for reactions in the solid state, it might be expected that such effects would be very sensitive to the difference between crystalline and glassy solids. From the results for acetonitrile and methanol considered here, this does not appear to be the case. However, a more definitive test of the importance of "cage effects" would result from a comparison of results for the same reaction in a crystalline and glassy matrix. Further work is planned on the methanol system with this idea in mind.

This work demonstrates that hydrogen atom abstraction can occur by a thermal reaction at low temperatures on a time scale which is short compared to the irradiation times commonly employed in many photochemical and radiation chemical experiments with solid matrices. Hence, under these conditions, caution should be exercised in attributing all the trapped intermediates present after photolysis or radiolysis at low temperatures to the results of primary processes and hot radical reactions. Also, since the present results in CD_3OD provide no evidence for abstraction by hot radical reactions in the photolysis of CH_3I and TMPD–CH_3Cl in methanol, it would seem that the importance of such processes[9,17] may be critically dependent on the nature of the matrix.

Acknowledgment. We thank Dr. C. M. L. Kerr for computational help and useful discussions during the course of this work.

Detritiation of Malononitriles in Mixed Aqueous Solvents and in Salt Solutions. A Kinetic Probe for Solvent Basicity[1,2]

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Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received February 3, 1972*

Abstract: The water-catalyzed detritiations of malononitrile and its *tert*-butyl derivative represent an interesting new probe for solvent basicity. The rates of detritiation have been measured in mixed solvents of water with dioxane, ethanol, and dimethyl sulfoxide. Replacement of water by the nonaqueous component leads to a rate maximum at about 0.2 mol fraction replacement, implying an initial increase in solvent basicity. The magnitudes of the maxima (dimethyl sulfoxide > ethanol > dioxane) and the solvent compositions at which they occur vary with the particular nonaqueous additive. In largely nonaqueous solution, the rate is reduced below its value in water; *i.e.*, the basicities decrease. The overall variation of the rate of detritiation with solvent composition in water–ethanol roughly follows the H_- indicator acidity function, but this correlation breaks down for water–dioxane solutions. In the presence of tetraalkylammonium halides the rate of the water-catalyzed detritiation of *tert*-butylmalononitrile is increased; the magnitude of the effect increases with the cationic radius of the salt. Alkali metal halides reduce the rate. These salt effects and the influences of mixed solvents on the rate of detritiation can be understood in terms of medium effects on the activity of the ion-pair transition state. The kinetic results also correlate closely with effects on the structure of water.

The detritiation of malononitriles in aqueous solution is a slow proton (triton) transfer reaction.[4]

$$\begin{array}{lll} RCT + B \xrightarrow{k} RC^- + BT^+ & \text{slow} & \\ RC^- + \text{proton species} \longrightarrow RCH & \text{fast} & \end{array} \quad (1)$$

The rate coefficient k of the base-catalyzed detritiation is directly proportional to the strength of the general base catalyst as measured by the dissociation constant of its conjugate acid (K_{HB}). In other words

$$k = \text{constant} \times (1/K_{HB})^{\beta} \quad (2)$$

where the Brønsted coefficient β is practically unity, 0.98 ± 0.02. Calculation of the reverse rates of recombination of the general acids with malononitrile anions showed these reactions to be virtually diffusion controlled (*e.g.*, $k_{H_3O^+} = 4 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ at 25°). Other properties of the reverse reaction confirm this conclusion. The transition state for proton transfer (eq 1) therefore resembles an ion pair in which the proton is almost completely transferred from the carbon acid.

In aqueous hydrochloric acid a "spontaneous" detritiation is observed. This has been identified as a simple base-catalyzed slow triton transfer in which the solvent, water, acts as the base catalyst.[4,5] For malononitrile ($pK^0 = 11.19$) and *tert*-butylmalononitrile ($pK^0 = 13.10$) the rate of this reaction can conveniently be measured. The existence of the water-catalyzed detritiation suggests the possibility of a new probe for solvent basicity. By studying the variation of the rate of detritiation with composition in a two-component aqueous solvent mixture, information about the basicity of the mixture is obtained. This type of study has been applied to three mixed aqueous solvents, water with dimethyl sulfoxide, ethanol, and dioxane, as well as to a number of aqueous salt solutions.

Previous information about the basicity of aqueous two-component solvent mixtures has been obtained

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(1) Work supported by a grant from the Atomic Energy Commission.

(2) A preliminary report of this work has been published: F. Hibbert, F. A. Long, and E. A. Walters, *J. Amer. Chem. Soc.*, **91**, 2381 (1969).

(3) To whom requests for reprints should be sent.

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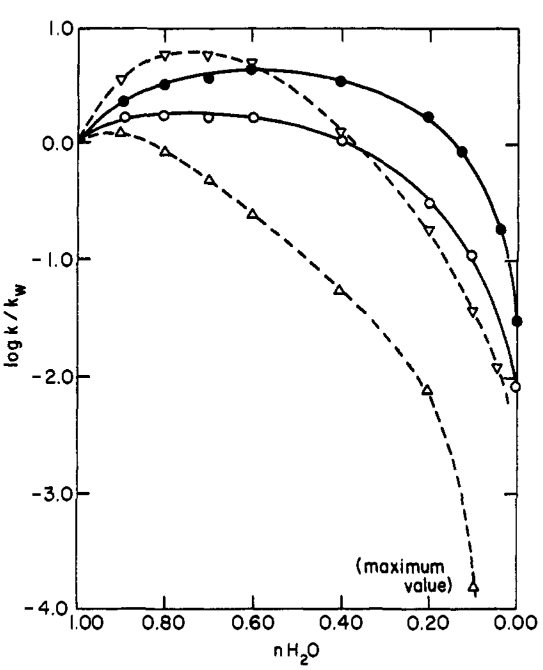

Figure 1. Detritiation of malononitriles in mixed solvents, all containing 0.001 *M* HCl. k and k_w are the rate coefficients in the mixed solvent and pure water, respectively. For *tert*-butylmalononitrile: water–dioxane, Δ; water–ethanol, O; water–dimethyl sulfoxide, ∇. For malononitrile: water–ethanol, ●.

by many different techniques.[6] Changes of solvent basicity can be further analyzed in terms of activity coefficient effects and, perhaps more fundamentally, in terms of the influence of added species on the structure of water.

Experimental Section

Materials. The preparation and purification of tritiated malononitriles has been previously described.[4] Dioxane was refluxed over sodium and distilled. Dimethyl sulfoxide was stirred with calcium hydride for several days and distilled under vacuum. Absolute ethanol was stirred with magnesium sulfate and distilled. The tetraalkylammonium salts were recrystallized and dried before use. 4-Chloro-2,6-dinitrophenol was recrystallized from ethanol.

Detritiation. All reactions were studied in the mixed solvent containing 1.00×10^{-3} *M* HCl at 25.0°. Solvent mixtures were usually made up by weight. The detritiation techniques have been described[4] and, as previously observed, detritiation was an accurately first-order process. All rate coefficients are in sec^{-1} units. For reference purposes k_w at 25° is 8.38×10^{-3} sec^{-1} for malononitrile and 3.27×10^{-4} sec^{-1} for *tert*-butylmalononitrile. In a solution of 0.9 mol fraction of dioxane, the reaction was inconveniently slow ($t_{1/2} \sim 100$ days). For this solvent, only a small percentage of the overall reaction was followed, and the resulting rate coefficient is an upper limit.

Measurement of Acidity Function (H_-). A method similar to that used by Bates and Schwarzenbach[7] was used to determine the H_- function for water–dioxane mixtures containing 1.00×10^{-3} *M* HCl. Measurements were taken at 25.0° in five different water–dioxane mixtures. In each mixture the extinction coefficients of the dissociated and undissociated forms of the indicator were determined at two wavelengths (3650 and 4450 Å) in solutions containing 0.1 *M* HCl or 0.1 *M* NaOH. At 3650 and 4450 Å absorption is predominantly by the acid and anionic forms, respectively. For each solvent mixture containing 1.00×10^{-3} *M* HCl, measurements of the optical density at both wavelengths were taken for at least five different indicator concentrations. Hence for each composition of water–dioxane usually ten measurements of the indicator ratio (average deviation usually about ±2%) and H_- were performed. In solutions where the indicator was largely undissociated, only measurements on the anion peak were made. We determined the pK^0 of 4-chloro-2,6-dinitrophenol as 2.97 ± 0.01 at 25°. Bates and Schwarzenbach obtained p$K^0 = 2.94 \pm 0.01$[7] compared with later values, p$K^0 = 2.97 \pm 0.01$[8] and 2.98.[9] We also determined an H_- value of one water–ethanol mixture and found good agreement with that of Bates and Schwarzenbach.

Solubility Measurements. The activity coefficients of *tert*-butylmalononitrile in 1 *M* solutions of potassium chloride and tetraethylammonium bromide and chloride were determined by measuring its solubilities (±1%) at 25° in these solutions and in pure water. All solutions contained 1.00×10^{-3} *M* HCl. The method has been described previously.[5]

Results

Basicity of Mixed Aqueous Solvents. Application of this kinetic probe for basicity to three aqueous solvent mixtures is illustrated in Figure 1. Rates for the water-catalyzed detritiation reaction at different solvent compositions are given relative to the rate of detritiation in pure aqueous solution. All three solvent systems show the same overall features. In highly aqueous solution, replacement of water by the organic component unexpectedly leads to a rate maximum, implying that initial addition of the nonaqueous component causes an increase in basicity. The magnitude of the rate maximum and the position on the composition axis at which it occurs is sensitive to the particular additive. At lower mole fractions of water in each of the three solvent mixtures the rates and hence the solvent basicities are reduced below their values in pure aqueous solution. A spontaneous detritiation is still observed in pure ethanol. This means that ethanol itself can act as a base catalyst, although its contribution for mixed solvents with mole fractions of water greater than 0.2 is probably negligible. Dioxane and dimethyl sulfoxide do not appear to be base catalysts. Hence the overall decrease in the rates of detritiation in Figure 1 is doubtless to some extent a result of the decrease in concentration of the water catalyst, and its replacement by less basic molecules.

Several equilibrium studies are available for comparison with the present probe for basicity.[7] Ethanol–water mixtures (containing 0.002 *M* HCl and 0.008 *M* NaCl) have been studied by two electrometric (pW$^+$ and pH$_{(\mathrm{conv})}$) and by two indicator (H_0 and H_-) techniques. The H_- and pH$_{(\mathrm{conv})}$ functions and data for the kinetic probe are shown in Figure 2. The H_- function and the kinetic probe agree well, especially considering the differences in ionic strength in the two cases. An H_- function determined in the present studies for the water–dioxane system is also compared in Figure 2 with the kinetic work in that solvent system. In order to understand these comparisons it is necessary to consider the functions more closely.

The H_- acidity function measures the effect of changing the solvent on the equilibrium (eq 3). An increase in H_-, as measured by an increase in the dissociation of the indicator, reflects the greater basicity of the medium. The function is defined by eq 4 where K_{ROH} is the dis-

$$\mathrm{H_2O + ROH \rightleftharpoons RO^- + H_3O^+} \tag{3}$$

$$H_- = \mathrm{p}K_{\mathrm{ROH}} - \log C_{\mathrm{ROH}}/C_{\mathrm{RO^-}} \tag{4}$$

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(6) R. G. Bates in "Hydrogen-Bonded Solvent Systems," A. K. Covington and P. Jones, Ed., Taylor and Francis, London, 1968.

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sociation constant of the indicator in pure aqueous solution, and C_{ROH} and $C_{\mathrm{RO^-}}$ are the measured indicator concentrations in the solvent under study. H_- is related to hydrogen ion activity in the solvent by eq 5 in which the activity coefficients are for transfer of the species between dilute aqueous solution and dilute solution in the mixed solvent.

$$H_- = -\log \frac{a_{\mathrm{H_2O^+}} f_{\mathrm{RO^-}}}{a_{\mathrm{H_2O}} f_{\mathrm{ROH}}} \tag{5}$$

At a fixed hydrogen ion concentration

$$H_- = \text{constant} - \log \frac{f_{\mathrm{H_3O^+}} f_{\mathrm{RO^-}}}{a_{\mathrm{H_2O}} f_{\mathrm{ROH}}} \tag{6}$$

Applying transition state theory to the detritiation of *tert*-butylmalononitrile (RCH) in mixed solvents, the rate coefficient measured in the mixed solvent (k) can be expressed by eq 7 in which k_w is the rate coefficient measured in aqueous solution, f_* is the activity coefficient of the transition state, and the activity coefficients (f) again refer to transfer between aqueous solution and the mixed solvent.

$$\log \frac{k}{k_w} = \log \frac{f_{\mathrm{RCH}} a_{\mathrm{H_2O}}}{f_*} \tag{7}$$

Hence the variation of the H_- function and the kinetic function $\log k/k_w$ with solvent composition are determined by the variation of the activity coefficient ratios in eq 6 and 7, respectively. The observed consistency of the two functions implies approximate constancy of the ratio

$$\frac{f_{\mathrm{H_3O^+}} f_{\mathrm{RO^-}} f_{\mathrm{RCH}}}{f_* f_{\mathrm{ROH}}}$$

Approximate cancellation of the activity coefficients of the undissociated acids is expected. Since the transition state is essentially an ion-pair $\mathrm{RC^- \cdots H_3O^+}$ with almost complete proton transfer,[4] it is plausible that there should be partial cancellation of its activity coefficient with the product of those for the species $\mathrm{H_3O^+}$ and $\mathrm{RO^-}$. This leads to the observed parallel behavior of the H_- function and the kinetic probe in ethanol–water. In dioxane–water solution, however, the two functions show fairly divergent behavior, and in ethanol–water the H_0 function departs from H_- and the kinetic probe. This latter is presumably due to the different charge type of the indicator used for the H_0 function.

The functions pW+ and $\mathrm{pH_{(conv)}}$ were determined by measurements of the emf of cells containing a hydrogen electrode with silver|silver chloride and calomel electrodes, respectively. Both relate to the hydrogen ion activity, *e.g.*

$$\mathrm{pH_{(conv)}} = -\log a_{\mathrm{H^+}} + \log f_{\mathrm{Cl^-}} \tag{8}$$

A decrease in hydrogen ion activity in the mixed solvent presumably indicates greater basicity than in water alone. The functions are complicated, however, by the additional term for chloride ion. This can be eliminated by making certain assumptions, and single hydrogen ion activities are then obtained.[10] These appear to indicate that methanol and dioxane and their mixtures with water are all more basic than pure water.

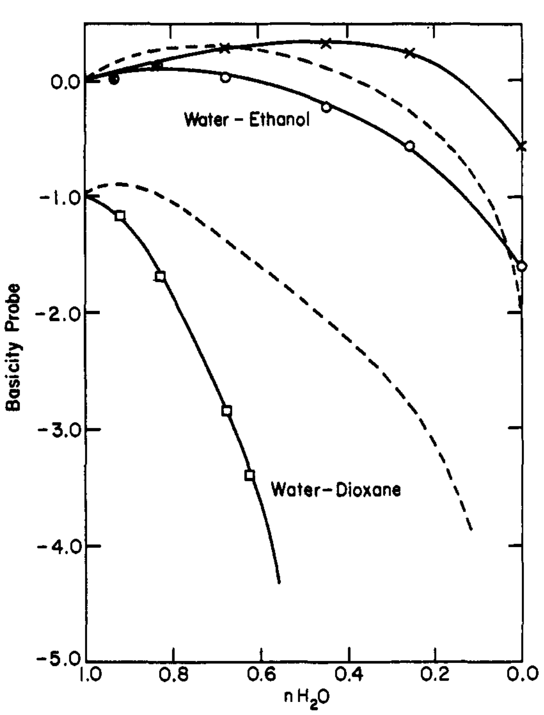

Figure 2. Comparison of the relative rate of detritiation of *tert*-butylmalononitrile with H_- and $\mathrm{pH_{(conv)}}$. For water–ethanol: $\log k/k_w$, - - - - - -; H_- −2.79, ○; $\mathrm{pH_{(conv)}}$ −2.75, ×. For water–dioxane: $\log k/k_w$, - - - - - -; H_- −3.97, □.

The variety of results obtained by these different studies illustrates the difficulty of separating solvent basicity from other inherent medium effects which result from changing the solvent. The present kinetic probe is no exception. The results are interesting, however, in that they indicate the operation of some unusual medium effects. With this in mind we turn to the study of the effects of salts on the detritiation of *tert*-butylmalononitrile.

Basicity Probe of Aqueous Salt Solutions. The effects of salts on the rate of the water-catalyzed detritiation of *tert*-butylmalononitrile are shown in Figure 3. The previously discussed measurements for mixed solvents refer to higher concentrations than those used for salts. However, the result obtained by interpolating the rate coefficient at the lowest mole fraction of dimethyl sulfoxide used to 1 *M* DMSO is shown in Figure 3. The effect of DMSO corresponds approximately to that of tetramethylammonium bromide.

The activity coefficients for *tert*-butylmalononitrile calculated from solubility studies in approximately 1 *M* salt solutions are shown in Table I. Using an expression similar to (7) and assuming the activity coefficient of water to be unchanged between water

Table I. Activity Coefficients at 25° in 1 *M* Salt Solutions[a]

Salt (concn, *M*)	Log f_{RCH}	Log f_*
$\mathrm{Et_4NCl}$ (0.996)	−0.04	−0.42
$\mathrm{Et_4NBr}$ (1.05)	−0.13	−0.41
KCl (0.996)	0.10	0.26

[a] Standard state: aqueous solution containing 1.00×10^{-3} *M* HCl. RCH represents *tert*-butylmalononitrile.

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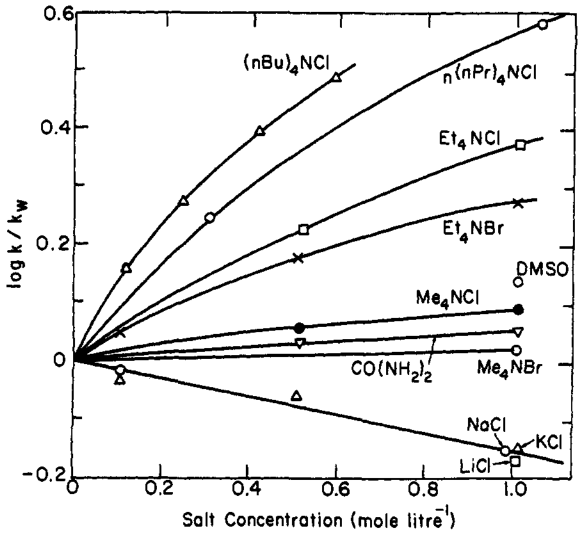

Figure 3. Relative rate of detritiation at 25° of *tert*-butylmalononitrile in salt solutions; k and k_w are the rate coefficients in salt solution and water, respectively. All solutions contain 0.001 M HCl.

and the 1 M salt solutions,[11] the activity coefficients for the transition state were calculated. Both the carbon acid and its transition state are salted-out by potassium chloride and salted-in by the tetraalkylammonium salts, although the magnitudes of the effects are very much larger for the transition state. Nonelectrolytes are frequently salted in by large ion salts[12] so the results for *tert*-butylmalononitrile are as expected. The transition state effects are discussed below.

Discussion

Maxima of the characters shown in Figure 1 are a common feature of solution properties measured in mixed aqueous media of varying composition.[13] For example, maximum values in the excess heats of mixing for these solvent mixtures have been observed at similar mole fractions to these kinetic maxima.[13a,b] Minima in the activation energies of reactions in which a nonpolar ground state leads to an ion-pair transition state have been observed in mixed aqueous solvents.[13a,d,e] In most of these cases, the effects have been postulated to originate from the structural properties of the solvent mixtures.

Two features of Figure 1 require explanation: the initial increase in rate, and hence solvent basicity at low mole fractions of the nonaqueous component, and the subsequent decrease at higher mole fractions. The ultimate decrease in rate can be looked upon as partly a consequence of replacing water by organic molecules which are relatively ineffective as base catalysts. In addition, for the type of ion-pair transition state involved, the decrease in dielectric constant as the medium becomes less aqueous is expected to reduce the rate of detritiation.[14] This reduction should be greater for mixtures of water (ϵ 78.4) with dioxane (ϵ 2.2) than with ethanol (ϵ 24.3) and dimethyl sulfoxide (ϵ 46.6). The observations for water–dioxane and water–dimethyl sulfoxide support this expectation. The water–ethanol results are not strictly comparable since, at high mole fractions of ethanol, catalysis by ethanol molecules is doubtless occurring, but qualitatively the results are similar. Thus the eventual decrease in rate brought about by changing the solvent is as expected; it is the initial increase at low mole fractions of the organic solvents which is less expected and more interesting.

In asking for an understanding of the initial effects of added salts and organic molecules, two approaches are possible. One is to analyze the effects in terms of the activity coefficients for transfer of the various species, attempting to identify the significant terms and, where possible, correlating these with structures of reactants and transition state. The alternative approach seeks an interpretation in terms of effects on the structure of solvent water. We turn first to the activity coefficient approach.

The comparatively small effects of salts and other additives on the solubility of the substrate species indicate that the kinetic behavior does not have its origin in changes in the degree of initial state solvation. We must explain the results in terms of the transition state effects which are much larger (Table I). Additions of tetralkylammonium halides and of organic solutes cause a strong decrease in the value of $f_{\ast}$ for the transition state, *i.e.*, a negative free energy of transfer (salting-in), whereas addition of alkali halides causes a strong increase in $f_{\ast}$ or a salting-out of the transition state species. Previous studies have shown that the transition state is an ion-pair or zwitterion-like structure of the type RC^{-}–H_3O^{+} with an almost fully transferred proton. Salting-in of such structures by large ion salts and by organic molecules would be expected and indeed has been observed for various dipolar species.[15] In contrast, alkali halides, as here, usually cause salting-out of dipolar species. We conclude that the observed rate changes (a) are principally to be explained by effects on the activity coefficient of the transition state and (b) are in the directions predicted by the structure of the transition state and by known salting-in and salting-out effects for dipolar species of its type.

This analysis offers a rationalization for the rate increase in salt solutions and at low mole fractions of organic solvents, but no real interpretation as to the nature of the underlying solvent effects is involved. One of the many factors which may determine free energies of transfer[10b,12] is the effect of changes in solvent structure, and we next turn to this.

No fully satisfactory model for liquid water has been devised. For our purposes it is sufficient to assume the extensive presence of hydrogen-bonded clusters of water molecules. It is generally agreed that the introduction into water of low concentrations of molecules containing nonpolar groups leads to an enhancement of the liquid structure.[16] According to the view

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[16] (a) H. S. Frank and W.-Y. Wen, *Discuss. Faraday Soc.*, 24, 133 (1957); (b) F. Franks in ref 6, p 31.

put forward by Frank and Wen, water molecules become ordered around the organic molecule with an increase in hydrogen bonding in this region. Any solute which increases the stability of the water clusters (as measured, for example, by an increase in the molecular reorientation time of liquid water) is said to be structure making. Speaking broadly, nonpolar molecules and large ion salts are structure makers. Small ion salts, as, for example, the alkali metal halides, are generally structure breakers.

A good indication of the effect of solutes on solvent structure is given by their effect on the dielectric dispersion wavelength.[16b,17] Interestingly the relative effects of the tetraalkylammonium and alkali metal halides on the structure of water, as measured by changes in the relaxation wavelength, are almost precisely the same as their relative effects on the rate of detritiation of the malononitriles. The effects of low mole fractions of alcohol and dioxane are similarly correlated. In other words, additives which increase water structure (the organic solvents and the tetraalkylammonium salts) lead to an increased rate of detritiation; the reverse is true for structure breakers. The relative effects of chloride and bromide ions as observed for the tetramethylammonium and tetraethylammonium halides are also in agreement with their expected effects on solvent structure (bromide ion is thought to be a more effective structure breaker).

The particular way in which enhanced water structure increases the rate of proton removal from a malononitrile can be persuasively explained as follows. In aqueous solution the malononitriles are probably surrounded by clusters of hydrogen-bonded solvent molecules. Proton transfer occurs to a water molecule in one of these neighboring clusters, and a solvated hydronium ion is formed. It is well known that the hydronium ion is heavily solvated in aqueous solution as a large hydrogen-bonded complex.[18] It is also likely that the almost fully formed hydronium ion of the transition state is stabilized by several solvent molecules. If proton transfer from malononitrile occurs to a cluster of water molecules, stabilization of the forming hydronium ion by solvent rearrangement within this cluster probably occurs. One would then expect salting-in of the transition state and increased rates in a solvent with greater structure since the stabilization of the hydronium ion is then accomplished more readily. This is observed in solutions of tetraalkylammonium salts and in solutions containing low mole fractions of organic solvents. In the presence of considerably larger mole fractions of organic solvents, however, the water structure is disrupted and this probably contributes to the decrease in rate which is then observed.

In water solutions, the detritiations of malononitrile and *tert*-butylmalononitrile occur with entropies of activation of -22 and -21 eu, respectively, when k values are in M^{-1} sec^{-1} units. These values are about a dozen entropy units more negative than normal, *i.e.*, than the value for a simple "collision theory" frequency factor. The most obvious explanation is that the dipolar transition states are more potent structure makers than the reactants themselves, *i.e.*, that this large negative entropy term is primarily a measure of the enhanced water structure which develops on formation of the transition state. From this point of view, addition of a structure maker such as tetraethylammonium bromide should decrease the required further structure making and hence cause a rate acceleration. The implication of this analysis, that the principal effect of additives will be on the entropies of activation, is now under investigation.

Acknowledgment. We wish to thank Mrs. Sue Garcia and Mrs. Diane Parchomchuk for technical assistance.

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Stopped-Flow Nuclear Magnetic Resonance Spectroscopy

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Abstract: A rapid mixing cell for nmr and a stopped-flow nmr spectrometer have been constructed. Stopped-flow nmr has been applied to the study of the reaction $Ni(NH_3)(H_2O)_5^{2+} + H_3O^+ \rightarrow Ni(H_2O)_6^{2+} + NH_4^+$. The rate constant obtained is in excellent agreement with the rate constant obtained using optical stopped-flow techniques. Several conditions for the applicability of stopped-flow nmr are discussed.

Nmr methods have been widely applied to the study of reactions in chemical and biochemical systems.[1,2] Virtually all of the applications, however, have been studies of exchange reactions at equilibrium. The advent of Fourier transform nmr techniques, which have greatly reduced the time required to obtain an nmr spectrum,[3] has focused attention on the possibility of using nmr to study rapid irreversible chemical reactions (and transient phenomena such as CIDNP).

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