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Kinetics of the pH-Independent Hydrolysis of Bis(2,4-dinitrophenyl) Carbonate in Acetonitrile−Water Mixtures: Effects of the Structure of the Solvent

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The pH-independent hydrolysis of bis(2,4-dinitrophenyl) carbonate, DNPC, in aqueous acetonitrile was studied spectrophotometrically from 20 to 45 °C. The binary solvent composition covers [H_2O] from 0.02 to 51.39 M, corresponding to the water mole fraction, χ_w, from 0.100 to 0.971. The dependence of log (k_{obs}), the observed rate constant, on χ_w is sigmoidal and is similar to the dependence of the solvent polarity scale $E_T(30)$ on χ_w for the same solvent mixture. As a function of decreasing χ_w, the Gibbs free energy of activation gradually increases, but $\Delta H^\ddagger$ and $\Delta S^\ddagger$ show a complex, quasi-mirror image dependence on χ_w. Plots of log (k_{obs}) versus log [water] do not allow calculation of *a single kinetic order* with respect to water over the entire range of [water]. The structure of the transition state was probed by a proton inventory study carried out at $\chi_w = 0.453$, 0.783, and 0.871, respectively. Plots of observed rate constants versus the atom fraction of deuterium in the solvent curve downward, and the results were fitted to a transition-state model that contains DNPC and two water molecules. Thus, the sigmoidal dependence of log (k_{obs}) on log [water] is not due to an increase in the number of water molecules in the transition state as a function of increasing [water]. The similarity of plots of log (k_{obs}) versus χ_w and $E_T(30)$ versus χ_w suggest similar solute−solvent interaction mechanisms, namely H-bonding and dipolar interactions. Kinetic results are discussed in terms of effects of the structure of acetonitrile−water mixtures on the solvation of reactant and transition states.

Introduction

Binary mixtures of water and organic solvents are extensively used in organic synthesis and in physical organic chemistry studies of, e.g., acyl-transfer reactions. The reasons are partially practical and are often connected with solubility constraints. On the other hand, there is an increasing interest in understanding the effects of pure solvents and their mixtures on chemical processes, i.e., on rates and equilibria of chemical reactions.[1−6] In the analysis of solvent effects, extensive use is made of their microscopic polarities determined with solvatochromic probes. The so called E_T scale is calculated from the relationship

$$E_T\,(\text{kcal/mol}) = 28591.5/\lambda_{max}\,(\text{nm}) \qquad (1)$$

where λ_{max} is the wavelength of maximum UV−vis absorption of the probe.[2] It is now realized, however, that solvent "polarity" is a deceptively simple term because calculated E_T values contain contributions from dipolarity/polarizability and H-bond donation (acidity) and acceptance (basicity) of both the solvent and the solvatochromic probe. Consequently, correlations between, e.g., rate constants or equilibrium constants and the solvent polarity are complex both in pure and mixed solvents. In the latter case, preferential solvation of the relevant species (probes, reactants, and transition states) by one component of the solvent mixture introduces additional complexity, and the importance of this factor has been only recently analyzed in some detail.[2,7−10]

We report here on the pH-independent hydrolysis of bis(2,4-dinitrophenyl) carbonate, DNPC, in acetonitrile−water mixtures over [H_2O] 0.02 to 51.39 M, corresponding to the water mole fraction range χ_w 0.100 to 0.971. We used DNPC because mechanisms of "water reactions" are relatively simple[1] and because data are available for the spontaneous hydrolysis of the structurally similar bis(4-nitrophenyl) carbonate, NPC.[11−13] Additionally, water is

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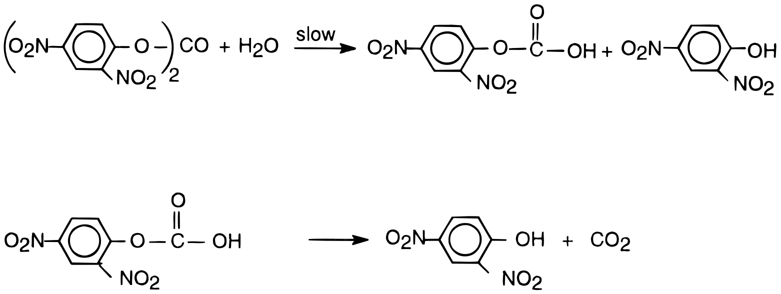
Scheme 1



(2)

(3)

a solvent and a reactant; therefore, kinetic results can be used to probe the properties of the binary solvent mixture and solute–solvent interactions. We show that the complex dependence of reaction rate constants and activation parameters on [H_2O] is not due to a change in the number of water molecules in the transition state. It reflects, however, effects of acetonitrile–water interactions on solvation of reactant and transition states.

Results And Discussion

The reaction investigated is given by Scheme 1. It is a water reaction over the entire χ_w range because k_{obs} is independent of [HCl] from 0.005 to 0.05 M for $\chi_w = 0.221$, 0.783, and 0.948, respectively. Hydrolysis of DNPC produces 2 equiv of 2,4-dinitrophenol, and the reaction shows a sharp isosbestic point at $\lambda = 272$ nm (25 °C, 30% acetonitrile in water). Additionally, excellent pseudo-first-order kinetics were always observed; identical rate constants were obtained in the presence or absence of 1.5×10^{-5} M 2,4-dinitrophenol; an initial rapid release of 2,4-dinitrophenol was not detected. Thus, by analogy to the pH-independent hydrolysis of NPC, the intermediate of the first step (the monoester of carbonic acid, eq 2) does not accumulate; i.e., the first step is rate limiting.[11–13]

There is some discrepancy between rate constants of the hydrolysis of NPC, which were reported by two different groups using almost identical experimental conditions;[12,13] inhomogeneity problems may have led to the reported differences in k_{obs}.[13] Because DNPC is more hydrophobic than NPC, we paid attention to solution homogeneity, especially in the water-rich region. We found that k_{obs} is independent of [ester] in the range $(1.0–4.0) \times 10^{-5}$ M. In the log (absorbance) versus time plots we judged the quality of fit *both* from value of the sum of squares of the residuals, ΣQ, and from change of residuals with time, always at random. The adverse consequences of solution inhomogeneity on the accuracy of rate data have been discussed elsewhere.[14]

Table 1 shows the dependence of k_{obs} on [water] or χ_w from 20 to 45 °C. A plot of log (k_{obs}) versus χ_w is shown in part (A) of Figure 1; the points are experimental, and the solid sigmoidal lines were calculated by a fourth power polynomial dependence of log (k_{obs}) on χ_w (eq 4),

$$\log (k_{obs}) = a + b(\chi_w) + c(\chi_w)^2 + d(\chi_w)^3 + e(\chi_w)^4 \quad (4)$$

where *a*–*e* are regression coefficients. Figure 1B shows the relationship between $E_T(30)$ values, plotted in its reduced dimensionless form [$E_T(30)_{red}$, eq 5], and χ_w. This

$$E_T\,(30)_{red} = [E_T(30)_{binary\ mixture} - E_T(30)_{acetonitrile}]/[E_T(30)_{water} - E_T(30)_{acetonitrile}] \quad (5)$$

polarity scale is based on 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate, RB, the most studied solvatochromic probe both in pure and in mixed solvents.[2] The points are from the literature,[2] and the solid sigmoidal line was calculated by a fifth power polynomial dependence of $E_T(30)_{red}$ on χ_w. Although this gives an excellent fit (correlation coefficient, cc, = 0.9998, ΣQ = 0.0056), a fourth power polynomial dependence also gives a satisfactory fit (cc = 0.9963, ΣQ = 0.0221) The plots in Figure 1A,B show a remarkable resemblance, a fact that will be discussed below.

Table 1. Dependence of the Observed Rate Constants (k_{obs}) on [Water] or the Mole Fraction of Water (χ_w) at Different Temperatures for the pH-Independent Hydrolysis of DNPC in Acetonitrile–Water Mixtures

[water], M/water mole fraction, χ_w	10^4k_{obs}, s^{-1}, 20 °C	10^4k_{obs}, s^{-1}, 25 °C	10^4k_{obs}, s^{-1}, 30 °C	10^4k_{obs}, s^{-1}, 35 °C	10^4k_{obs}, s^{-1}, 45 °C
[2.02]/0.1	0.22	0.29	0.32	0.41	0.71
[4.91]/0.221	1.44	1.98	2.70	3.60	6.20
[8.74]/0.351	3.41	4.89	6.98	9.62	18.23
[12.29]/0.453	4.92	7.38	10.49	15.13	28.54
[16.31]/0.552	6.39	9.75	14.74	20.50	40.08
[21.86]/0.649	8.24	12.97	19.13	27.30	51.02
[25.25]/0.701	10.01	15.39	22.29	32.51	63.11
[28.36]/0.746	11.65	18.36	28.55	38.81	79.71
[31.31]/0.783	14.70	22.89	34.38	45.59	97.25
[39.52]/0.871	27.89	42.18	63.81	78.26	168.38
[42.81]/0.902	37.62	56.27	84.58	105.57	225.85
[48.43]/0.948	62.03	93.53	135.26	160.80	320.37
[51.39]/0.971	83.34	123.04	162.11	207.94	396.17

The slope of a linear plot of log (k_{obs}) versus log [water] is the reaction kinetic order with respect to water; however, such plots (not shown) are sigmoidal for DNPC. An order of 2.1 has previously been calculated for the spontaneous hydrolysis of NPC in aqueous acetonitrile for χ_w from 0.23 to 0.43.[13] For χ_w from 0.100 to 0.453, our data yield a similar order (1.9 ± 0.2), but for χ_w 0.871 to 0.971 they yield temperature-dependent orders that decrease from 4.1 at 20 °C to 3.2 at 45 °C. Thus, a *single* kinetic order with respect to water cannot be obtained from our data over the *entire range* of [H_2O]!

The dependence of the activation parameters on χ_w is listed in Table 2 and is shown graphically in Figure 2. As a function of increasing χ_w, $\Delta G^‡$ gradually decreases due to complex variations, i.e., an initial increase then decrease of *both* $\Delta H^‡$ and $\Delta S^‡$.

How can the dependence of log (k_{obs}) and of the activation parameters on χ_w be explained? The above-mentioned kinetic orders may be taken to indicate that

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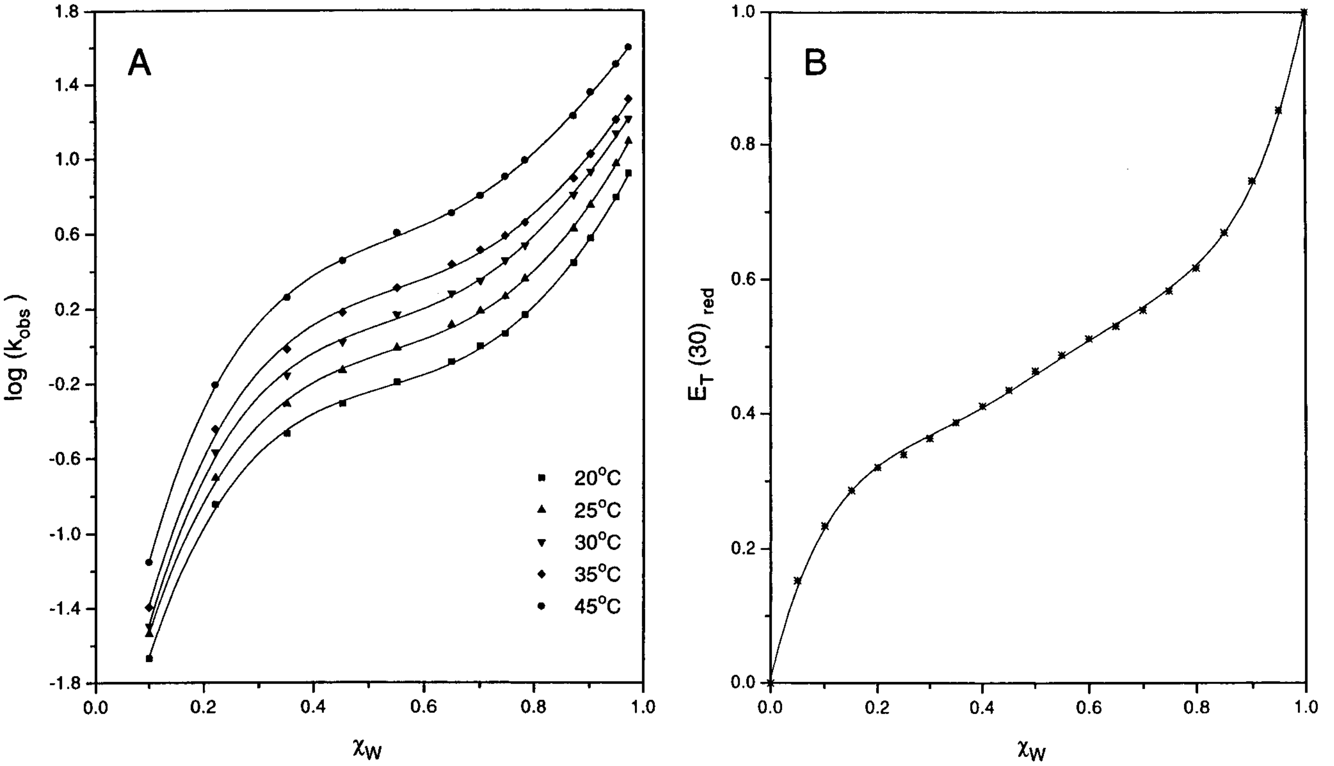

Figure 1. (A) Dependence of log (k_{obs}), the observed rate constant on χ_w, the mole fraction of water in aqueous acetonitrile, at different temperatures. The points are experimental and the solid curve was calculated from eq 4. (B) Dependence of the solvent polarity scale $E_T(30)$ on χ_w. The points were taken from ref 20b, and the solid curve was calculated from a fifth power polynomial dependence of $E_T(30)$ on χ_w.

Table 2. Activation Parameters for the pH-Independent Hydrolysis of DNPC in Acetonitrile−Water Mixtures[a]

water mole fraction, χ_w	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, cal/K mol	$\Delta G^\ddagger$, kcal/mol
0.1	7.8	−53.1	23.6
0.221	10.2	−41.2	22.5
0.351	11.8	−34.0	21.9
0.453	12.4	−31.3	21.7
0.552	13.0	−28.8	21.6
0.649	12.9	−28.7	21.5
0.701	13.0	−27.8	21.3
0.746	13.5	−25.7	21.2
0.783	13.2	−26.4	21.1
0.871	12.4	−27.7	20.7
0.902	12.4	−27.1	20.5
0.948	11.2	−30.2	20.2
0.971	10.7	−31.5	20.1

[a] The errors are ± 0.1 kcal/ mol ($\Delta H^\ddagger$ and $\Delta G^\ddagger$) and 0.5 cal/K mol ($\Delta S^\ddagger$).

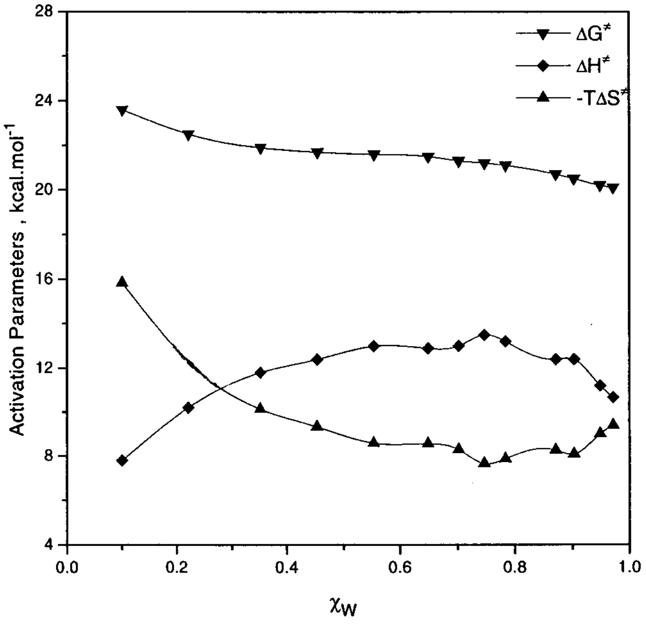

Figure 2. Dependence of the reaction activation parameters on χ_w.

the number of water molecules in the transition state, TS, depends on [H_2O]. Examples of such dependence are known, e.g., the kinetic order with respect to water for the spontaneous hydration of chloral varies from ca. 4 to ca. 2 when [water] is increased from 0.25 to 46.3 M.[15] The TS for the hydration of 1,3-dichloroacetone contains the ketone and either one, two, or three molecules of water, depending on whether the reaction is carried out in the presence of detergent aggregates in *n*-hexane (i.e., reverse micelles and water-in-oil microemulsion) or in aqueous dioxane, respectively.[16,17] Finally, the number of water molecules in the transition state of the imidazole-catalyzed hydrolysis of 4-nitrotrifluoroacetanilide in aqueous acetonitrile was reported to increase from one to four as a function of increasing [water].[18]

In order to probe the number of water molecules in the TS, we subjected the reaction to a proton inventory study that we carried out at χ_w = 0.453, 0.783, and 0.871, respectively. The use of proton inventory to probe the structure of TS is documented,[13,16,19] and only a brief

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Table 3. Dependence of the Rate Constants (k_n) for the Hydrolysis of DNPC on the Atom Fraction of Deuterium (n) in Mixtures of Acetonitrile−H_2O−D_2O at Different Water Mole Fractions, χ_w, at 25 °C

atom fraction of deuterium, n	10^4k_n, s^{-1}, $\chi_w = 0.453$	10^4k_n, s^{-1}, $\chi_w = 0.783$	10^4k_n, s^{-1}, $\chi_w = 0.871$
0.000	7.380	22.891	42.181
0.167	6.652	20.423	37.824
0.327	5.978	18.165	34.143
0.477	5.366	16.413	30.689
0.662	4.655	14.098	26.806
0.834	4.061	12.308	23.631
0.998	3.252	10.400	20.690

account will be given here. One uses the observed solvent kinetic isotope effect to estimate the number of hydrogens (hence water molecules in our case) that participate in the TS. This number, and other chemical information, e.g., activation parameters, enable one to suggest a structure for the TS. The observed rate constant, k_n, in a H_2O−D_2O mixture is related to the observed rate constant in pure H_2O, k_o, by the equation

$$k_n/k_o = \prod_{i}^{TS}(1 - n + n\varphi_i^{\ddagger})/\prod_{j}^{GS}(1 - n + n\varphi_j) \qquad (6)$$

where n is the atom fraction of deuterium in the solvent. All TS hydrogens (i) that contribute to the isotope effect possess a term in the right-hand numerator of eq 6. These terms are multiplied, as are the terms in the right-hand denominator, corresponding to the exchangeable ground state, GS, hydrogens (j). Each hydrogen site is associated with a fractionation factor defined as, e.g., for an exchangeable site (s);

$$\varphi_S = [D/H]_s/[D/H]_{solvent} \qquad (7)$$

i.e., φ_s expresses the preference of deuterium for the site (s) relative to that of bulk solvent. Analysis of the present water reaction is simplified by the fact that DNPC carries no exchangeable hydrogens, and the other reactant, water, has a $\varphi = 1$ by definition. Consequently, the denominator of eq 6 is unity, and we need consider only hydrogens of the TS.

Table 3 and Figure 3 show the dependence of k_n on n for three different χ_w.

The next step is to fit our data to a *chemically plausible* model for the transition state.[20] Before doing this, it is instructive to discuss proton inventory results of the spontaneous hydrolysis of NPC.[12,13] Menger and Venkatasubban adjusted their data to a straight line. This would lead to a TS that contains one water molecule, a suggestion that was discarded in favor of a TS containing NPC and two water molecules. In order to account for the linearity of their k_n versus n plot, they argued that the TS is reached at an early stage of the reaction, i.e., when there is little transfer of H_a from the "nucleophilic" water to the "general base" water, as shown in Figure 4 (for sake of simplicity, we draw H_a symmetrically between the two water molecules). According to their assumption, the observed isotope effect is essentially due to H_a, whereas H_b is expected to have a fractionation factor of unity and should not contribute to the observed kinetic isotope effect.[12] Gopalakrishnan and Hogg studied the hydrolysis of NPC under almost identical experimental conditions and found that the k_n versus n plot curves downward. They fitted their data to eq 8

$$k_n = k_o(1 - n + n\varphi_a^{\ddagger})(1 - n + n\varphi_c^{\ddagger})^2 \qquad (8)$$

where H_a contributes a primary isotope effect ($\varphi_a^{\ddagger}$ = 0.565), H_b does not contribute an isotope effect, and H_c contributes a secondary isotope effect ($\varphi_c^{\ddagger} = 0.889$).[13] That is, both groups agree that the TS contains NPC and two water molecules, but there is discrepancy regarding the degree of transfer of H_a. It is interesting to note that although Menger's data were fitted to a straight line, they can be made to fit eq 8 with $\varphi_a^{\ddagger} = 0.51$ and $\varphi_c^{\ddagger} = 0.92$ simply by taking into account the reported error in k_o! We attribute these possibilities of fit to the small degree of curvature of the k_n versus n plot.

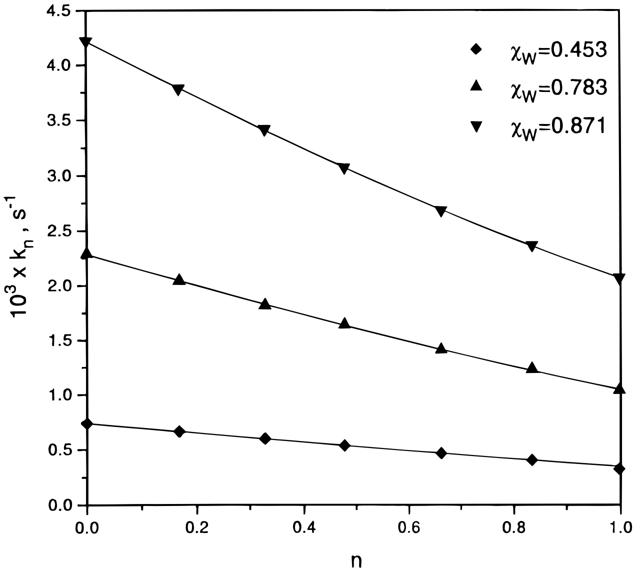

Figure 3. Results of the proton inventory study of the reaction, showing the dependence of observed rate constant (k_n) on the atom fraction of deuterium (n) in acetonitrile−H_2O−D_2O mixtures. The points are experimental, and the solid curves were calculated by eq 8.

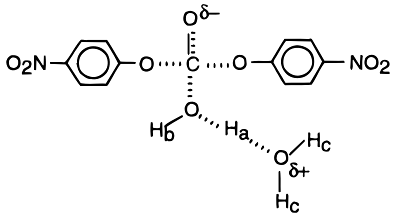

Figure 4. Structure of TS for the spontaneous hydrolysis of NPC.[13]

Because of the structural similarity between NPC and DNPC and the similarity of their solvent kinetic isotope effects, 2.2 for NPC,[13] 2.27, 2.20, and 2.04 for the hydrolysis of DNPC at χ_w = 0.453, 0.783, and 0.871, respectively, we fitted our data, Figure 3, to eq 8 The quality of the data fit is shown by $\sum Q$, between 1.2×10^{-6} and 5×10^{-5}, and the resulting fractionation factors are $\varphi_a^{\ddagger} = 0.583$, 0.588, and 0.708 and $\varphi_c^{\ddagger} = 0.901$, 0.818, and 0.832 for χ_w = 0.453, 0.783, and 0.871, respectively. These fractionation factors are similar to those obtained for NPC; they show some dependence on χ_w, probably because of slight differences in the degree of transfer of

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H_a. The relevant point is that three hydrogens are contributing to the kinetic solvent isotope effect, i.e., the *TS contains DNPC and two water molecules, over the entire range of* χ_w.

Before addressing solvent effects on the hydrolysis of DNPC, we discuss some relevant aspects of the structure of acetonitrile−water mixtures:[2,7−10,21−24] when the organic solvent is added to water it replaces the uncoordinated water molecules. The limit of χ_W beyond which acetonitrile cannot be accommodated within the cavities of ordinary water is $\chi_w \approx 0.85$.[10,21] Below this χ_w limit solvent microheterogeneity sets in, and there exists two “microdomains”, one highly structured consisting predominantly of coordinated water molecules and a relatively disordered one containing mostly acetonitrile H-bonded to water molecules.[21,22] Calculations of the Kirkwood−Buff integral functions showed that the probability of finding a water molecule close to an acetonitrile molecule is minimum at $\chi_w \approx 0.65$.[10,23a,b] Addition of more acetonitrile leads to a change in the relative concentrations of the two microdomains, but their compositions do not vary appreciably. At $\chi_w \leq 0.3$ the water clusters have become so few and far apart that new interactions set in. Water−acetonitrile interactions become important; this results in the formation of complexes, e.g., $(CH_3CN)_m - H_2O$ where $m = 1-4$.[10,23c,24a,b] At still lower χ_w values, the structure of acetonitrile dominates, and species such as $(CH_3CN)_m$ and CH_3CN are abundant.[23c] It should be born in mind, however, that the onset of formation of the different regions is not sharp and is dependent on the method used to study the system.[10]

In addressing the results shown in Figures 1 and 2, the following points are relevant: (i) A detailed analysis of solvent kinetic effects on hydrolysis of DNPC *over the whole* χ_w range is beyond the scope of the present work and may not even be possible because of the abovementioned solvent microheterogeneity. This explains the fact that studies in which overall solvent kinetic effects have been separated into contributing interactions of solvent components with GS and TS have been confined to the water-rich region.[6c,25,26] Additionally, experimental determination of thermodynamic functions of transfer of DNPC from a reference solvent to aqueous acetonitrile mixtures that could shed light on solvent interactions with GS and TS[27] is not feasible because of the facile hydrolysis of this ester. (ii) Our results indicate that solvatochromism of RB in acetonitrile−water mixtures is very different from that of the small, hydrophilic probe 1-methyl-3-oxypyridinium betaine.[8c] This indicates that RB, being very hydrophobic (solubility in water $= 7.2 \times 10^{-6}$ M),[2] is solubilized in the ranges $0.4 \geq \chi_w \geq 0.8$ by acetonitrile−water complexes that are either rich in acetonitrile (for $\chi_w \leq 0.4$) or rich in water (for $\chi_w \geq 0.8$). Alternatively, it is solubilized by the acetonitrile clusters in the region of microheterogeneity ($0.4 \leq \chi_w \leq 0.8$). On the other hand, 1-methyl-3-oxypyridinium betaine (solubility in pure water >2.0 M)[8a] forms its own solvation sphere, the composition of which is always rich in water.[8c] The remarkable similarity of Figure 1A,B indicates that both processes, i.e., solvation of RB and hydrolysis of DNPC are sensitive to the same interaction mechanisms, mainly H-bonding and dipolar interactions. (iii) Both RB and DNPC are hydrophobic substrates, and there are certainly solvent effects both on GS and TS. One way to explain our data is that solvation of the TS does not change much as a function of χ_w, but the observed solvent effects could be due to the smaller number of GS molecules with adequate solvation to reach the TS. This limiting case does not fit our results because it implies an almost constant $\Delta H^{\ddagger}$;[6a] this is not observed, Table 2. Because the Gibbs free energies of transfer of several nonelectrolytes from water to mixtures of water and aprotic solvents are relatively insensitive to the binary solvent composition,[27,28] it is plausible that kinetic solvent effects on the GS are not dominant in the present reaction, so that we concentrate on solvation of the TS.[6b−e] (iv) In the acetonitrile molecule the partial negative dipole charge is localized on the nitrogen while the positive charge of the dipole is diffused onto the methyl group. Hence, it can solvate positive centers much stronger than negative centers. On the other hand, the water molecule is capable of solvating both types of centers effectively. In the TS shown in Figure 4, the partial negative charge is still localized on the carbonyl oxygen while the positive charge is diffused; i.e., the TS is more efficiently solvated by water, and solvent kinetic effects should be sensitive to the state of water in the binary solvent mixture.

The initial addition of acetonitrile to water (χ_w from 0.971 to 0.871) results in a decrease of k_{obs} and increase in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ since uncoordinated water molecules would be considerably more polar (i.e., of higher kinetic reactivity) and form stronger H-bonds than their coordinated counterparts.[1,29] In the intermediate χ_w region (χ_w from 0.783 to 0.552), the structure of each microdomain should remain relatively constant so long as they exist.[21] Consequently, the solvent-dependent process, i.e., hydrolysis of DNPC or solvation of RB, may vary little as shown in Figure 1A,B. Addition of more acetonitrile ($\chi_w \leq 0.453$, Table 2) results in formation of mobile acetonitrile−water clusters. In this acetonitrile−rich region the rate constant decrease simply reflects the decrease in [water]. The observed decrease of $\Delta H^{\ddagger}$ may be due to the fact that water−acetonitrile interactions are weaker that water−water interactions.[21−24] The accompanied entropy decrease occurs because the reactant water has more degrees of freedom. It is interesting that the gradual increase in $\Delta G^{\ddagger}$ ($\Delta\Delta G^{\ddagger} = \Delta G^{\ddagger}\chi_{w0.1} - \Delta G^{\ddagger}\chi_{w0.453}$) is due to a loss of entropy ($T\Delta\Delta S^{\ddagger} = -6.5$ kcal/mol, Table 2) not compensated by a gain in enthalpy ($\Delta\Delta H^{\ddagger} = -4.6$ kcal/mol, Table 2).

Conclusions

(i) Calculation of the kinetic order with respect to one component of a binary solvent mixture should be based

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on rate constants obtained over the entire range of solvent composition.[6b] Care should be exercised when kinetic orders with respect to water are interpreted in terms of the number of water molecules in the TS. The reason is that slopes of plots of log k versus log [water] may be affected by the nonideal behavior of the solvent mixture and by preferential solvation of GS and/or TS by one component of the mixture.[7−10] The proton inventory technique can be fruitfully used to solve this problem. (ii) The TS of the present reaction contains DNPC and two water molecules, independent of [water] in the binary solvent mixture. (iii) Solvation of RB and hydrolysis of DNPC seem to be sensitive to the same solute−solvent interactions, namely, H-bonding and dipolar interactions; these are modulated by the water−acetonitrile interactions.

Experimental Section

Materials. All chemicals were obtained from Aldrich or Merck and were purified as described elsewhere.[30] DNPC was prepared by stirring a suspension of sodium 2,4-dinitrophenoxide (20 mmol) with phosgene (15 mmol) in toluene for 6 h at room temperature. The solvent was evaporated and the residue recrystallized from benzene. It was further purified by sublimation under reduced pressure. The impurity, i.e., 2,4-dinitrophenol, sublimes, leaving the pure carbonate ester as a slightly yellowish solid, mp 137−138 °C. Several melting points are reported for DNPC in the literature, e.g., 125.5 °C,[31a] 148 °C,[31b] and 130−131 °C.[31c] IR (KBr, Perkin-Elmer FT-1750): 3116, 1803, 1617, 1540, 1346 cm^{-1}. Anal. Calcd for $C_{13}H_6N_4O_{11}$: C, 39.59; H, 1.53; N, 14.22. Found: C, 39.61; H, 1.53; N, 14.24.

Kinetic Measurements. Glass double-distilled water was used throughout. Binary solvent mixtures were prepared by weight; they contained 0.01 M HCl or 0.01 M DCl in order to suppress any base-catalyzed hydrolysis. The deuterium content of D_2O and DCl in D_2O was determined by NMR (Bruker AC-200) by the internal reference method.[19] The DNPC stock solution was 0.005 M in dry acetonitrile.

Kinetic runs were carried out with a Beckman DU-70 UV−vis spectrophotometer, interfaced to a microcomputer and fitted with a thermostated cell holder whose temperature was kept constant to ± 0.05 °C (checked with a Lauda R 42/2 digital thermometer). All runs were carried out in triplicate, under pseudo-first-order conditions, and were initiated by injecting 20 μL of the DNPC stock solution into 7 mL of the thermally equilibrated binary solvent mixture, contained in a 5 cm path length quartz cell. The reaction mixture was homogenized by a hand-held, battery-operated Hellma-type 338.004 microstirrer. The reaction was followed by monitoring the liberation of 2,4-dinitrophenol at $\lambda = 302$ nm as a function of time. The log (absorbance) versus time plots were rigorously linear over more than 5 half-lives. Values of k_{obs} were calculated from the slopes of these plots. The relative standard deviation in k_{obs}, i.e., ((standard deviation/k_{obs})100), was $\leq$0.2%, that between k_{obs} of a triplicate was $\leq$0.5%.

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