AP(IV) =

$$\frac{\Delta H_f(\mathrm{IV}) + \Delta H_f(91) + \Delta H_f(\mathrm{CO}) - \Delta H_f(\mathrm{I})}{23.06} \quad (16)$$

The appearance potential of the benzoyl ion in the mass spectrum of I was found to be 9.98 ± 0.12 eV and leads to a ΔH_f(IV) of 182.2 ± 3.1 kcal/mol. These values are close to the previously reported values of 9.7 eV and 186 kcal/mol.[26a] The ΔH_f(119) was estimated to be 18.2 ± 2.0 kcal/mol from the ΔH_f of the benzoyl radical and the difference (−7.9 kcal/mol) in the heats of formation of the 4-methylbenzyl and benzyl radicals.[45] Likewise it was necessary to use the value −7.9 and ΔH_f of the C_6H_5 radical (72 kcal/mol) to estimate the heat of formation of the 4-methylphenyl radical (64.1 ± 3.6 kcal/mol). Equations 15 and 16 lead to values of 10.02 ± 0.17 and 10.86 ± 0.22 eV, respectively, for AP(IV).

The appearance potential for formation of V from II was calculated using eq 17. Values of 232 kcal/mol

AP(V) =

$$\frac{\Delta H_f(\mathrm{V}) + \Delta H_f(105) + \Delta H_f(\mathrm{CO}) - \Delta H_f(\mathrm{I})}{23.06} \quad (17)$$

from the ionization-dissociation of toluene and 209 kcal/mol from the ionization of the cycloheptatrienyl radical[45] for ΔH_f(V) lead to values of 11.37 ± 0.52 and 10.37 ± 0.47 eV for AP(V).

Equation 18 is applicable to the formation of VI from

AP(VI) =

$$\frac{\Delta H_f(\mathrm{VI}) + \Delta H_f(119) + \Delta H_f(\mathrm{CO}) - \Delta H_f(\mathrm{I})}{23.06} \quad (18)$$

II. A value of 299 kcal/mol is obtained for ΔH_f of the C_6H_5 ions in the mass spectra of benzaldehyde and acetophenone.[38] Thus a value of 13.95 ± 0.66 eV is calculated for the AP(VI).

Ionic Association in Low-Dielectric Media. I. Ultrasonic Absorption Studies of Nitrates in Tetrahydrofuran

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Abstract: Ultrasonic absorption studies of lithium nitrate solutions in tetrahydrofuran at 25° have been carried out. In the frequency range 10–150 MHz there is a single concentration-independent relaxation which is not found in a number of other lithium salts. A very similar effect is found in THF solutions of tetramethyl- and tetrabutylammonium nitrates. The relaxations have been attributed to a process, possibly a desolvation, characteristic of nitrate ion within an ion pair. The influence of quadrupole formation upon the observed effect is discussed.

The Eigen multistep mechanism for ionic association[1] involves either two or three steps. The first step is the diffusion-controlled approach of free ions to form a solvent-separated ion pair (outer-sphere complex). The final step in this process is the collapse of a solvent-separated pair expelling the solvent molecule and forming a contact (inner sphere complex). In a three-step mechanism there is a third process which may be due to desolvation of the anion. Three-step and two-step mechanisms have been applied to data for $MnSO_4$ in water.[2,3]

Ultrasonic absorption has been the technique most often used for the experimental investigation of the kinetics of the first step in this process. Single relaxation processes corresponding to this step have been observed in a number of cases.[4,5] Relaxations essentially due to the formation of inner sphere complexes are common in both ultrasonic and jump methods.[6] Relaxations due to anion desolvation and which are not closely coupled to other processes have never been reported previously. We believe that we have formed a process which is characteristic only of the anion and may be a desolvation.

Experimental Section

The ultrasonic instrumentation consists of a Matec Model 6000 pulse generator-receiver, Model 666 B attenuator, and Model 120 syncronizer. The ultrasonic cell was similar to one used in earlier work.[2] A Z cut quartz delay line was used as opposed to the earlier fused quartz rod. This improved the signals at higher frequency.[7] A Hewlett-Packard Model 180 oscilloscope with a Model 1820B time base and Model 1803A amplifier was used in all measurements. The instrument was checked by measuring the absorption of both water and aqueous $MnSO_4$ solutions.

Tetrahydrofuran was distilled from lithium aluminum hydride. It was found that the value of α_0/f^2, where α_0 is the sound absorption coefficient and f the frequency, was a sensitive means of detecting moisture in the solvent. Freshly opened bottles of THF gave values about 123×10^{-17} neper cm^{-1} sec^2 which rose to 133×10^{-17} neper cm^{-1} sec^2 for distilled THF. Addition of more substantial quantities of water to THF led to relaxation processes in the solvent similar to those found for water–dioxane solutions.[8]

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The measured sound velocity was in excellent agreement with literature data[9] but was not sensitive to small amounts of moisture.

The tetraalkylammonium salts were prepared by reacting the corresponding halides with silver nitrate in water–ethanol solution. Evaporation of the solvent ultimately yielded crystals. The solids were dried in a vacuum oven at 40° for at least 48 hr.

The lithium nitrate was reagent grade product, dried at 110° for no less then 8 hr. All salts were analyzed by passing an aqueous solution of the weighed material through a cation-exchange resin and titrating the resulting nitric acid with standard base. The lithium nitrate was found to be anhydrous. All other chemicals were reagent grade and used as received. Temperatures were regulated to better than 0.1° with a Forma temperature bath.

Results and Discussion

For a single relaxation process, the excess absorption per wavelength, μ, is given by the equation[1]

$$\mu = (\alpha - \alpha_0)\lambda = \frac{2\mu_{\max}(f/f_r)}{1 + (f/f_r)^2} \qquad (1)$$

where α is the sound absorption coefficient of the solution, α_0 is the sound absorption coefficient in the absence of a relaxation process, normally the solvent value, λ is the wavelength, f is the frequency of the ultrasonic wave, f_r is the relaxation frequency, and $\mu_{\max}$ is the maximum value of μ and is related to thermodynamic functions of the system.

When solutions of lithium nitrate in THF are investigated at 25°, a single, *concentration-independent* relaxation is observed in the frequency range 10–150 MHz. Values of f_r and $\mu_{\max}$ are reported in Table I. Experimental values of α can be obtained from the authors on request.

Table I. f_r and $\mu_{\max}$ for $LiNO_3$ in THF at 25°

C_T, M	f_r, MHz	$\mu_{\max} \times 10^5$ (±5%)
0.200	29 ± 2	270
0.100	29 ± 2	178
0.050	29 ± 2	108

The high-frequency value of α/f^2 was equal to the solvent value within experimental error for all solutions.

Due to the low dielectric constant of THF the lithium nitrate was expected to be highly associated to ion pairs and perhaps higher aggregates. It was also possible that the ion pairs could exist as solvent-separated and contact pairs. Hence, it was expected that the association process could be described by a mechanism of the form

$$M^+(solv) + L^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} M(solv)L \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} ML$$

where M^+(solv) is the free solvated cation, L^- is the free anion, M(solv)L is the solvent-separated ion pair, ML is the contact pair, and the k's are the rate constants.

For such a mechanism there are two relaxation times given by the equation

$$\tau_{I,II}^{-1} = {}^1/_2(S \pm \sqrt{S^2 - 4P}) \qquad (2)$$

where $S = k_{12}\theta + k_{21} + k_{23} + k_{32}$, $\theta = 2\alpha C\gamma^{\pm}$, $\gamma^{\pm}$ is the mean actively coefficient, α is the degree of dissociation, and $P = k_{12}\theta(k_{23} + k_{32}) + k_{21}k_{32}$.

If we assume that k_{12} is a diffusion-controlled rate constant, then an estimate of its magnitude can be obtained *via* the Debye equation.[10] In order of magnitude $k_{12} = 10^{10}\ M^{-1}\ \text{sec}^{-1}$. If the ion pair formation constant $K_0 = k_{12}/k_{21}$ is very large and the ratio of contact ion pairs to solvent-separated ones is not very much greater than unity, then the overall association constant K_T can be simply related to the degree of dissociation α, the total concentration of salt, and the value of K_0. In general eq 3 applies where K is the

$$K_T = K_0(1 + K) = (1 - \alpha)/\alpha^2 C\gamma^{\pm 2} \qquad (3)$$

ratio of contact pairs to solvent-separated pairs and is also equal to k_{23}/k_{32}. Hence, if K_0 is large and K not very much greater than 1, then in order of magnitude

$$\alpha\gamma^{\pm} = 1/(CK_T)^{1/2} \cong 1/(CK_0)^{1/2}$$

Thus $\theta \cong 2(C/K_0)^{1/2}$. For lithium nitrate in THF, K_T is[11] $1 \times 10^{10}\ M^{-1}$. Thus for a 0.1 M solution, $\theta = 6 \times 10^{-6}$. The term $k_{12}\theta$ is therefore on the order of 6×10^4. Since $K_0 = k_{12}/k_{21}$, k_{21} is on the order of unity. Thus, unlike the case of electrolytes in water and other high-dielectric solvents, in THF the values of $k_{12}\theta$ and k_{21} are relatively small. Hence relaxations due to the first step of the association mechanism are far too slow to appear in the ultrasonic region. It is also expected that the values of k_{23} and k_{32} will be relatively high for lithium, since according to the Eigen mechanism[1] k_{23} is equal to the rate of solvent exchange for the cation which is quite high for lithium ion in water[12] and is probably not too different in other solvents. If the value of k_{23} is similar to the exchange rate in water (about[12] $10^8\ \text{sec}^{-1}$) and if K is about unity, then in eq 2

$$S^2 \gg 4P$$

$$\tau_I^{-1} \cong S \cong k_{23} + k_{32} \qquad (4)$$

In low-dielectric media therefore we expect to find a fast relaxation process which is concentration independent. When this result was obtained experimentally it was assumed that the process under observation was the solvent-separated ion pair–contact ion pair transformation with the cation being desolvated.

Additional experiments were carried out to prove this contention. If this process was indeed the cause of the relaxation, then addition of very strong cation solvating agents would displace the nitrate ion from the inner sphere of the lithium ion and thus interfere with the ion pair transformation. Addition of 2 mol of DMSO or 2 mol of 1,2-dimethoxyethane/mol of $LiNO_3$ caused virtually no change in relaxation effect. This effect was quite disturbing since the two ligands are known to be quite effective in displacing carbanions from the inner sphere of lithium ion.[13] This observation could not be explained by invoking a tremendously more stable inner sphere complex for lithium nitrate compared with the carbanion. If

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this were the case, then K would have to be large. Since large values of K would lead to a very small magnitude of the relaxation effect,[14] this explanation is unlikely.

Another test of the process deals with the effect of changing anions and cations. One of the central features of the Eigen mechanism is that, for cation desolvation, k_{23} is virtually independent of anion and is approximately equal to the rate of solvent exchange. According to eq 4

$$2\pi f_r = \tau^{-1} = k_{23} + k_{32} = k_{23}(1 + K^{-1})$$

thus f_r can vary with anion even if k_{23} is constant due to variations of K. Since very large or very small values of K would lead to negligible amplitude of the relaxation effect, we might expect that all measureable relaxations would be in about the same frequency range. We therefore tested a number of diverse lithium salts such as the chloride, cyclohexane butyrate, and 9-fluorenyl derivative (LiFl). No effect was observed for any salts in the frequency range studied. For the first two salts it was possible that K could be far too large or small to give an effect. For the last salt, however, this was not the case since K was available from spectrophotometry.[13] The absence of the effect in the carbanion case and the presence of the effect for the nitrate could be explained only if K for nitrate was much smaller than for the carbanion. We can estimate the necessary value of K by taking the ratio of the relaxation frequency expression for the two salts.

$$\frac{f_r(\mathrm{LiNO_3})}{f_r(\mathrm{LiFl})} = \frac{1 + K^{-1}(\mathrm{LiNO_3})}{1 + K^{-1}(\mathrm{LiFl})}$$

If there is a relaxation frequency for LiFl it must be considerably below 10 MHz. Using 10 MHz as the upper limit for this frequency leads to the prediction that K^{-1} for lithium nitrate would be at least 13 and probably more than 20. This value for K^{-1} is rather unlikely in view of the rather small ultrasonic magnitude expected from any equilibrium which lies so far to one side.

In view of the effect of cation solvating agents, and change of anions, the assumption of a cation-desolvation process being the cause of the observed relaxation was no longer considered tenable. Other possibilities were considered including the formation of triple ions and quadrupoles according to the reaction

$$2\mathrm{ML} \rightleftharpoons \mathrm{ML_2^-} + \mathrm{M^+}$$

or

$$2\mathrm{ML} \rightleftharpoons \mathrm{M_2L^+} + \mathrm{L^-}$$

$$2\mathrm{ML} \rightleftharpoons (\mathrm{ML_2})$$

In both cases, however, there is at least one second-order rate constant. Thus the relaxation time would be concentration dependent. In addition, conductance studies have shown[11] that the concentration of triple ions would be very small and thus the magnitude of an ultrasonic relaxation would be far too small to be detectable. These possibilities were therefore discarded.

We therefore adopted the assumption that the process under observation was an ion pair desolvation process but of the following type

$$\mathrm{Li(sol)^+} + \mathrm{(sol)NO_3^-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{Li(sol)(sol)NO_3} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \mathrm{Li(sol)NO_3} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \mathrm{LiNO_3}$$

where sol = solvent molecule. An anion-desolvation process such as k_{23} in the above would be expected to be little affected by addition of DMSO, which is a poor anion solvating agent.[15] Dimethoxyethane is also expected to be a relatively poor solvating agent for anions. A final and most convincing test lies in the prediction that such a process should be cation independent. The first observation of this independence is the fact that the two cation solvating agents gave no appreciable change in the relaxation despite the fact that the first coordination sphere of the cation is being substantially changed. As a further test of the assumed cation independence we measured the ultrasonic absorption of THF solutions of tetrabutylammonium nitrate (TBA nitrate) and tetramethylammonium nitrate (TMA nitrate). In the former case a concentration-independent relaxation at 32 MHz was found. For the latter salt a concentration-independent relaxation at 22 MHz was found. The differences in relaxation frequency are probably due to differences in equilibrium constant for the different salts. The magnitudes of the effects at comparable concentrations are also similar. Above 0.1 M, TBA nitrate shows an additional relaxation probably due to quadrupole formation. Conductivity measurements[11] strongly support this last assignment as does the strong concentration dependence of the new effect.

Calculations of the Ultrasonic Absorption Magnitude

The magnitude of a single ultrasonic relaxation effect is given by[1]

$$\mu_{\max} = \frac{\pi}{\beta RT}(\Delta V_s)^2\Gamma \qquad (5)$$

where β is the compressibility of the solvent and ΔV_s is the adiabatic volume change.

$$\Delta V_s = \Delta V_T - \frac{\alpha}{\rho C_p}\Delta H$$

where ΔV_T is the isothermal volume change, α is the coefficient of thermal expansion, C_p is the heat capacity, and ΔH is the enthalpy change.

$$\Gamma^{-1} = \frac{\partial A/RT}{\partial \xi} = \sum_i \frac{\nu_i^2}{a_i}$$

where A is the chemical affinity, ξ is the degree of advancement of the reaction, ν_i is the stoichiometric coefficient, and a_i is the activity of the species. For our case the concentration of free ions is so small that they can be neglected. Hence

$$\Gamma = \left(\frac{1}{[\mathrm{M,L}]} + \frac{1}{[\mathrm{ML}]}\right)^{-1} = \frac{[\mathrm{M,L}][\mathrm{ML}]}{[\mathrm{M,L}] + [\mathrm{ML}]} \qquad (6)$$

where concentrations are now being used in place of activities, [M,L] is the concentration of solvent-

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separated ion pairs, and [ML] is the concentration of the contact ion pair. In view of this last equation, it is evident that when either [ML] or [M,L] is very small Γ will be very small, and hence the magnitude of the ultrasonic relaxation will be very small. This concentration term is going to be quite important for ion pair transformation processes since ΔV_T for this process is expected to be small.[16]

According to eq 5 and 6, the logarithm of μ_max should be linear function of log C_T with a slope of unity. The plot for $LiNO_3$ data was linear but the slope was 0.78. The corresponding plot for tetrabutylammonium nitrate was 0.70.

An explanation of the slope of less than unity can be found by considering other species in the solution besides the two types of ion pairs and free ions. Electrical conductance results show that the concentrations of triple ions and free ions are extremely small in these solutions and thus such species are neglected in further discussion.

Considering only ion pair types we can write

$$C_\mathrm{T} = [\mathrm{ML}] + [\mathrm{M,L}] + [\mathrm{M,,L}] \qquad (7)$$

where ML is the species with Li^+ and NO_3^- in direct contact and each comma represents an intervening solvent molecule. This situation thus considers both anion and cation solvation. Designating $K_1 = [\mathrm{M,L}]/[\mathrm{M,,L}]$ and $K_2 = [\mathrm{ML}]/[\mathrm{M,L}]$, the concentrations of the ion pair species which are involved in the process observed in the ultrasonic region are

$$[\mathrm{M,,L}] = \frac{C_\mathrm{T}}{1 + K_1 + K_1K_2}$$

$$[\mathrm{M,L}] = \frac{K_1C_\mathrm{T}}{1 + K_1 + K_1K_2}$$

The concentration-dependent contribution to the magnitude of the ultrasonic effect is therefore

$$\Gamma = \frac{K_1C_\mathrm{T}}{(1 + K_1)(1 + K_1 + K_1K_2)}$$

Thus even when other types of ion pairs are considered, the slope of a log μ_max *vs.* log C_T plot should still be unity. Only a concentration-dependent equilibria can lead to an apparent decrease in slope. The most likely species present in a resonable concentration which is formed in low-dielectric solvents is a quadrupole, an ion pair dimer. If we write the mass balance equation of a system in which M,,L dimerizes we have (neglecting free ions and triples)

$$C_\mathrm{T} = [\mathrm{ML}] + [\mathrm{M,L}] + [\mathrm{M,,L}] + 2[\mathrm{M_2L_2}]$$

if

$$K_\mathrm{q} = \frac{[\mathrm{M_2L_2}]}{[\mathrm{M,,L}]^2}$$

$$C_\mathrm{T} = K_1K_2[\mathrm{M,,L}] + K_1[\mathrm{M,,L}] + [\mathrm{M,,L}] + 2K_\mathrm{q}[\mathrm{M,,L}]^2$$

or

$$[\mathrm{M,,L}] = \frac{1}{2}\left\{-\frac{(1 + K_1 + K_1K_2)}{2K_\mathrm{q}} \pm \sqrt{\left(\frac{1 + K_1 + K_1K_2}{2K_\mathrm{q}}\right)^2 + \frac{2C_\mathrm{T}}{K_\mathrm{q}}}\right\} \qquad (8)$$

if

$$\frac{2C_\mathrm{T}}{K_\mathrm{q}} \ll \frac{1 + K_1 + K_1K_2{}^2}{2K_\mathrm{q}}$$

The radical can be expanded in series to give

$$[\mathrm{M,,L}] \cong C_\mathrm{T}/(1 + K_1 + K_1K_2)$$

which gives

$$\Gamma = \frac{K_1C_\mathrm{T}}{(1 + K_1)(1 + K_1 + K_1K_2)}$$

Hence the magnitude of the ultrasonic absorption is proportional to the total concentration. If in eq 8

$$\frac{2C_\mathrm{T}}{K_\mathrm{q}} \gg \frac{1 + K_1 + K_1K_2}{2K_\mathrm{q}}$$

then

$$[\mathrm{M,,L}] \cong \sqrt{C_\mathrm{T}/2K_\mathrm{q}}$$

and

$$\Gamma = \frac{K_1}{1 + K_1}\sqrt{\frac{C_\mathrm{T}}{2K_\mathrm{q}}}$$

The magnitude of the ultrasonic effect is thus proportional to $C_\mathrm{T}^{1/2}$. Thus, if log μ_max is plotted *vs.* log C_T the slope at low concentrations is 1 and it decreases as C_T increases approaching 0.5 at high concentrations. Since our measurements are restricted to a small variation in C_T, a nearly linear plot is understandable as is the value of the slope. The presence of quadrupoles is likely in $LiNO_3$ solutions and very pronounced in tetrabutylammonium nitrate as shown by conductance measurements.

In conclusion, we believe that we have observed an anion-desolvation process which accounts for all of the experimental observations. The fact that the relaxation is observed in tetraalkylammonium salts is proof that the process is not due to second solvation shells of the cation. There is some cation dependence on the relaxation frequency. Since molecular models indicate that the effective radius of THF solvated Li ion is intermediate between that of TMA and TBA ions, the relaxation frequency would increase with cation radius.

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