δ 16.46. In Me$_2$SO-d_6 solution, two doublets were observed for DNBF: H$_5$, δ 9.19; H$_7$, δ 8.92; $^4J_{5,7}$ = 1.8 Hz. The singlet of TNB was at δ 9.13.

Acknowledgment. The authors thank the North Atlantic Treaty Organization for a grant (NATO Res. 1540) to F.T. and M.J.S. supporting this research.

Registry No. **5**, 77902-62-6; **6a**, 77902-63-7; **6b**, 77902-64-8; **9a/9b**, 77902-65-9; **11**, 77902-66-0; **12a/12b**, 77902-67-1; **13**, 77902-68-2; **14a/14b**, 77902-69-3; **15a/15b**, 77902-70-6; 4,6-dinitrobenzofuroxan, 5128-28-9; 3-hydroxycyclopent-2-en-1-one, 5870-62-2; 2,4-pentanedione, 123-54-6; 4-hydroxypent-3-en-2-one, 1522-20-9; 3-methyl-2,4-pentanedione, 815-57-6; 4-hydroxy-3-methyl-3-penten-2-one, 1522-25-4.

Comparative Study of the Water-Catalyzed Hydrolysis of [(*p*-Nitrophenyl)sulfonyl]methyl Perchlorate in 1,4-Dioxane–Water and in 1,3-Dioxane–Water

Klaas Remerie and Jan B. F. N. Engberts*

Department of Organic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Received December 29, 1980

Pseudo-first-order rate constants (k_{obsd}) and thermodynamic activation parameters have been compared for the water-catalyzed hydrolysis of [(p-nitrophenyl)sulfonyl]methyl perchlorate (1) in 1,4-dioxane–water and in 1,3-dioxane–water. Characteristic differences in the kinetic basicities of both reaction media are only observed below n_{H_2O} = 0.80 and most likely reflect the specific hydrogen bonding interactions between water and the organic cosolvent. The structural properties of both aqueous binaries are critically discussed, and it is concluded that the maxima in k_{obsd} at about n_{H_2O} = 0.80 in both solvent mixtures do not reflect an enhanced degree of water structure at this solvent composition.

The wide range of dielectric constants (ϵ = 2.2–78, 25 °C) that can be attained in mixtures of 1,4-dioxane with water, together with their excellent solubilizing properties, seem to make them ideal media for synthetic and mechanistic studies in organic chemistry. However, the 1,4-dioxane–water system exhibits pronounced deviations from ideal behavior in the thermodynamic sense,[1] which especially complicate mechanistic investigations. In the water-rich region, the anomalies have been frequently attributed[2] to "water-structure effects". Unfortunately, however, there is strong controversy in the literature concerning the interpretation of kinetic solvent effects in this popular mixed aqueous system since in different studies, 1,4-dioxane has been characterized either as a water-structure breaker or as a water-structure promotor.[3] Structure-making properties have been claimed on the basis of ultrasonic absorption measurements,[4] infrared, raman,[5,6] and NMR spectroscopic studies,[7] and dielectric relaxation measurements.[8] The results of these studies were interpreted in terms of structure promotion upon the addition of 1,4-dioxane to water down to a mole fraction of water (n_{H_2O}) of ca. 0.8. By contrast, several properties of the 1,4-dioxane–water system have been rationalized by assuming a destabilizing effect of the organic cosolvent on the three-dimensional hydrogen bond regime. Strong evidence for this idea is provided by the structural part of the temperature of maximum density (TMD) depression[9] and by studies of the solubility of argon in 1,4-dioxane–water mixtures.[10] Evidence in favor of structure breaking is also provided by X-ray diffraction studies,[11] the effect of pressure on density,[12] apparent molar heat capacities,[13] partial molal excess heat capacities,[14] excess molar volumes,[15] enthalpies of transfer of slightly soluble salts,[16] and the enthalpies of hydrophobic interaction in combination with partial molar volumes.[17]

Described herein is a comparative study of the rates and thermodynamic activation parameters of the water-catalyzed hydrolysis of [(*p*-nitrophenyl)sulfonyl]methyl perchlorate (1) in 1,4-dioxane–water and 1,3-dioxane–water.

$$\underset{\textbf{1}}{p\text{-}NO_2C_6H_4SO_2CH_2OClO_3} + H_2O \xrightarrow{\text{slow}} p\text{-}NO_2C_6H_4SO_2\bar{C}HOClO_3 + H_3O^+ \xrightarrow[\text{fast}]{H_2O} p\text{-}NO_2C_6H_4SO_2H + HCO_2H + ClO_3^-$$

The mechanism of this reaction involves general-base catalysis by water, implying rate-determining deprotonation at the α-sulfonyl carbon.[18] In previous studies, the process

---

[1] Franks, F., Ed. "Water, a Comprehensive Treatise"; Plenum: New York, 1973; Vol. 2.

[2] Already suggested by: Stallard, R. D.; Amis, E. S. *J. Am. Chem. Soc.* **1952**, *74*, 1781–1790.

[3] A useful definition of water structure is given in: Ben-Naim, A. *Biopolymers* **1975**, *14*, 1337–1355. See also: Ben-Naim, A. "Hydrophobic Interaction"; Plenum, New York, 1980; p 222.

[4] Baumgartner, E. K.; Atkinson, G. *J. Phys. Chem.* **1971**, *75*, 2336–2340.

[5] Gorbunov, B. Z.; Naberukhin, Y. I. *J. Mol. Struct.* **1972**, *14*, 113–116; *J. Struct. Chem. (Engl. Transl.)* **1972**, *13*, 16–22.

[6] Naberukhin, Y. I.; Shuiskii, S. I. *J. Struct. Chem. (Engl. Transl.)* **1967**, *8*, 544–549.

[7] Glew, D. N.; Mak, H. D.; Rath, N. S. *J. Chem. Soc., Chem. Commun.* **1968**, 264–265.

[8] (a) Garg, S. K.; Smyth, C. P. *J. Chem. Phys.* **1965**, *43*, 2959–2965. (b) Rizk, H. A. *Z. Phys. Chem.* **1969**, *66*, 257–268.

[9] Franks, F.; Watson, B. *Trans. Faraday Soc.* **1967**, *63*, 329–334.

[10] Ben-Naim, A.; Yaacobi, M. *J. Phys. Chem.* **1975**, *79*, 1263–1267.

[11] Cennamo, F.; Tartaglione, E. *Nuovo Cimento* **1959**, *11*, 401–409.

[12] Pearce, P. J.; Strauss, W. *Aust. J. Chem.* **1968**, *21*, 1213–1219.

[13] Cabani, S.; Conti, G.; Martinelli, A.; Matteoli, E. *J. Chem. Soc., Faraday Trans. 1*, **1973**, 2112–2123.

[14] Mohanty, R. K.; Sarma, T. S.; Subrahmanyam, S.; Ahluwalia, J. L. *Trans. Faraday Soc.* **1971**, *67*, 305–315.

[15] Cabani, S.; Conti, G.; Lepori, L. *J. Phys. Chem.* **1972**, *76*, 1338–1343.

[16] Bright, L. L.; Jezorek, J. R. *J. Phys. Chem.* **1975**, *79*, 800–808.

[17] Oakenfull, D.; Fenwick, D. E. *J. Chem. Soc., Faraday Trans. 1*, **1979**, 636–645.

0022-3263/81/1946-3543$01.25/0

has already been utilized as a probe for the kinetic basicity of mixtures of water with organic solvents[19] and of aqueous electrolyte solutions.[20]

An attempt will be made to analyse the kinetic consequences of a relatively small structural change in the organic cosolvent (1,3-dioxane instead of 1,4-dioxane). This type of approach is not frequently followed. Quite generally there are large changes in the organic cosolvent (for example, EtOH, Me_2SO, DMF, MeCN) when comparative studies are carried out on solvent effects in aqueous binaries. Although these studies may be highly valuable, it must be realized that there occur large changes in all types of solute–solvent and solvent–solvent interactions which determine the overall kinetic response to solvent variation. Very often, all these contributions will be partly compensating, but the complexity of the problem remains rather frustrating. Therefore, a comparison of solvent effects on a mechanistically very simple reaction in 1,4-dioxane–water and 1,3-dioxane–water over a large solvent composition range was deemed worthwhile.

Experimental Section

Materials. The synthesis of the covalent perchloric acid ester 1 has been reported previously.[20,21] The compound was stored in the dark at -20 °C. 1,4-Dioxane (Merck, Uvasol) was distilled under dry nitrogen, filtered through active, neutral alumina in a nitrogen atmosphere, and stored under nitrogen in the dark at 3 °C. 1,3-Dioxane was prepared by a literature procedure[22] and was purified and stored as described for 1,4-dioxane. Water was demineralized and distilled twice in an all-quartz distillation unit. The solvent mixtures were all made up by weight.

Kinetic Measurements. Pseudo-first-order rate constants (reproducible to within 3%) were determined by using the UV technique reported previously.[20,23] Substrate concentrations were in the range 10^{-4}–10^{-5} M. In all solvent mixtures small amounts of HCl (pH ~2.1) were present to suppress hydroxide ion catalysis. No solvolysis of 1 occurred in pure 1,4-dioxane and 1,3-dioxane. No reproducible rate constants could be obtained in 1,3-dioxane–water below $n_{H_2O} = 0.11$. The thermodynamic activation parameters were obtained from rate constants at four different temperatures in the range 20–40 °C. The accuracy of $\Delta H^{\ddagger}$ is ±0.3 kcal mol^{-1} and that of $\Delta S^{\ddagger}$ is ±1 eu. Kinetic data for hydrolysis of 1 in 1,4-dioxane–water have been reported previously.[19]

Results and Discussion

Before we discuss the kinetic solvent effects in the hydrolysis of 1 in 1,4-dioxane–water and 1,3-dioxane–water, we will examine the relevant literature on both solvent systems, focussing special attention on their solvent structural properties.

1,4-Dioxane-H_2O. Those authors who assume a stabilizing effect of 1,4-dioxane on the water structure almost generally base their arguments on the observation of extrema in solvent properties around $n_{H_2O} = 0.80$. This mole fraction would then be the solvent composition for which all cavities in the water structure are occupied by 1,4-dioxane molecules.[8b,24,25] However, it is known that at temperatures below -13 °C 1,4-dioxane forms with water clathrate II structures (1,4-dioxane–$17H_2O$).[26] X-ray studies have revealed that these clathrate II lattices for 1,4-dioxane are slightly expanded as compared with those for smaller guest molecules,[27] most likely as a result of steric strain. These results imply that at high mole fractions of water, 1,4-dioxane does not fit into normal hexagonal lattice cavities and that the water lattice must transform into a dynamic clathrate II structure.[28] Thus, a maximum in the stiffness of the water hydrogen bond network is expected around $n_{H_2O} = 0.95$ which is at a substantially higher water concentration than that suggested by the studies mentioned above ($n_{H_2O} = 0.80$). Interestingly, a small degree of structure making at about $n_{H_2O} = 0.98$ has been suggested by measurements of internal pressures[29] and adiabatic compressibilities.[30]

We submit that at least part of the controversy is caused by the assumption[25] that 1,4-dioxane–water hydrogen bonding interactions are weaker than water–water interactions. However, there is now strong evidence that 1,4-dioxane is more basic than water.[31] This leads us to propose the following model: when small amounts of 1,4-dioxane are added to water, water–water hydrogen bonds are replaced by 1,4-dioxane–water hydrogen bonds, and the degree of water structure is diminished, at least at $n_{H_2O} < 0.95$. Furthermore, the interaction between 1,4-dioxane and water will be accompanied by an enhanced basicity of the complexed water.[32] It is reasonable to assume that around $n_{H_2O} = 0.80$ a maximum number of waters will be hydrogen bonded to 1,4-dioxane (di) in dynamic complexes of the type $di{\cdot}4H_2O$. This is in accord with the observation that maxima in the excess molar heat capacity at constant pressure and at constant volume are reached at $n_{H_2O} = 0.82$ (25 °C).[33] At still higher concentrations of 1,4-dioxane, the number of water molecules hydrogen bonded to 1,4-dioxane will decrease continuously as expressed in the equilibrium shown in eq 1. From n_{H_2O}

$$di{\cdot}4H_2O \underset{-di}{\overset{+di}{\rightleftharpoons}} di{\cdot}3H_2O \underset{-di}{\overset{+di}{\rightleftharpoons}} di{\cdot}2H_2O \underset{-di}{\overset{+di}{\rightleftharpoons}} di{\cdot}H_2O \underset{-di}{\overset{+di}{\rightleftharpoons}} 2di{\cdot}H_2O \quad (1)$$

≈ 0.80 to $n_{H_2O} \approx 0.30$ hydrogen bonding between 1,4-dioxane and water becomes increasingly important at the expense of water–water hydrogen bonding. Below $n_{H_2O} \approx 0.30$ the dilution of the $2di{\cdot}H_2O$ complexes will result in a strong decrease in overall hydrogen bonding. The infrared studies of Gorbunov and Naberukhin[5] are consistent with this model. Although these authors suggest an increase in water structure at low concentrations of 1,4-dioxane, the change in the integrated intensity of the O–D stretch vibration between $n_{HDO} = 1.00$ and 0.80 in 1,4-dioxane–HDO can be easily reconciled with competitive 1,4-dioxane–HDO and (weaker) HDO–HDO hydrogen bonding. Upon addition of more 1,4-dioxane ($n_{HDO} \approx$ 0.80–0.30) the integrated intensity decreases regularly, as expected on the basis of the equilibria suggested above.

---

(18) Bruggink, A.; Zwanenburg, B.; Engberts, J. B. F. N. *Tetrahedron* **1969**, *25*, 5655–5667.

(19) Menninga, L.; Engberts, J. B. F. N. *J. Org. Chem.* **1976**, *41*, 3101–3106.

(20) Menninga, L.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1976**, *98*, 7652–7657.

(21) Engberts, J. B. F. N.; Morssink, H.; Vos, A. *J. Am. Chem. Soc.* **1978**, *100*, 799–802.

(22) Laurent, P. A.; Tarte, P.; Rodrigues, B. *Bull. Soc. Chim. Fr.* **1959**, 946–947.

(23) Menninga, L.; Engberts, J. B. F. N. *J. Phys. Chem.* **1973**, *77*, 1271–1274.

(24) Emel'yanow, M. I.; Mikolaev, I. N.; Samigullin, F. M. *J. Struct. Chem.* (*Engl. Transl.*) **1971**, *12*, 138–140.

(25) Clemett, C. J. *J. Chem. Soc. A* **1969**, 761–765.

(26) Gough, S. R.; Ripmeester, J. A.; Davidson, D. W. *Can. J. Chem.* **1975**, *53*, 2215–2226.

(27) Davidson, D. W.; Gough, S. R.; Lee, F.; Ripmeester, J. A. *Rev. Chim. Miner.* **1977**, *1*, 447–463.

(28) Davidson, D. W. *Can. J. Chem.* **1971**, *49*, 1224–1242.

(29) Dack, M. R. J. *Aust. J. Chem.* **1976**, *29*, 771–778.

(30) Murthy, N. M.; Subrahmanyam, S. V. *Can. J. Chem.* **1978**, *56*, 2412–2416.

(31) Levitt, L. S.; Levitt, B. W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 614–620. See also: Campbell, A. N.; Bhatnagar, O. N. *Can. J. Chem.* **1972**, *50*, 1627–1632.

(32) Das, A. K.; Kundu, K. K. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 730–735.

(33) Murthy, N. M.; Subrahmanyam, S. V. *Indian J. Pure. Appl. Phys.* **1979**, *17*, 620–622.

Table I. Pseudo-First-Order Rate Constants and Activation Parameters for the Neutral Hydrolysis of 1 in 1,3-Dioxane-H_2O at 25 °C

n_{H_2O}	$10^4 k_{obsd}$, s^{-1}	$\Delta G^{\ddagger}$, kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
1.000	32.5	20.85	17.8	−10
0.898	106	20.17	16.9	−11
0.801	161	19.92	13.0	−23
0.799	160			
0.656	135	20.01	10.4	−32
0.502	116	20.10	13.1	−23
0.399	91.6			
0.390	90.0[a]			
0.345	84.1	20.26	12.8	−25
0.250	79.9[b]			
0.203	70.3	20.39	13.9	−22
0.180	73.8			
0.115	63.6			

[a] $k_{obsd}^{H_2O}/k_{obsd}^{D_2O} = 1.24$. [b] $k_{obsd}^{H_2O}/k_{obsd}^{D_2O} = 1.1$.

The more rapid decrease in the integrated intensity below $n_{H_2O} \approx 0.30$ apparently reflects the continuous decrease in the number of hydrogen bonds upon further dilution with the organic cosolvent. Important changes in hydrogen bonding behavior around $n_{H_2O} = 0.85$ and 0.33 are also suggested by the nonlinear electric field effect of the relative permittivity of aqueous 1,4-dioxane (as measured by the Piekara factor $\Delta\epsilon/E^2$) and by a plot of the dipole correlation factor against n_{H_2O}.[34]

1,3-Dioxane–H_2O. Relatively few studies have been made of the 1,3-dioxane–water system. However, from the effect of 1,3-dioxane on the TMD of water[35] it may be concluded that the structure-breaking properties of 1,3-dioxane are more pronounced than those of 1,4-dioxane. The solvent dependence of the excess enthalpy of mixing is rather similar for mixtures of water with 1,3- and 1,4-dioxane.[36] The basicities of both dioxanes are also almost equal.[37] Therefore, the model suggested for the hydrogen bonding interactions in 1,4-dioxane–water is, in principle, also applicable for the 1,3-dioxane–water system. The most important differences comprise the dielectric constants (1,3-dioxane, $\epsilon = 24$;[38] 1,4-dioxane, $\epsilon = 2.2$; 25 °C) and the dipole moments (1,3-dioxane, $\mu = 2.18$ D;[39] 1,4-dioxane, $\mu \approx 0$).

Hydrolysis of 1 in 1,4-Dioxane–H_2O and 1,3-Dioxane–H_2O. Pseudo-first-order rate constants (k_{obsd}) and activation parameters for the neutral hydrolysis of 1 in 1,3-dioxane–water at 25 °C are listed in Table I. The kinetic solvent deuterium isotope effects at low water concentration are similar to those at high water concentration and to those observed in 1,4-dioxane–water.[19] This suggests that in the whole solvent composition range no medium-induced changes in mechanism are involved. Kinetic data for 1,4-dioxane–water were taken from a previous study.[19,40] Figure 1 portrays the change of k_{obsd} for hydrolysis of 1 as a function of solvent composition in both aqueous binaries. These rate constants pertain to water-induced processes since 1 is not solvolyzed in the pure dioxanes. In the region $n_{H_2O} = 1.00$–0.80 the response of k_{obsd} to variation of n_{H_2O} is very similar for both reaction media despite the substantial differences in dielectric constants. This behavior of k_{obsd} is consistent with our model for both aqueous binaries.[41] Water structure is gradually broken down and the kinetic basicity of the water molecules is enhanced as a result of hydrogen bond interactions with the dioxanes. Also in these kinetic studies it is only below $n_{H_2O} = 0.80$ that significant differences between both solvent systems arise, especially when the solvent dependence of the second-order rate constants (k_2

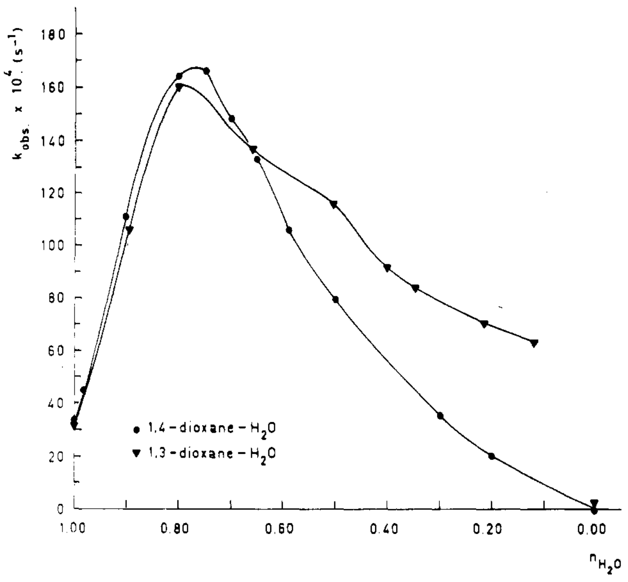

Figure 1. Plots of k_{obsd} vs. n_{H_2O} for the neutral hydrolysis of 1 in 1,4-dioxane–H_2O (●) and in 1,3-dioxane–H_2O (▼) at 25 °C.

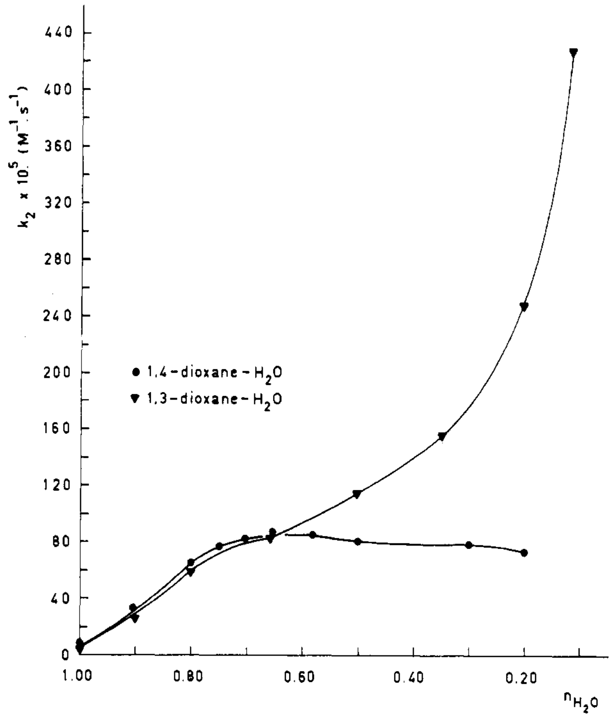

Figure 2. Plots of k_2 vs. n_{H_2O} for the neutral hydrolysis of 1 in 1,4-dioxane–H_2O (●) and in 1,3-dioxane–H_2O (▼) at 25 °C.

---

(34) Bradley, P. A.; Jones, G. P.; Kolodziej, H. A. *J. Chem. Soc. Faraday Trans. 2* **1975**, 1200–1211.

(35) Kuppers, J. R. *J. Phys. Chem.* **1975**, *79*, 2105–2107.

(36) Morcom, K. W.; Smith, R. W. *Trans. Faraday Soc.* **1973**, *66*, 1073–1080.

(37) Wong, K. F.; Pong, T. S.; Soon, N. G. *Chem. Phys. Lett.* **1975**, *30*, 309–313.

(38) Walker, R.; Davidson, D. W. *Can. J. Chem.* **1959**, *37*, 492–495.

(39) Vertut, M. C.; Fayet, J. P.; Chassaing, G.; Cazaux, L. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1973**, 635–637.

(40) Engberts, J. B. F. N. In "Water. A Comprehensive Treatise"; Franks, F., Ed.; Plenum: New York, 1979; Vol. 6, pp 139–237.

(41) Alternatively, attempts have been made to explain the kinetic solvent effects in 1,4-dioxane–water by considering the effect of 1,4-dioxane on an equilibrium between completely hydrogen bonded water molecules and water molecules containing "free" OH groups and "free" lone pairs. See: Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1978**, 418–420; *J. Chem. Res., Synop.* **1978**, 140–141. Compare also ref 40.

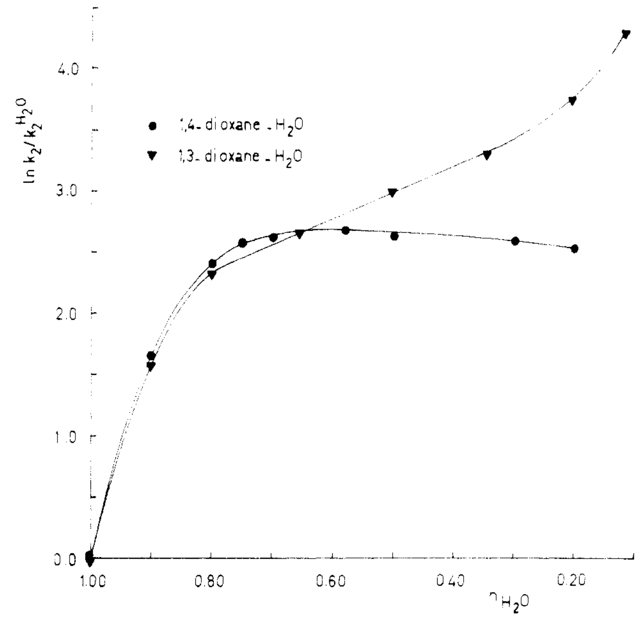

Figure 3. Plots of $\ln k_2/k_2^{H_2O}$ vs. n_{H_2O} for the neutral hydrolysis of 1 in 1,4-dioxane–H_2O (●) and in 1,3-dioxane–H_2O (▼) at 25 °C.

$= k_{obsd}c_{H_2O}^{-1})^{41}$ is considered (Figure 2). In 1,4-dioxane–water, k_2 becomes almost independent on n_{H_2O} below $n_{H_2O} \approx 0.85$, while k_2 increases continuously in 1,3-dioxane–water with decreasing n_{H_2O} until $n_{H_2O} = 0.11$ (see Experimental Section). It has been suggested that preferential solvation of 1 by the apolar 1,4-dioxane[19,42] could account for the independence of k_2 for changes in solvent composition. The different solvent effects in both solvent systems are also illustrated by plots of $\ln(k_2/k_2^{H_2O})$ vs. n_{H_2O} (Figure 3). The plot for 1,3-dioxane–water suggests a relatively high kinetic basicity of the 2di·H_2O complex, probably as a result of the high dipole moment of the organic component which will encourage proton transfer to the complex.

Figure 4 shows a plot of the thermodynamic activation parameters as a function of n_{H_2O} for hydrolysis of 1 in 1,4-dioxane–water. The corresponding data for hydrolysis in 1,3-dioxane–water are displayed in Figure 5. In both solvent systems, extrema in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are observed at about $n_{H_2O} = 0.7$. As expected, the decrease of $\Delta H^{\ddagger}$ between $n_{H_2O} = 1.00$ and $n_{H_2O} = 0.7$ is greater in 1,3-dioxane–water than in 1,4-dioxane–water, but this effect is completely compensated by a greater loss of entropy, leading to almost equal changes in $\Delta G^{\ddagger}$. Between $n_{H_2O} = 0.7$ and 0.2, k_2 remains almost constant in 1,4-dioxane–water, as a result of a delicate balance of solvent effects on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (if the latter parameter is corrected for the changes in water concentration). By contrast, the changes in $\Delta S^{\ddagger}$ dominate the increase in k_2 at low water content in 1,3-dioxane–water. Probably the enhanced kinetic basicity of the 1,3-dioxane–water complexes (relative to the 1,4-dioxane–water complexes) will impose less constraints on the solvent orientation in the transition state for deprotonation of 1.

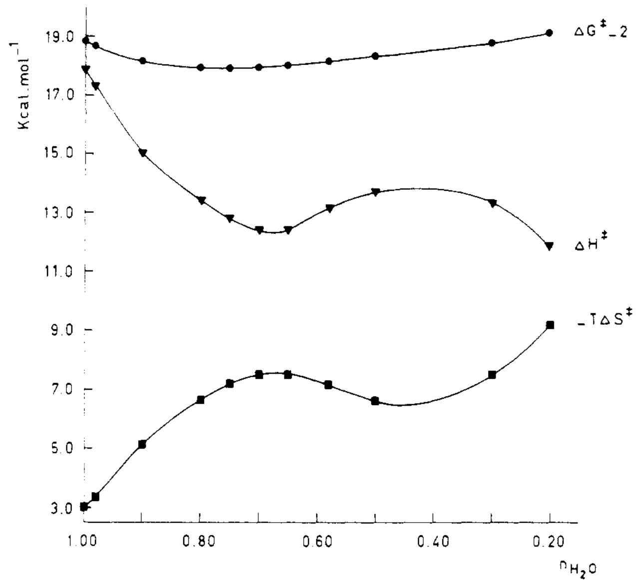

Figure 4. Plots of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $-T\Delta S^{\ddagger}$ vs. n_{H_2O} for the neutral hydrolysis of 1 in 1,4-dioxane–H_2O (25 °C).

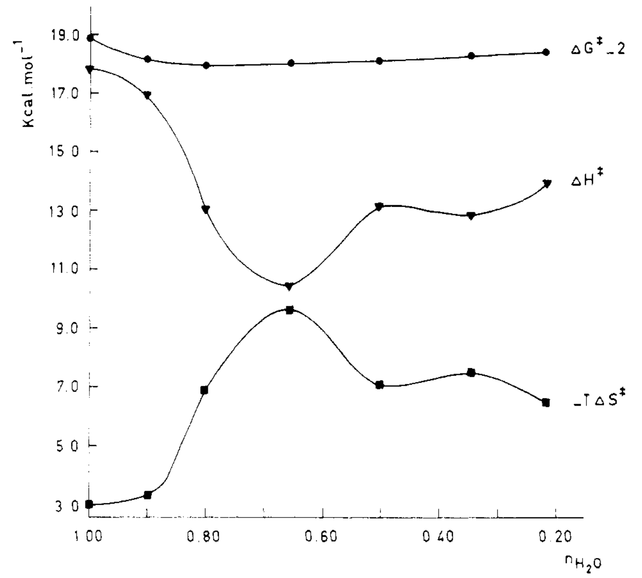

Figure 5. Plots of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $-T\Delta S^{\ddagger}$ vs. n_{H_2O} for the neutral hydrolysis of 1 in 1,3-dioxane–H_2O (25 °C).

In conclusion, we note that solvent effects on the water-catalyzed hydrolysis of 1 in 1,4-dioxane–water and 1,3-dioxane–water can be interpreted without implying a dominant role of cosolvent-induced changes in the three-dimensional water–water hydrogen bond network. Instead, the solvent dependence of the rate constants and thermodynamic activation parameters specifically reflects cosolvent–water hydrogen bonding interactions which ultimately determine the kinetic basicity of the aqueous mixtures.

Acknowledgment. The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. 1, 26452-84-6.

---

[42] The physical significance of k_2 is uncertain, especially at high water contents when the substrate is almost completely surrounded by water, and no diffusion together of the reactants is required. Nevertheless, the variation of k_2 provides an impression of the influence of varying water concentration on k_{obsd}. At low water concentration, water molecules will behave more and more as a second substrate molecule. For a discussion of this problem, see: Langford, C. H.; Tong, J. P. K. *Acc. Chem. Res.* 1977, *10*, 258–264.

[43] Compare: Karzijn, W.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* 1977, *96*, 95–100.