neutral, dried over Na_2SO_4 and evaporated to give a yellow oil (**3**), bp 55-63 °C (86-111 torr), yield 1.72 g (67%). The exo-endo ratio was ca. 3:2 as judged from the relative magnitude of the CH_3 peaks in the NMR spectrum.

3-Acetyl-4-oxatetracyclo[4.2.1.$0^{2,5}$.$0^{3,7}$]nonane (10). A solution of 0.37 g of **4** in 1 mL of benzene was irradiated at 300 nm for 65 h. Evaporation of the solvent gave a colorless oil which was purified by gas chromatography (D, 123 °C) to give 80 mg (22%) of **10**: NMR δ 2.24 (s, CH_3), 4.72 (q, HCO). Anal. ($C_{10}H_{12}O_2$) C, H.

The same product was isolated from photolyses at 430 nm and from the benzophenone-sensitized irradiations. Identification was by NMR comparisons.

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Isobaric and Isochoric Activation Parameters for the Water-Catalyzed Hydrolysis of *p*-Methoxyphenyl 2,2-Dichloropropionate in Typically Aqueous Solutions

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Abstract: Isobaric thermodynamic activation parameters ($\Delta G_p^\ddagger$, $\Delta H_p^\ddagger$, $\Delta S_p^\ddagger$) and volumes of activation ($\Delta V^\ddagger$) have been measured for the water-catalyzed hydrolysis of *p*-methoxyphenyl 2,2-dichloropropionate (**1**) in water and in *t*-BuOH–H_2O (n_{H_2O} = 0.950 and 0.925) and 2-*n*-butoxyethanol–H_2O (n_{H_2O} = 0.980) at 25 °C. These data, in combination with the isobaric thermal expansivities (α) and the isothermal compressibilities (β) of the solvent, were used to calculate the isochoric activation parameters $\Delta U_v^\ddagger$ and $\Delta S_v^\ddagger$. It is found that the solvent dependence of the sets ($\Delta H_p^\ddagger$, $\Delta S_p^\ddagger$) and ($\Delta U_v^\ddagger$, $\Delta S_v^\ddagger$) is widely different as a result of the large changes in α/β and in $\Delta V^\ddagger$. The results are interpreted mainly in terms of hydrophobic interactions between **1** and the organic cosolvent and the large electrostriction, as expressed in the strongly negative $\Delta V^\ddagger$ values. The analysis is facilitated by consideration of thermodynamic parameters for transfer of a model substrate (*p*-nitrophenyl propionate) from water to the *t*-BuOH–H_2O system. It is concluded that both isobaric and isochoric activation parameters contain fundamental information about the solvation changes during the activation process. There is no compelling evidence to prefer either of these sets for an analysis of kinetic solvent effects on the hydrolysis of **1** in the solvent systems used.

The interpretation of rate constants (k) and thermodynamic activation parameters for organic reactions in typically aqueous (TA) solutions[1] of high water content constitutes a long-standing problem of utmost difficulty.[2] A fundamental approach in recent studies involves a rationalization of changes in thermodynamic activation parameters like Gibbs free energies ($\Delta G_p^\ddagger$), enthalpies ($\Delta H_p^\ddagger$), entropies ($\Delta S_p^\ddagger$), volumes ($\Delta V^\ddagger$), and heat capacities of activation ($\Delta C_p^\ddagger$) with solvent composition in terms of interactions of the substrate(s) and the transition state with the TA solvent systems.[2-6] But the results are often a matter of considerable controversy which has its seat in the peculiar features of TA solutions.[1]

Previously, the question has also been asked whether isobaric (constant pressure) or isochoric (constant volume) activation parameters best reflect the actual solvation changes during the activation process.[7,8] We define

$$\Delta U_v^\ddagger = RT^2\left(\frac{\delta \ln (k/T)}{\delta T}\right)_v$$

$$\Delta H_p^\ddagger = RT^2\left(\frac{\delta \ln (k/T)}{\delta T}\right)_p$$

$$\Delta V^\ddagger = -RT\left(\frac{\delta \ln k}{\delta P}\right)_T$$

then it follows from the mathematical relations between derivatives[8] that

$$\Delta U_v^\ddagger = \Delta H_p^\ddagger - (T\alpha\Delta V^\ddagger)/\beta$$

$$\Delta S_v^\ddagger = \Delta S_p^\ddagger - (\alpha\Delta V^\ddagger)/\beta$$

in which α is the isobaric thermal expansivity and β the isothermal compressibility of the solvent system. In the high water concentration region of TA solutions, α/β varies strongly with changes

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[1] For a definition of TA solutions and a summary of their properties, see: Franks, F. In "Water. A Comprehensive Treatise"; Franks, F., Ed.; Plenum Press: New York, 1973; Vol. 2, Chapter 1.

[2] (a) Blandamer, M. J.; Burgess, J. *Chem. Soc. Rev.* **1975**, *4*, 55. (b) Engberts, J. B. F. N. In "Water. A Comprehensive Treatise"; Franks, F., Ed.; Plenum Press: New York, 1979, Vol. 6, Chapter 4.

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[6] During the last decades, many attempts have been made to correlate rate constants with solvent parameters: (a) Reichardt, C. "Solvent Effects in Organic Chemistry"; Verlag Chemie: Weinheim, 1979. (b) Symons, M. C. R. *Acc. Chem. Res.* **1981**, *14*, 179. Although sometimes useful trends have been found, the physical significance of these correlations is usually far from clear since no distinction is made between solvation effects on the reactant molecule(s) and the transition state.

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Table I. Pseudo-First-Order Rate Constants for the Neutral Hydrolysis of *p*-Methoxyphenyl 2,2-Dichloropropionate in *t*-BuOH–H_2O and 2-BE–H_2O as a Function of Pressure (25 °C)

t-BuOH–H_2O						2-BE–H_2O	
$n_{H_2O} = 1.000^a$		$n_{H_2O} = 0.950^b$		$n_{H_2O} = 0.925^a$		$n_{H_2O} = 0.980^a$	
P, bar	$k_{obsd} \times 10^5$, s^{-1}	*P*, bar	$k_{obsd} \times 10^5$, s^{-1}	*P*, bar	$k_{obsd} \times 10^5$, s^{-1}	*P*, bar	$k_{obsd} \times 10^5$, s^{-1}
1	119	1	8.0^c	1	1.42	1	6.2
100	135	100	12.9	250	2.82	250	13.5
260	166	270	18.4	500	5.77	500	24.5
525	234	540	32.1	1000	12.7	1000	69.8
1025	401	1040	65.6	1500	27.6	1500	138
1525	578	1540	125	2000	60.9	2000	242
2025	827	2040	245			2500	413

[a] No HCl added. [b] In the presence of 8×10^{-3} mol kg^{-1} HCl. [c] Measured in the conventional kinetic apparatus.

Table II. Isobaric and Isochoric Activation Parameters for the Neutral Hydrolysis of *p*-Methoxyphenyl 2,2-Dichloropropionate in *t*-BuOH–H_2O and 2-BE–H_2O at 25 °C

medium	$k_{obsd} \times 10^5$, s^{-1}	$\Delta G_p^\ddagger$, kcal/mol	$\Delta H_p^\ddagger$, kcal/mol	$\Delta S_p^\ddagger$, eu	$\Delta V^\ddagger$, cm^3/mol	$10^6\alpha$, K^{-1}	$10^6\beta$, bar^{-1}	$-T\alpha\Delta V^\ddagger/\beta$, kcal/mol	$\Delta U_v^\ddagger$, kcal/mol	$\Delta S_v^\ddagger$, eu
H_2O	119	21.46	7.8	−46	−32 ± 2	257	44.6	1.3 ± 0.1	9.1	−41
t-BuOH–H_2O, $n_{H_2O} = 0.950$	7.97	23.05	5.3	−59	−63 ± 3	560	42.7	5.9 ± 0.4	11.2	−40
t-BuOH–H_2O, $n_{H_2O} = 0.925$	1.46	24.05	10.0	−47	−69 ± 3	703	45.6	7.6 ± 0.5	17.6	−22
2-BE–H_2O, $n_{H_2O} = 0.980$	6.19	23.20	$[0.8]^a$	$[-75]^a$	−77 ± 6	429	42.5	5.5 ± 0.5	$[6.3]^a$	$[-57]^a$

[a] $\Delta C_p^\ddagger = 342 \pm 51$ cal K^{-1} mol^{-1}, 20–48 °C.[5b,15]

in the mole fraction of water (n_{H_2O}).[9] If $\Delta V^\ddagger$ is sufficiently large, the variation of this ratio of *macroscopic* solvent parameters can already be the sole reason for a significant difference in the solvent dependence of the sets ($\Delta H_p^\ddagger$, $\Delta S_p^\ddagger$) and ($\Delta U_v^\ddagger$, $\Delta S_v^\ddagger$).

In the present study we compare the changes in the isobaric and isochoric activation parameters with n_{H_2O} for the pH-independent hydrolysis of *p*-methoxyphenyl 2,2-dichloropropionate (**1**) in water-rich *t*-BuOH–H_2O and 2-*n*-butoxyethanol (2-BE)–H_2O. The difference in the solvent dependence of both sets of activation parameters was found to be very large indeed. The strong electrostriction during the activation process is primarily invoked to explain these results.

Experimental Section

Pseudo-first-order rate constants (k_{obsd}; ±1.5%) for neutral hydrolysis of **1** under atmospheric pressure were obtained between 20 and 48 °C by following the change in absorbance at 290 nm.[5b] Isobaric activation parameters were obtained by standard procedures. The estimated error in $\Delta H_p^\ddagger$ is 0.3 kcal mol^{-1} and in $\Delta S_p^\ddagger$ 1 eu.

The hydrolysis reactions under pressure were followed spectrophotometrically at 290 nm in a Novaswiss high-pressure flowcell (provided with sapphire windows, path length 1.0 cm, volume ca. 2 mL) which was built in a Zeiss PMQII spectrophotometer.[10] The light from the monochromator was transmitted into the cell by means of a UV light guide. The optical cell formed part of a stainless steel high-pressure system (a closed circuit) in which pressures up to 4000 bar (monitored by two high-pressure transducers, one in the range 0–1000 bar, accuracy 1.5 bar, and one in the range 0–4000 bar, accuracy 6 bar) could be generated manually (two Nova pumps). During all reactions the pressure could be kept constant within 6 bar. The optical cell was surrounded by a copper cylinder through which water (25.00 ± 0.05 °C) was circulated. The reaction medium (in most cases containing 8×10^{-3} mol kg^{-1} of HCl; vide infra) was circulated through the system with the aid of a membrane pump (Prominent Electronic Type A1002). Pseudo-first-order rate constants were measured in the high-pressure system up to 2000 bar in water and the *t*-BuOH–H_2O mixtures and up to 2500 bar in 2-BE–H_2O at $n_{H_2O} = 0.98$. After all the air had been removed from the system (by compression and decompression of the solution), the hydrolysis was initiated by adding ca. 200 μL of a concentrated stock solution of **1** in acetonitrile. For the relatively fast reactions, the rate constants were reproducible to within 2.5%. However, for the relatively slow reactions in the low-pressure region there were problems with the stability of the reaction products during the required long reaction times. Therefore, the rate constants were determined in the absence of HCl. Control experiments at 1 bar showed that the rate constants in acidic and neutral media were equal within experimental error. This is indicative for catalysis only by water molecules. Generally, the rate constants for the slow reactions were reproducible between 4 and 10% The $\Delta V^\ddagger$ values were determined graphically[11] from the low-pressure part (1 to ca. 500 bar) of plots of ln k_{obsd} vs. pressure and refer to 1 bar. Pressure effects on the autoprotolysis constant of water are too small[12] for invoking the possibility of hydroxide ion catalysis at higher pressures. The errors in $\Delta U_v^\ddagger$ and $\Delta S_v^\ddagger$ can be calculated from those in $\Delta H_p^\ddagger$ and $\Delta S_p^\ddagger$, respectively, and those in $-T\alpha\Delta V^\ddagger/\beta$ and $-\alpha\Delta V^\ddagger/\beta$, respectively (Table II).

The α and β values for *t*-BuOH–H_2O were calculated from data given in the literature.[13] The corresponding data for 2-BE–H_2O were kindly provided by Professor J. E. Desnoyers, University of Sherbrooke. The estimated error in the values of α/β used in Table II is ±2%.

The thermodynamic transfer parameters for *p*-nitrophenyl propionate (**2**) given in Table III were obtained from solubilities of **2** between 10 and 30 °C. The standard state is a hypothetical ideal solution of 1.0 mol kg^{-1} of **2**.

All solutions were made up by weight. The water used in all experiments was deionized and distilled twice in an all-quartz distillation unit.

Results and Discussion

The mechanism of the single-step, neutral hydrolysis of **1** has been well established[14] and involves water-catalyzed nuceophilic attack of water on the ester carbonyl. Previous studies[5] have shown large variations of $\Delta H_p^\ddagger$ and $\Delta S_p^\ddagger$ for hydrolysis in *t*-BuOH–H_2O and 2-BE–H_2O and of the apparent heat capacity of activation for hydrolysis in 2-BE–H_2O[5b,15] between $n_{H_2O} = 0.900$ and 1.000.

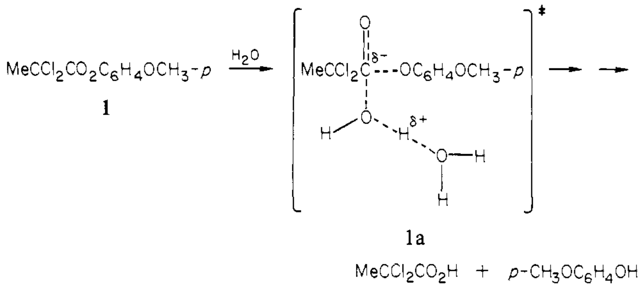

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Table III. Free Energies, Enthalpies, and Entropies of Transfer[a] of 2 from Water to *t*-BuOH–H_2O at 25 °C

n_{H_2O}	$\Delta G_p{}^{\theta}{}_{tr}$, kcal/mol	$\Delta H_p{}^{\theta}{}_{tr}$, kcal/mol	$\Delta S_p{}^{\theta}{}_{tr}$, eu	$T\Delta S_p{}^{\theta}{}_{tr}$, kcal/mol
0.96	−0.41	6.5	23	6.9
0.95	−0.52	7.4	27	7.9

We have now determined volumes of activation for the hydrolysis of **1** in both solvent systems from the pressure dependences of the pseudo-first-order rate constants (k_{obsd}, Table I). These results were used to calculate $\Delta U_v^{\ddagger}$ and $\Delta S_v^{\ddagger}$ (Table II). The extremely large and negative $\Delta V^{\ddagger}$ values are indicative for strong electrostriction, as expressed in the Drude–Nernst equation.[16] The formation of the dipolar transition state **1a** will result in a partial disruption of the hydrogen-bonded structure of the solvent, and the transition state will, therefore, occupy a relatively small volume. It is likely that the reduction of $\Delta V^{\ddagger}$ upon addition of *t*-BuOH or 2-BE is caused by zwitterion–dipole forces as well as by a negative volume contribution due to increased hydrogen bond formation.[17,18] Most importantly, the large variations of $\Delta V^{\ddagger}$ with n_{H_2O} lead to a dramatic difference in the solvent dependence of the isobaric and isochoric activation parameters.[19] In the *t*-BuOH–H_2O system, for which $\Delta C_p^{\ddagger}$ is only small,[5b] $\Delta U_v^{\ddagger}$ increases by 8.5 kcal mol^{-1} going from pure water to n_{H_2O} = 0.925, whereas $\Delta H_p^{\ddagger}$ increases by only 2. 2 kcal mol^{-1}. In the case that $\Delta V^{\ddagger}$ would not have changed, $\Delta U_v^{\ddagger}$ would still have varied by 4.4 kcal mol^{-1} in this solvent composition range. Going from n_{H_2O} = 1.000 to n_{H_2O} = 0.950, $\Delta H_p^{\ddagger}$ and $\Delta U_v^{\ddagger}$ even vary in opposite direction.

Since $T\alpha/\beta = P_i$ and $P_i = (\delta U/\delta V)_T$, in which P_i represents the internal pressure of the solvent, it is clear that the addition of small amounts of *t*-BuOH or 2-BE to water is accompanied by a large increase of P_i. As argued by Dack,[20] this is indicative for substantial strengthening of those cohesion forces that vary rapidly with a small isothermal volume change (i.e., the "nonchemical" forces: repulsion, dispersion, and weak polar interactions). Dissolution of the cosolvent molecules in the interstitial cavities within the three-dimensional hydrogen-bond network of water will be primarily responsible for this effect.

Consideration of the data listed in Table II leads to the possibility of framing a scheme of ideas for the interpretation of the observed kinetic solvent effects. At constant pressure, the relatively small solvent dependence of $\Delta G_p^{\ddagger}$ is the result of large, almost compensatory, changes in $\Delta H_p^{\ddagger}$ and $\Delta S_p^{\ddagger}$. Assuming that the solvation behavior of **1** can be reasonably mimicked by that of *p*-nitrophenyl propionate (**2**),[21] the thermodynamic transfer parameters listed in Table III show that particularly the changes of the initial state enthalpy are still larger than $\Delta\Delta H_p^{\ddagger}$. This loss of initial state enthalpy is overcompensated by a gain in $T\Delta S_p{}^{\ominus}{}_{tr}$. These *trends* are consistent with disruption of the hydrophobic hydration spheres around the ester and *t*-BuOH (hydrophobic interaction), the effect being at a maximum near n_{H_2O} = 0.950. At constant volume (i.e., the volume of an equilibrium mixture of initial and transition states),[19b] the large electrostriction involved in the activation process comes into play, and, as anticipated, this effect increases upon addition of the nonaqueous solvent component (i.e., with increasing P_i).[20] Now the solvent volume in regions far from the transition state must be expanded in order to compensate the decrease in volume as a result of electrostriction. Thus, for hydrolysis of **1** at constant volume an increase in temperature will be accompanied by a larger temperature dependence of the rate constant than at constant pressure (i.e., $\Delta U_v^{\ddagger} > \Delta H_p^{\ddagger}$).[23] Upon increase in cosolvent concentration, short-range interactions (as expressed in P_i) increase, and consequently, $\Delta U_v^{\ddagger}$ will increase (Table II). Even at n_{H_2O} = 0.950 in *t*-BuH–H_2O, this effect apparently overwhelms the energy changes involved in hydrophobic interaction between the initial state and *t*-BuOH.

We contend that the question[7,8] whether isobaric or isochoric activation parameters must be preferred in the analysis of kinetic solvent effects in aqueous binary systems cannot be answered in general terms. Of course, thermodynamics provide no reason for preferring one set over the other. Important differences between both sets of activation parameters only arise if $|\Delta V^{\ddagger}|$ is large and if the internal pressure varies significantly in the solvent composition range examined. Under these conditions, each set contains ultimate facts about the solvation changes during the activation process. However, a *quantitative* dissection of these (pseudo)-thermodynamic data into contributions of different types of solute–solvent interactions must await further developments in our understanding of these aqueous solvent systems.[24]

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Registry No. 1, 75265-14-4; *p*-nitrophenyl propionate, 1956-06-5; water, 7732-18-5.

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(15) The large and positive $\Delta C_p^{\ddagger}$ for hydrolysis[5b] of **1** in 2-BE–H_2O at n_{H_2O} = 0.98 has recently been reinterpreted in terms of association of **1** with aggregates ("moving units") of 2-BE which start to form at about this mole fraction and for which the concentration is strongly temperature dependent: Holterman, H. A. J.; Engberts, J. B. F. N., to be published. See also ref 10.

(16) (a) Drude, P.; Nernst, W. *Z. Phys. Chem.* (*Leipzig*) **1894**, *15*, 79. (b) Asano, T.; Le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407. It may be assumed that dielectric saturation of the dielectric is unimportant.

(17) Compare: Dollet, N.; Juillard, J.; Zana, R. *J. Solution chem.* **1980**, *9*, 827.

(18) The variation of $\Delta V^{\ddagger}$ with solvent composition cannot be reconciled with changes in the pressure dependence of hydrophobic interactions. See: (a) Ben-Naim, A. "Hydrophobic Interactions"; Plenum Press: New York, 1980; p 209. (b) Morild, E.; Aksnes, G. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 169.

(19) Previously, much smaller differences between ($\Delta H_p^{\ddagger}$, $\Delta S_p^{\ddagger}$) and ($\Delta U_v^{\ddagger}$, $\Delta S_v^{\ddagger}$) have been noted for the acid-catalyzed hydrolysis of methyl acetate and some S_N displacement reactions in acetone–H_2O or EtOH–H_2O. See: (a) Baliga, B. T.; Withey, R. J.; Poulton, D.; Whalley, E. *Trans. Faraday Soc.* **1965**, *61*, 517. (b) Whalley, E. *Ber. Bunsenges. Phys. Chem.* **1966**, *70*, 958. (c) Baliga, B. T.; Whalley, E. *J. Phys. Chem.* **1967**, *71*, 1166. (d) Baliga, B. T.; Whalley, E. *Can. J. Chem.* **1970**, *48*, 528, 2021.

(20) Dack, M. R. J. *Chem. Soc. Rev.* **1975**, *4*, 211.

(21) Replacement of the chlorine atoms in **1** by hydrogen has only little effect on the hydrogen-bonding ability of the ester moiety.[14b] The *p*-MeO group was replaced by a *p*-NO_2 substituent since *p*-methoxyphenyl propionate gave an oil upon contact with *t*-BuOH–H_2O, thereby preventing accurate solubility measurements. Consideration of hydrophobicity constants (f_x), as defined by Rekker,[22] indicates that this structural change has no substantial effect on the overall hydrophobicity of the ester molecule ($f_{NO_2} = -0.078$; $f_{MeO} = 0.269$).

(22) Rekker, R. F. "The Hydrophobic Fragmental Constant"; Elsevier: Amsterdam, 1977; p 350–355.

(23) The volume contraction (and evolution of heat) upon mixing of *t*-BuOH or 2-BE with water (n_{H_2O} = 0.900–1.000) are well documented: (a) *t*-BuOH—Nakanishi, K.; Kato, N.; Maruyama, M. *J. Phys. Chem.* **1967**, *71*, 814. (b) 2-BE—Chu, K. Y.; Thompson, A. R. *J. Chem. Eng. Data* **1960**, *5*, 147. (c) For a review of volumes of mixing, see: Tager, A. A.; Adamova, L. V. *Usp. Khim.* **1980**, *49*, 618. Battino, R. *Chem. Rev.* **1971**, *71*, 1.

(24) The peculiar behavior[15] of the hydrolysis of **1** in 2-BE–H_2O at n_{H_2O} = 0.98 at the moment precludes a semiquantitative analysis of $\Delta V^{\ddagger}$ and both sets of activation parameters.