc.*, **16**, 163 (1962).

(2) A. J. Parker and R. Alexander, *J. Amer. Chem. Soc.*, **90**, 3313 (1968).

(3) G. Choux and R. L. Benoit, *ibid.*, **91**, 6221 (1969).

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(8) J. D. Payzant, R. Yamdagni, and P. Kebarle, *Can. J. Chem.*, **49**, 3308 (1971).

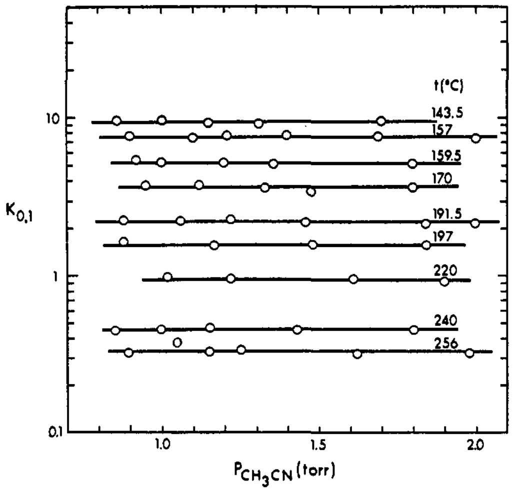

Figure 1. Equilibrium constant $K_{0,1}$ for reaction $Cl^- + CH_3CN = Cl^- \cdot CH_3CN$ (0,1). Constants are seen to be invariant with pressure. The values of $K_{0,1}$ are in $Torr^{-1}$.

detection, which has been described in previous publications.[5,8] Acetonitrile at pressures from 0.8 to 2 Torr was added to a slowly flowing O_2 carrier gas at 5 Torr (flow rate −15 cm^3/min at STP). Approximately 0.1 Torr of a compound RX containing the desired halogen atom was also added to the gas stream. The stream was passed through the ion source, where it was irradiated with a 2000-V electron beam. Primary ionization leads predominantly to positive ions and electrons (approximately 50 pairs per primary electron). The secondary electrons are rapidly degraded to subexcitation levels. The negative ions X^- are produced by dissociative electron capture of these electrons as indicated by eq 2. The compounds

$$e + RX = R + X^- \quad (2)$$

RX used for the production of F^-, Cl^-, Br^- and I^- were NF_3, CCl_4, CH_2Br_2, and CH_3I, respectively. The oxygen is added in order to increase the gas pressure. High pressure is required to speed up the thermalization of the electrons, slow down diffusion to the wall, and provide third bodies for the clustering reactions. The clustering reactions require third-body deactivation in the forward and second-body activation in the reverse direction. The ions engage in the clustering reactions ($n - 1,n$) (see introduction) as they diffuse toward the walls of the ion source. One of the walls is provided with a very narrow ion exit slit (~8 μ × 2 mm) through which some of the ions escape into an evacuated chamber containing the mass analysis and ion detection apparatus. There the ion intensities of the ions are measured and their ratios assumed proportional to the ratio of the concentrations in the ion source.

The time required for the establishment of clustering equilibrium is estimated at some 100 μsec.[8] The average residence time of the ions in the ion source is a few milliseconds. In some of the runs, the electron beam was pulsed[8] and the time dependence of the different ion species detected with the multiscaler. The intensity ratio of the cluster ions n and $n - 1$ was found to be constant with time for $t > 100$ μsec. A time-independent ratio indicates achievement of equilibrium.

The ion source temperature was measured by thermocouples inserted in the massive ion source block. The total ion source pressure was determined by a directly connected capacitance manometer. The partial pressure of the acetonitrile was determined by weight loss measurement of the acetonitrile storage bulb, assuming that the flow velocity of acetonitrile through the ion source was the same as that of O_2.

Results and Discussion

The $\Delta H_{n,n-1}$, $\Delta S°_{n,n-1}$, and $\Delta G°_{n,n-1}$ determined from the temperature dependence of the equilibrium constants $K_{n-1,n}$ for the reactions ($n - 1,n$), $X^-(CH_3CN)_{n-1} + CH_3CN = X^-(CH_3CN)_n$, are shown in Table I. Given in Figure 1 are some representative data for $K_{0,1}$ involving the association of acetonitrile with Cl^-. The plot shows that the equilibrium constants remain invariant with pressure within the experimental range. Given in Figure 2 are the van't Hoff plots for the reactions ($n - 1,n$) involving Cl^-. van't Hoff plots of similar appearance were obtained for the other negative ions. In Figure 3 the $\Delta H_{n,n-1}$ values are plotted as a function of n. For comparison, the enthalpies for the reactions $X^-(H_2O)_n = X^-(H_2O)_{n-1} + H_2O$ determined in earlier work[5] are also included in Figure 3.

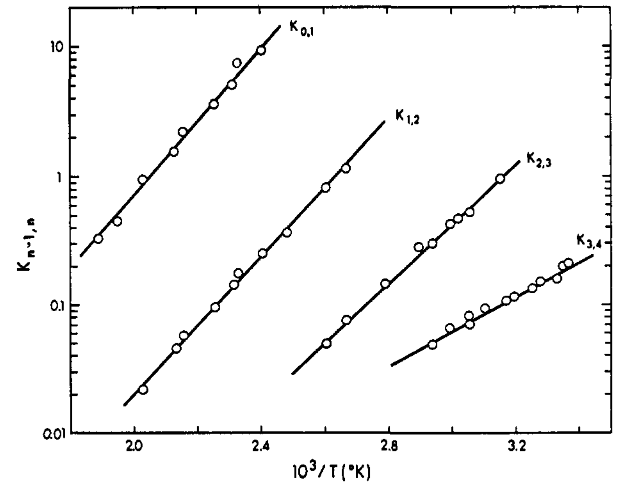

Figure 2. van't Hoff plots of equilibrium constants for reactions ($n - 1,n$): $Cl^-(CH_3CN)_{n-1} + CH_3CN = Cl^-(CH_3CN)_n$.

Table I. Thermodynamic Data Obtained from the Temperature Dependence of the Equilibria ($n,n - 1$), $X^-(CH_3CN)_n = X^-(CH_3CN)_{n-1} + CH_3CN$

$n, n - 1$	F^-	Cl^-	Br^-	I^-
		$\Delta H_{n,n-1}$[a]		
1, 0	16.0	13.4	12.9	11.9
2, 1	12.9	12.2	11.8	10.5
3, 2	11.7	10.6	10.0	9.3
4, 3	10.4	6.2	5.5	
5, 4	5.3			
		$\Delta G°_{n,n-1}$[b]		
1, 0	12.0	9.2	8.0	6.4
2, 1	8.5	6.6	5.8	4.3
3, 2	6.4	4.6	3.6	2.7
4, 3	4.5	3.0	2.2	
5, 4	3.1			
		$\Delta S°_{n,n-1}$[c]		
1, 0	13.4	14.3	16.5	18.2
2, 1	14.8	18.9	20.4	20.8
3, 2	17.9	20.1	21.7	22.1
4, 3	19.6	10.8	10.9	
5, 4	7.4			

[a] kcal/mol. [b] kcal/mol, standard state 1 atm, 298°K. [c] eu; standard state 1 atm. $\Delta S°$ is constant for the temperature range covered in experiment.

The data in Figure 3 show that the acetonitrile solvation energies follow the familiar order with ionic size, *i.e.*, they decrease from F^- to I^-. A similar conclusion concerning the total single-ion enthalpies of solvation for the halide ions in several aprotic solvents has been reached by Fuchs and coworkers[9] and Choux and Benoit.[3]

Comparing the acetonitrile with the water results, one notices that the acetonitrile $\Delta H_{n,n-1}$ values for

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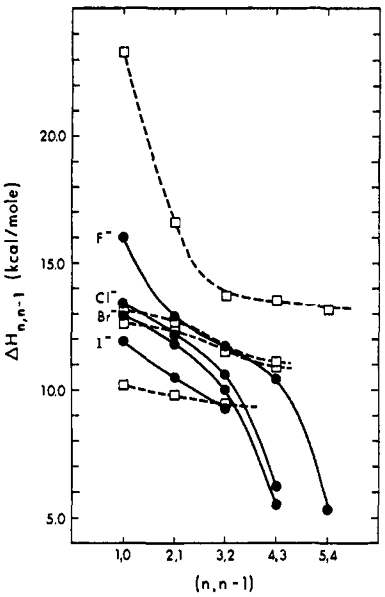


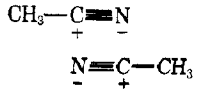
Figure 3. $\Delta H_{n,n-1}$ for halide ions solvated by acetonitrile (—) and water molecules (---).

F^- remain lower than those for water over the total observed range. For Cl^- and Br^- the $\Delta H_{1,0}$ for acetonitrile is higher, but then a crossover occurs, and $\Delta H_{2,1}$, $\Delta H_{3,2}$, etc., for water become progressively larger. The I^-, acetonitrile values are initially considerably higher, so that the crossover occurs later, *i.e.*, at $\Delta H_{3,2}$. Thus, two general trends are evident. First, solvation by water is favored in all cases at large n. Second, the acetonitrile interactions become relatively stronger as one moves from small to large ions, *i.e.*, from F^- to I^-. The observation that acetonitrile becomes the poorer solvent at high n is not surprising. One could understand it as a steric effect caused by the large size of the molecule and the specific location of the acetonitrile dipole, $CH_3C^+N^-$, which is such that most of the positive charge is on the nitrile carbon, *i.e.*, "inside" the molecule.

The trend toward better solvation by acetonitrile (relative to water) with increasing size of the ion, observed in the present results, is in the same direction as that found for the enthalpies of ion transfer from protic to aprotic solvents. Choux and Benoit[3] have deduced transfer enthalpies (water–aprotic solvent) which are positive for Cl^- and Br^- but decrease with increasing size of the ion, generally becoming negative for I^-. The present results indicate that the differences in the transfer enthalpies are due to close interactions, *i.e.*, interactions involving the first few solvent molecules.

The observed acetonitrile $\Delta H_{n,n-1}$ values (Figure 3) show a large falloff for Cl^- and Br^- after $\Delta H_{3,2}$, while the F^- curve has a considerable drop after $\Delta H_{1,0}$ and then a second falloff after $\Delta H_{4,3}$. In attempting to rationalize these observations, one is hampered by the already mentioned location of the acetonitrile dipole. The orientation of the acetonitrile molecules relative to the negative ion cannot be easily established from *a priori* considerations. Fortunately, there is some experimental information which might be pertinent. Roche and Van Huong[10] have studied infrared spectra of halide salts containing the ions Cl^-, Br^-, and I^- in liquid acetonitrile. The absorption bands attributed to the acetonitrile X^- complex involved the CH_3 group frequencies. The authors concluded that the complex has C_{3v} symmetry. This meant that the acetonitrile attaches itself to the ion through the methyl hydrogens and that the three hydrogens are symmetrically involved, *i.e.*, there is three-point attachment with the ion lying on the acetonitrile axis. Assuming that the same mode of attachment occurs for Cl^- and Br^- also in the gas phase, we may explain the falloff after $\Delta H_{3,2}$ by crowding which occurs after three acetonitrile molecules or nine H atoms have surrounded the ion. Unfortunately, Roche and Van Huong did not study F^-. But for F^- the situation may be expected to be different. The larger $\Delta H_{1,0}$ could be due to considerable contribution from covalent bonding between F^- and one H atom. In this case, the attachment is not symmetric. The attachment of a second acetonitrile molecule weakens the covalent bonding. The small size of F^- might require continued attachment of acetonitrile molecules by one H atom only. Thus, an inner shell could be completed after four molecules have been attached.

The outer-shell enthalpies, $\Delta H_{4,3}$ for Cl^- and Br^- and $\Delta H_{5,4}$ for F^-, are all around 5 kcal/mol. This is much smaller than the heat of evaporation of acetonitrile: $\Delta H_{\text{evap}} = 8$ kcal/mol. The very low outer-shell $\Delta H_{n,n-1}$ values may reflect a peculiarity of acetonitrile. There is considerable evidence that acetonitrile molecules tend to associate, forming the antiparallel dimer I. The existence of the dimer has been



$$\begin{array}{l} CH_3{-}\underset{+}{C}{\equiv}\underset{-}{N} \\ \quad\;\; \underset{-}{N}{\equiv}\underset{+}{C}{-}CH_3 \end{array}$$

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postulated in the gas phase, on the basis of the large second virial coefficient[11] and dipole moment variation with temperature,[12] and in pure liquid acetonitrile on the basis of changes in CN vibrational frequencies[13] and viscosity and boiling point comparisons.[14] The dissociation energy of the dimer has been estimated to be in the range 4–7 kcal/mol.[11,12,14] The breakup of the dimer may be expected to contribute a substantial amount to the heat of evaporation. The tendency toward antiparallel dimerization could lead to relatively poor bonding in the second shell of the ion cluster, since the acetonitrile molecules cannot arrange in antiparallel fashion for steric reasons, and also the fact that this arrangement would lead to an opposing dipole interaction with the negative ion. The second-shell molecules therefore probably go in coaxial positions to the first-shell molecules. This results in large ion–dipole and dipole–dipole distances and low binding energy.

The entropies $\Delta S°_{n,n-1}$ given in Table I are found to be small when the $\Delta H_{n,n-1}$ is small, *i.e.*, the outer shell $\Delta H_{n,n-1}$ values are distinguished by small $\Delta S°_{n,n-1}$ values. Such an effect is expected and should indicate

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[10] J. P. Roche and P. Van Huong, *J. Chim. Phys. Physicochim. Biol.*, 67, 211 (1970).

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the greater freedom in the outer shell. Owing to the mutually compensating character of the ΔH and ΔS values, one finds that the ΔG values change much less than the ΔH values.

As was mentioned in the introduction, there is considerable evidence that positive ions are solvated better by aprotic solvents than negative ions. It should be noted that the negative end of the dipole in all aprotic solvents is located at a much more accessible place than the positive end. Thus, as mentioned earlier, the negative charge in acetonitrile is on the nitrogen atom. Better solvation of positive ions is to be expected on this basis. The difference between positive and negative ions should be particularly noticeable in first-shell solvation. Some measurements[15] of the equilibria $M^+ + CH_3CN = M^+CH_3CN$ confirm this view. For $M^+ = K^+$, $\Delta H_{1,0} = 24$ kcal/mol. This is about 80% higher than $\Delta H_{1,0}$ for Cl^-, the isoelectronic negative ion which is of similar size. $\Delta H_{1,0}$ for K^+ is also considerably larger than $\Delta H_{1,0} = 18$ kcal/mol for the same ion solvated by a water molecule.

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(15) W. R. Davidson and P. Kebarle, unpublished work.

Pyrolysis of Cyclobutane[1a]

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Abstract: The pyrolysis of cyclobutane has been studied by the VLPP technique between 969 and 1280 K. It was found that the Arrhenius parameters which give best agreement between the present results and those of previous workers are $\log (k_\infty, \text{sec}^{-1}) = 16.5 - 65.5/\theta$. Estimates consistent with the above parameters have been made of the Arrhenius parameters for reactions 2, −2, and 3, $c\text{-}C_4H_8 \rightleftharpoons \cdot C_4H_8\cdot \rightarrow 2C_2H_4$ (2, forward; −2, reverse). Studies on the pressure dependence of the rate constant in the 22,400-collision reactor indicate a gas-collision efficiency of about 0.1 relative to the wall, while the good agreement expressed above indicates approximately unit efficiency. By lowering the high-pressure Arrhenius parameters, we can reconcile such a low collision efficiency with the falloff data of other workers. However, such low parameters would not fit our other VLPP data, and there appears to be no way to reconcile the discrepancy.

The thermal decomposition of cyclobutane has been shown to be a homogeneous, unimolecular reaction.[2–6] Although ethylene is the major product, there have been reports of the formation of small amounts of other alkenes.[2b,4,5] Between 693 and 740 K, the high-pressure rate constant[2b] has been given by

$$\log k_\infty = 15.6 - 62.5/\theta$$

where $\theta = 2.303RT$ (R in kilocalories per degree per mole). The rate constant has been shown to be independent of pressure above approximately 20 Torr.[2b–4] Because of the apparent simplicity of the reaction, it has been used several times to test unimolecular reaction rate theories. Butler and Ogawa[4] measured the rate constant between 1.7×10^{-4} and 43 Torr at 722 K. Using the parameters $A_\infty = 2 \times 10^{-15}$ sec^{-1}, $k_\infty = 4.9 \times 10^{-4}$ sec^{-1}, $s = 14$, $E_\infty = 61{,}700$ cal mol^{-1}, and collision diameter $\sigma = 5.5$ Å, they found that RRK theory fitted the data well down to 10^{-3} Torr. Slater theory was found to give just as good a fit when n was taken to be 16. Below 1 μ, the experimental rate constant was greater than the calculated one. A similar effect was noted by Vreeland and Swinehart[5] below about 20 μ. They used rather different parameters ($A_\infty = 7.02 \times 10^{15}$, $E_\infty = 63{,}200$ cal mol^{-1}, $s = 18$, and $\sigma = 5.8$ Å), but obtained a curve very similar to that of Butler and Ogawa. It was suggested[5] that this strange behavior at low pressures could be due to competition between the alternative pyrolysis routes, simultaneous rupture of two bonds or consecutive rupture (tetramethylene biradical mechanism). These deviations, however, are much more likely to be due to a wall-promoted reaction which would be caused by the limiting low collision frequency determined solely by the geometry of the reaction vessel. Maloney and Rabinovitch[7] have discussed this effect in relation to the ethyl isocyanide thermal isomerization, and it has been shown to be important in the thermal decomposition of methylcyclobutane.[8] Swinehart and his coworkers,[8] who demonstrated this, also emphasized that there was no evidence for chemical reactions occurring on the wall and that the only process important at the wall was the transfer of vibrational energy. The most extensive theoretical study of the reaction's falloff behavior has been made by Lin and Laidler,[9] who studied several small ring compounds. Using the reaction scheme

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(1) (a) This work was supported in part by Grant No. AP 00353-07 from the Environmental Protection Agency, Air Pollution Control Administration; (b) Postdoctoral Research Associate.

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