

EFFECT OF POLARITY AND OTHER SOLVENT PARAMETERS ON THE KINETICS OF THE ALKALINE DECOMPOSITION OF A QUATERNARY PHOSPHONIUM CHLORIDE IN AQUEOUS ALCOHOLIC SOLVENTS

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ABSTRACT

The reaction between Benzyltriphenylphosphonium chloride and hydroxide ions was studied kinetically in mixtures of ethanol and n-propanol with water at several temperatures. The reaction rate increases and the activation energy decreases progressively with increasing alcohol content in the mixed solvent. The change is described in the light of the solvation phenomena and the internal solvent structure. A comparative discussion is presented of the specific solvent effects in the two solvent systems under consideration, based on the respective polarity values as given by the parameter ΔE_T . The relative extents of the preferential solvation of the reactants or the transition state has an important influence and is suggested as a reason for the dependence of the rates of reaction on the mixed-solvent structure.

Keywords: Polarity effect, Solvent parameters, Reaction rates.

INTRODUCTION

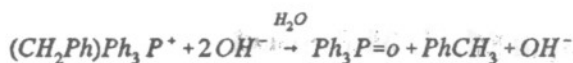
It has been accepted recently that the solvent polarity has an important effect upon chemical reactions and there have been several attempts to correlate empirical and experimental parameters of solvents with their polarity and solvation properties [1-5]. One of the most successful approaches to solvent polarity is that of the E_T values [3,4] which depend upon the solvatochromic behaviour of the betaine [3] [2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate]. The term solvatochromism refers to the shift of an electronic absorption band when varying the polarity of the medium; and the E_T values (in kcal mol⁻¹) are calculated from the absorption band position of the betaine (λ in nm) by the relationship:

$$E_T = 28590 / \lambda_{\max}$$

The solvatochromic changes result from intermolecular solute-solvent interaction forces which usually involve alterations in the electronic ground state or may also involve the excited state of the

absorbing species. It is well known that most bimolecular chemical reactions involve transition states having some form of charge separation in parts of the molecule relative to the reactants. It is possible, therefore, that preferential solvation of reactants or transition state will occur by one of the components of the solvent mixture, and consequently this could influence the reaction rate. Dawber and coworkers [5] estimated the extent of preferential solvation, p , of the betaine, by one of the components of some binary solvent mixtures and showed that such preferential solvation was likely to be exerted in a parallel manner by other polar solutes, and might be used as a useful index in the interpretation of kinetic studies in mixed solvents, particularly when the reactants and transition state were significantly different in their polarities. In order to examine the correlation between the observed rate constants and ΔE_T values in mixed solvents, among various theories [6-9] pertaining to the reaction in aqua-organic binaries, the system benzyltriphenylphosphonium chloride in alkaline

ethanol-water or n-propanol-water mixtures was chosen for study. This compound reacts with sodium hydroxide to give the corresponding phosphine oxide and a hydrocarbon, toluene in this case [10]:



The fact that this type of reaction represents an ion-ion interaction involving a polar charge-separated activated complex implies that strong solvent effects are to be displayed.

EXPERIMENTAL AND CALCULATIONS

Benzyltriphenylphosphonium chloride (Aldrich) was obtained in a pure form and was used without further purification. Technical ethanol was purified by refluxing for several hours over sodium hydroxide pellets and then distilled. The distillate was refluxed again for several hours over sodium metal and redistilled. The ethanol was finally refluxed over calcium metal for several hours and then distilled under dry conditions in an all-glass Pyrex apparatus; head and tail portions were rejected and the quantity boiling at 79°C at 760 mm Hg was collected and kept out of contact with moisture. The AnalaR "May and Baker" n-propanol was used without further purification. The concentration of Benzyltriphenylphosphonium chloride used was always 0.02 M in all experiments. The composition of binary mixtures of organic solvents and water was determined on a weight basis. Appropriate volumes of the organic solvents were measured by means of a grease-free burette and the weights determined. Calculated volumes of 1N NaOH were then added, followed by calculated amounts of distilled water, such that the solutions were always 0.02 N with respect to NaOH. The weights were determined, from which the weight per cent and, accordingly, the mole per cent of the organic solvent were calculated. Because of considerable sensitivity of the reaction rate toward solvent composition, each reaction mixture was prepared in such a quantity as to be sufficient for all experiments carried out with this mixture at different temperatures. These mixed solvents were kept as stock solutions in brown glass-

stoppered bottles. From each mixture a sample was withdrawn, and titrated against the standard hydrochloric acid solution before the start of each kinetic run. In order to test for the reproducibility of measurements, several runs were made in duplicate and the results were found to be concordant within $\leq \pm 2\%$. Experimental details of the procedure used for the evaluation of the rate constants were described elsewhere [11].

The activation energies, E, were calculated by the least-squares method as applied to the Arrhenius plots of the respective experiments. The free energies, the entropies and the enthalpies of activation were computed using the thermodynamic expressions of the absolute reaction rate theory [12], namely,

$$k' = \frac{kT}{h} e^{-\Delta G^\ddagger/RT} \quad \text{l}^2 \text{ mol}^{-2} \text{sec}^{-1},$$

$$\Delta H^\ddagger = E - RT \quad \text{kJ mol}^{-1}, \text{ and}$$

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger - \Delta G^\ddagger}{T} \quad \text{J mol}^{-1} \text{ deg}^{-1}$$

where, ΔG^\ddagger , kJ mol⁻¹, is the free energy of activation, k being the Boltzmann's constant, h, the Plank's constant, ΔH^\ddagger and ΔS^\ddagger the enthalpy and entropy of activation, respectively.

RESULTS AND DISCUSSION

The third-order rate coefficients, the values of activation energies E and activation parameters ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger for the reaction investigated in the two alcohol-water mixtures are given in Tables (1) and (2), where it is evident that the rate constant increases and the activation energy decreases progressively with gradual increase of the alcoholic component in the solvent mixture. The role of the organic cosolvent on the rate of the enhancement of the reaction under study is principally the most important observation obtained in the present, as well as in other solvent systems [13,14]. A considerable desolvation of the reactants ($(\text{CH}_2\text{Ph})\text{Ph}_3\text{P}^+$ and HO^-) as well as a marked increase in the solvation of the activated complex [12,13] can both well explain the drop in the overall

activation energy of the reaction from, e.g., 121.1 KJ mole⁻¹ in pure water to 23.0 KJ mole⁻¹ in 70% (v/v) ethanol-water or 42.6 KJ mole⁻¹ in 50% (v/v) n-propanol-water mixtures. The activation energy in the former solvent system is always higher than that in the latter containing, the same mole % of the organic cosolvent. However, this difference in the E values is strongly dependent on the solvent composition, being much larger in media rich in the alcoholic part. This may be rationalised on the basis of a difference in the solvation abilities of the two sets of solvent mixtures. By infrared spectroscopy [15,16], it was shown that the association of alcohols tends to decrease with increasing molecular weight, and in the sequence primary, secondary and tertiary [15]. In other words, the association decreases down from ethanol to n-propanol and hence the solvation of the reactants, through hydrogen bonding, will decrease in the same direction causing a rate acceleration through a decrease in activation energy. As visualised in Tables (1) and (2), the smooth and gradual decrease of the ΔG^\ddagger values runs parallel to the rate enhancement with increasing the mole% of the alcohol. The latter will help in breaking more of the hydrogen bonds around reactants, and hence the free energy, ΔG^\ddagger associated with breaking such bonds will decrease progressively. Moreover, this slow decrease in the ΔG^\ddagger values reflects a partial compensating behaviour between the enthalpy ΔH^\ddagger and entropy ΔS^\ddagger of activation and reflects the progressive disruption of the water liquid structure. The strong lowering of ΔS^\ddagger indicates a decrease in the extent of expulsion of solvent molecules in the transition state as the medium becomes enriched in alcohol. In the water-rich solvents the more positive values of ΔS^\ddagger presumably show a considerable decrease in order as water molecules bonded to HO⁻ ions are partially released in attaining the transition-state structure.

It is noteworthy that two different ranges of rate change with solvent composition are identified. In the first range, (0-15 mole% ethanol or 0-6 mole% n-propanol), the combined hydrophobic interaction of the alkyl group and the hydrogen-bonding interaction of the OH group enhance the three-dimensional structure of water and stiffen it [17]. In other words, at low alcohol contents, there is enough H₂O to solvate the reactants HO⁻ ions and maintain

the three-dimensional structure of the water clusters. Consequently, the activity of the HO⁻ ion is inhibited by its extensive hydration and the rate increases slowly in this range of solvent composition. On the other hand, at high alcohol contents, the water molecules bind with the nearest alcohol molecules and increase the extent of structured water-alcohol system, and hence the solvation sheath around the hydroxide ions will be gradually lost, thus rendering them more reactive with the result of a sharp increase in rate.

The dependence of the physical properties of the water-alcohol solutions upon composition [15,18,19] renders the solvent influence on the reaction kinetics rather complex. Such physical properties [17] are exemplified in excess enthalpy of mixing, which is always negative in the water-rich solvent, but, in the alcohol-rich solvent, it is negative for ethyl alcohol and positive for n-propyl alcohol [15,18,19]; viscosity, where a maximum always occurs at 70-80 mole% water [20,21]; mutual diffusion coefficients, which have a minimum at 70-80 mole% water [22]; and dielectric relaxation, where the relaxation time of alcohols increases with the addition of a small amount of water and the relaxation time of water increases with the addition of a small amount of alcohol [23,24]. The behaviour of these structured solutions depends on the balance between the effects of the two functional parts of the alcohol molecules and of the network structure of water. Summing up, it is to be concluded that although the increase in rates of the present reaction with increasing the alcohol content of the medium is, at least, attributable to the apparently major factor, which is the decrease in the catalytic activity of the HO⁻ ions through its extensive hydration, the above physical properties can affect the rate to one degree or another.

It is clear from Tables (1) and (2), that the rate in presence of n-propanol is always faster than that in presence of ethanol when both media contain the same amount of the organic solvent. This could be related with the difference in the solvent polarity values ΔE_T in the two media as shown in Table (3), where the ΔE_T values are listed for the whole range of the solvent composition. These values are derived from the solvatochromic behaviour of a pyridinium betaine and prove that the latter is preferentially

solvated by the less-polar alcohol than with water (negative ΔE_T values) [5]. However, the p values (preferential solvation numbers), calculated by Dawber and coworkers [5] to be 0.26 in 50 % EtOH and 0.11 in 50 % PrOH indicate that although betaine is preferentially solvated by the ethanol or propanol component, there is more water associated with the betaine in the aqueous PrOH than in the aqueous EtOH. Thus, in the case of the hydrolysis of the phosphonium salt under investigation, if the same principle applies, the effect of a greater

additional solvation of the activated complex by water in the *n*-propanol-water, as compared to the ethanol-water mixtures may be sufficient to accelerate the reaction in *n*-PrOH by presenting more water for solvation. In other words, the water molecules present with *n*-PrOH as cosolvent will be more free to solvate the transition state, together with the alcohol molecules, than those present with C_2H_5OH cosolvent and, hence, the lower E values in the former medium is rationalised.

Table 1. Third-Order Rate Constants, Activation Energies and Activation Parameters for the Alkaline Decomposition of benzyyltriphenylphosphonium Chloride in EtOH-H₂O Mixtures.

$k' \times 10^3, l^2 \text{ mol}^{-2} \text{ sec}^{-1}$							
Ethanol, Vol % Wt % mole %	0	10	20	30	40	50	70
35°C	3.7 ±0.3	7.1 ±0.2	14.3 ±0.1	22.8 ±0.4	36.5 ±0.2	108.1 ±1.2	481.2 ±0.9
40°C	8.2 ±0.4	14.5 ±0.8	26.1 ±0.2	40.6 ±0.5	65.9 ±0.4	151.4 ±1.9	549.5 ±0.8
45°C	16.6 ±0.1	28.2 ±0.4	47.9 ±0.8	71.4 ±1.0	107.0 ±0.9	217.3 ±1.1	645.7 ±1.9
50°C	33.3 ±0.4	51.3 ±0.5	83.3 ±1.0	123.0 ±1.4	175.9 ±0.9	305.6 ±1.2	724.4 ±2.1
$E, \text{ kJ mol}^{-1}$	121.4 ±1.4	109.4 ±1.2	98.1 ±1.1	93.6 ±1.2	86.2 ±0.4	57.9 ±0.6	23.0 ±0.2
$\Delta G^\ddagger, \text{ kJ mol}^{-1}$ at 40°C	89.3 ±0.9	87.8 ±1.0	86.3 ±1.0	85.1 ±0.8	83.9 ±0.9	81.7 ±1.3	78.3 ±0.9
$\Delta H^\ddagger, \text{ kJ mol}^{-1}$ at 40°C	118.8 ±0.3	106.8 ±0.5	95.5 ±1.1	91.0 ±1.0	83.6 ±1.2	55.2 ±0.9	20.4 ±0.4
$\Delta S^\ddagger, \text{ J mol}^{-1} \text{ deg}^{-1}$ at 40°C	94.3 ±1.2	60.7 ±0.7	29.5 ±0.5	18.8 ±1.1	- 0.9 ±1.0	- 84.4 ±1.8	- 185.1 ±0.7

Table 2. Third-Order Rate Constants, Activation Energies and Activation Parameters for the Alkaline Decomposition of benzyltriphenylphosphonium Chloride in n-PrOH-H₂O Mixtures.

$k' \times 10^3, l^2 \text{ mol}^{-2} \text{ sec}^{-1}$						
n-propanol, Vol % Wt % mole %	0	10	20	30	40	50
35°C	3.7 ±0.3	12.9 ±0.3	30.2 ±0.1	70.7 ±0.5	163.7 ±1.1	362.4 ±1.3
40°C	8.2 ±0.4	22.6 ±0.3	48.4 ±0.2	102.3 ±1.0	216.3 ±1.3	457.1 ±0.9
45°C	16.6 ±0.1	37.6 ±0.6	79.4 ±0.8	153.2 ±1.1	304.7 ±1.5	206.1 ±1.3
50°C	33.3 ±0.4	64.7 ±0.3	120.2 ±1.2	223.9 ±2.1	416.9 ±1.9	776.2 ±1.8
E, kJ mol ⁻¹	121.4 ±0.6	88.1 ±1.1	76.8 ±0.6	64.3 ±0.5	52.4 ±1.0	42.6 ±0.9
ΔG^\ddagger , kJ mol ⁻¹ at 40°C	89.3 ±1.4	86.7 ±1.3	84.7 ±0.8	82.7 ±1.1	80.8 ±0.7	78.7 ±0.1
ΔH^\ddagger , kJ mol ⁻¹ at 40°C	118.8 ±0.3	85.5 ±1.1	74.2 ±1.4	61.7 ±2.0	49.8 ±1.7	40.0 ±1.2
ΔS^\ddagger , J mol ⁻¹ deg ⁻¹ at 40°C	94.3 ±1.2	- 3.7 ±0.8	- 33.5 ±0.7	- 67.2 ±0.9	- 99.0 ±1.0	- 124.1 ±0.1

 Table 3. Solvent ΔE_T Values in Alcohol-Water Mixtures at Various Concentrations.

Solvent mixture*	$\Delta E_T, \text{ k cal mol}^{-1}$								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Water-EtOH	- 0.8	- 1.6	- 2.1	- 2.5	- 2.7	- 2.6	- 2.5	- 1.9	- 1.1
Water-n-PrOH	- 1.0	- 2.0	- 3.0	- 4.0	- 5.0	- 6.0	- 6.8	- 7.2	- 6.0

* mole fraction of water : 0.1 - 0.9

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