

COMPARATIVE STUDY OF CHEMICAL DYNAMICS OF THE REACTION BETWEEN PHOSPHONIUM SALTS AND HYDROXIDE IONS IN METHANOL-WATER AND TERT-BUTANOL-WATER MIXTURES

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SUMMARY

The rate constants for the alkaline decomposition of tetraphenylphosphonium bromide in a series of methanol-water, and tert-butanol-water systems were determined, as functions of temperature and solvent composition, covering the range 10-80% (v/v) of the alcoholic solvent. The reaction shows a large increase in rate as the organic content of the binary solvent mixture is increased. The rate enhancement brought about by gradual addition of the alcohol is attributed to a considerable drop in activation energy caused by an increase both in the desolvation of reactant anions and the solvation of the transition state. A comparative discussion of the specific solvent effects on the reaction in methanol-water, and tert-butanol-water mixtures, using the same anion, was made to explain the relative changes in the solvation states of the reactants, and the transition state, as criteria for the kinetic parameters of the reaction.

INTRODUCTION

Solvents are known to exert pronounced effects on rates, particularly of ion-ion reactions, by affecting the activation parameters [1-3]. Their study throws considerable light on the mechanism of reactions in solution. Several attempts were made to correlate the relative catalytic efficiency of different solvents towards particular reactions with certain properties of the solvent or of the solution [4-6]. Our previous work [7-9] has established that tremendous rate acceleration can be obtained, giving rise to rate factors as large as 5-10 powers of 10, on addition of a dipolar aprotic solvent to the reaction medium. Such an observation has also been reported for many organic reactions involving anions [10,11], and has often been attributed to changes in the solvation of the reactant anion as well as the transition state [12,13]. In the present study, rate measurements were made of the alkaline decomposition of tetraphenylphosphonium bromide, in a series of alcohol-water mixtures, including primary and tertiary monohydric alcohols. The reaction of the phosphonium salt and sodium hydroxide involves a rate-determining decomposition of a transition pentacovalent phosphorus anion, into a phosphine oxide and a phenyl anion which is protonated to give benzene [14]. The major

effect of the alcoholic solvent on the rate is a consequence of the modifying effect on the water structure and hence on the hydrogen-bonding ability of the mixed solvent [10]. The aim of this investigation is to clarify the role of protic solvents on the reaction, and to have more insight concerning the reaction behavior in protic media. The results obtained are also discussed in the light of the Arrhenius parameters and thermodynamic functions of the activated complex. A comparative discussion is presented of the specific solvent effects of the two solvent systems under consideration.

EXPERIMENTAL

Tetraphenylphosphonium bromide (Fluka) was obtained in an adequately pure form and was used without further purification. Methanol (BDH) for kinetic measurements was purified according to the method described by Danniell and Hildebrand [15]. Super dry alcohol was obtained after applying the method reported by Lund and Bjerrum [16]. Tertiary butyl alcohol (BDH) was purified [17] by refluxing for 24 hours with calcium hydroxide and then distilling.

The product was redistilled from benzoic acid and the middle fraction contained less than 10^{-5} M acid and less than 0.002 M water, b.p. 82 °C. The kinetic procedure for following the reaction rate was described before [18]. The dielectric constant data were obtained by interpolation from the findings of Åkerlof [19].

RESULTS AND DISCUSSION

The rates of the reaction were determined in binary solvent mixtures of alcohol and water covering the range 10-80% (v/v) in steps of 10%. The temperatures at which the reaction was studied depended on the rates in different media and varied from 45 to 60 °C. The rate constants were obtained from the graphical representation of the third-order kinetic law. Linearity of the kinetic plots was observed only in the ranges below 25% completion in H₂O-rich solvents, while in alcohol-rich solvents the plots were linear up to 70% completion. The reason for this discrepancy is that, in more aqueous media, the produced tetraphenylphosphonium oxide precipitated and had a catalysing effect on the reaction, causing a marked deviation of the linear third-order plots towards higher rate. In less aqueous media, however, the produced oxide remained in solution and had no such effect. The activation energies were determined from the appropriate Arrhenius plots and the results are set forth in Table (1). The enthalpies (ΔH^\ddagger), entropies (ΔS^\ddagger) and free energies (ΔG^\ddagger) of activation were calculated using the absolute reaction rate theory [20].

Examination of Table (1) shows large increases in rate with addition of alcohol to the solvent mixture. Such rate increases can be as high as 2×10^2 and 3×10^3 times at 50 °C in 80 % MeOH-H₂O and tert-butanol-H₂O mixtures, respectively. The table shows a relatively slow increase in rate in the water-rich solvents followed by a rapid increase when the alcohol content exceeds about 50 % (v/v) in MeOH and 30 % (v/v) in tert-butanol. It is well known that water has an extensive tendency to solvate ions strongly and to form hydrogen bonds with hydroxide anions [10,21]. This is favoured by the high dielectric constant of water which, in turn, is due to the polar nature of this solvent and to the fact that the dimensions of the water molecule favour a tetrahedrally coordinated structure

[21]. Diluting water with alcohol decreases the solvating power of the medium progressively until it reaches a minimum in slightly aqueous or nonaqueous media. Consequently, the retarding effect of the solvation sheath around the anion will drop causing a large enhancement in the reaction rate. On the other hand, as the composition of the solvent is gradually altered from pure water to a mixture of water and alcohol cosolvent, the activation energy E decreases continuously. Table (1). This is to be ascribed to a considerable decrease in solvation of the reactants, as well as to a marked increase in the solvation of the activated complex [22]. The hydroxide anion, being the strongest base that can exist in water, and its catalytic activity greatly inhibited by its extensive hydration, will gradually lose its solvation sheath, particularly in high alcohol contents, and thereby will be much more reactive. The effect is, of course, relatively slight at high water concentrations in which there is enough water to hydrate the HO⁻ anions as well as to form hydrogen bonds with the cosolvent alcohol. This explains the initial slow rise in the rate followed by a relatively larger increase in rate in high alcohol-content solvents. Thus, decreasing the polarity, and hence the dielectric constant, leads to more solvation of the transition state, where there is a charge dispersal, as the solvent changes from water to alcohol-water mixtures [23]. As a result, the potential energy of the transition state will decrease [20] and hence the activation energy will drop more and more as the medium is enriched in methanol or tert-butanol. The lowering (about 40 kJ mol⁻¹ in methanol and 38 kJ mol⁻¹ in tert-butanol) of E over the whole range of solvent composition is thus rationalised in terms of some combination of these two factors, namely, reactant desolvation and increased transition - state solvation. The latter effect, however becomes more evident at sufficiently low dielectric constants where the alcohol cosolvent prevails. In this range of solvent composition, there is not enough water to solvate the transition state efficiently and, therefore, solvation of the latter will take place mainly with the alcohol solvent. No doubt, such a large decrease in E (Table 1) manifests the internal structural changes, and hence the alterations in hydrogen - bonding ability of the solvent mixture as the latter is varied in dielectric constant.

Table 1. Rate Constants and Activation Energies for the Alkaline Decomposition of Tetraphenylphosphonium Bromide at different Temperatures.**A. Methanol-Water Mixtures**

CH ₃ OH Content			$k/\times 10^3$ (l ² mol ⁻² min ⁻¹)			E, kJ mol ⁻¹
vol %	wt %	mol %	50 °C	55 °C	60 °C	
10	8.02	4.67	13.2	24.5	46.3	121
20	16.29	9.86	20.8	38.5	72.4	116
30	24.71	15.57	30.3	55.5	93.3	106
40	33.48	22.04	50.1	91.2	158	103
50	42.80	29.59	95.5	166	275	98
60	52.48	38.29	199.5	331	575	93
70	62.75	48.62	525	871	1450	90
80	73.81	61.29	2090	3162	5250	81

B. tert-Butanol-Water Mixtures

tert-BuOH Content			$k/\times 10^3$ (l ² mol ⁻² min ⁻¹)				E, kJ mol ⁻¹
vol %	wt %	mol %	45 °C	50 °C	55 °C	60 °C	
10	7.81	2.02	15.9	29.6	52.6	91.4	108
20	15.73	4.34	30.5	55.5	95.2	179	103
30	23.67	7.00	69.2	132	208	350	96
40	32.22	10.35	200	355	595	966	93
50	41.52	15.68	643	1160	1910	3167	88
60	51.24	20.33	1610	2750	4170	7143	84
70	60.56	27.16	6940	10830	16250	25120	77
80	71.49	37.85	72440	109650	162500	251189	70

It is of interest, in this stage, to compare the effects of methanol and tert-butanol contents of the solvent mixture on the reaction rate under investigation. Although protic solvents, such as methanol and tert-butanol are strong hydrogen-bond donors [23], the latter solvent is less polar ($\mu = 1.66$ D) [24] than the former ($\mu = 2.87$ D) [25] and its effect is especially remarkable. The dielectric constant of methanol (34) is much higher than that of tert-butanol (12.5) [19] whose molecular weight is higher. The effective hydrogen-bond donor acidity (α) is 0.93 and 0.68 for methanol and tert-butanol bonds, respectively [5]. In the light of the above comparative data, Figure (1) illustrates the effect of the alcoholic component of the solvent on the rate in MeOH-H₂O and tert-butanol-H₂O mixtures. It is clear that the rate in tert-butanol-water is always higher than that in methanol-water mixtures containing the same mol % of the alcoholic solvent, accompanied by an opposite trend in the activation energy. Thus, the rate in tert-butanol-H₂O solvent is about 38 times higher at 50 °C in 15.6 mol % than in methanol-water solvent, at the same temperature and solvent

composition. This is caused by the difference in activation energies in the two solvents. In the same solvent composition, the reaction in methanol has an activation energy which is 18 kJ mol⁻¹ higher than that in tert-butanol. Also, the frequency factor, log A, which is independent of temperature, decreases from 13.8 l² mol⁻² sec⁻¹ in methanol to 12.5 l² mol⁻² sec⁻¹ in tert-butanol (Table 2). The relatively less negative activation entropy in methanol, compared to tert-butanol, favours again the assumption of a stronger solvation of the transition state in the latter solvent. The difference in rate should then be ascribed to a difference in the transition-state solvation. The latter effect increases as the alcoholic solvent is successively added to cause a much higher rate in tert-butanol than in methanol when the mol % of the alcoholic solvent approaches about 40. The value of E, which is not only lower but also more dependent on solvent composition in tert-butanol-H₂O than in methanol-H₂O, indicates that, apart from the increased desolvation of reactant HO⁻ ions, the transition-state solvation in tert-butanol-H₂O is larger than in methanol-H₂O.

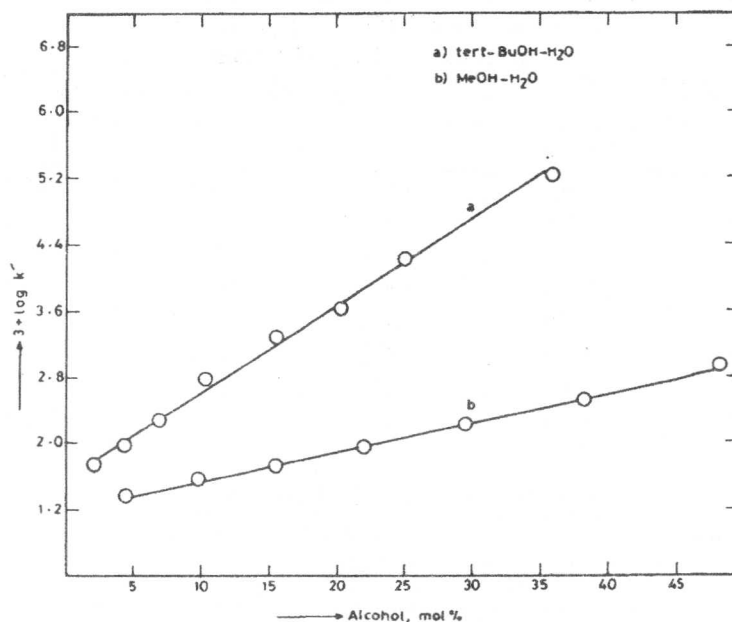


Figure 1. Comparative plots of the rate constant, $\log k'$ against the mol % of the alcoholic solvents at 55°C.

Table 2. Thermodynamic Parameters of Activation and Preexponential Factors of the reaction at 50 °C.
A CH₃OH-H₂O mixtures

Parameter	CH ₃ OH, wt %							
	8.02	16.29	24.71	33.48	42.80	52.48	62.75	73.81
ΔG^\ddagger , kJ mol ⁻¹	101.6	100.4	99.4	98.0	96.3	94.3	91.8	88.0
ΔH^\ddagger , kJ mol ⁻¹	118.4	112.9	103.3	100.1	95.4	89.8	87.2	78.7
ΔS^\ddagger , J mol ⁻¹ deg ⁻¹	52.2	39.0	12.2	6.5	- 2.7	- 13.9	- 12.9	- 28.9
$\log A$, l ² mol ⁻² sec ⁻¹	15.9	15.3	13.8	13.6	13.1	12.5	12.5	11.7

B. t-BuOH-H₂O mixtures

Parameter	t-BuOH-H ₂ O, wt %							
	7.81	15.73	23.67	32.22	41.52	51.24	60.56	71.49
ΔG^\ddagger , kJ mol ⁻¹	99.5	97.7	95.4	92.8	89.6	87.3	83.6	77.4
ΔH^\ddagger , kJ mol ⁻¹	105.2	100.1	93.7	90.5	85.2	81.0	74.4	67.4
ΔS^\ddagger , J mol ⁻¹ deg ⁻¹	17.9	7.4	- 5.4	- 7.3	- 13.7	- 19.0	- 28.6	- 31.1
$\log A$, l ² mol ⁻² sec ⁻¹	14.2	13.6	12.9	12.8	12.5	12.2	11.8	11.6

The extent of the solvation of the activated complex, can better be discussed by considering the thermodynamic activation parameters. Table (2) collects the values of the free energies ΔG^\ddagger , enthalpies ΔH^\ddagger and entropies ΔS^\ddagger of activation together with the preexponential factor A. All parameters show a considerable dependence on the solvent composition. Thus, the increase in the reaction rate, on addition of methanol or tert-butanol to water, is associated with a decrease in the activation enthalpy ΔH^\ddagger by about 40 kJ mol⁻¹ in the former, and 38 kJ mol⁻¹ in the latter solvent mixtures, which is partially compensated [26,27] through the decrease of ΔS^\ddagger by about 81 and 49 J mol⁻¹ deg⁻¹ over the whole range of medium composition, thus causing ΔG^\ddagger to decrease only by 14 and 22 kJ mol⁻¹ in the two alcoholic solvents, respectively. The considerable changes in these functions imply that the contributions from relative changes in the solvation shells of reactants and transition state, during the course of the reaction, are very important factors in the rate process. It is possible to correlate the trend in each of these parameters with the ionising power, or hydrogen bonding ability of the solvent system. Thus, the decrease in ΔG^\ddagger with successive addition of alcohol is a direct consequence of the decrease in the free energy involved in breaking the hydrogen bonds associated with the ground state. The latter energy will definitely decrease, as the mixed solvent is made less hydrogen bonding, by decreasing its water content. The large decrease in the value of ΔH^\ddagger , depicted in Table (2), as the medium composition passes from 4.7 to 61.3 mol % MeOH, or from 2.0 to 37.9 mol% t-BuOH, indicates that, in water-rich solvents, more energy has to be overcome before the transition state can be formed. The substantial diminution of the ΔS^\ddagger values with the addition of MeOH or t-BuOH is also indicative of remarkable changes in the solvation effects.

REFERENCES

- [1] E.S. Amis and J.F. Hinton, "Solvent Effects on Chemical Phenomena", Academic Press, New York and London 1973.
- [2] E.M. Arnett, "Physico-Chemical Processes in Mixed Aqueous Solvents", ed. F. Franks, Heinemann Educational Books, London 1967.
- [3] M.J. Blandamer, *J. Burgess and J.B.F.N. Engberts, Chem. Soc. Rev.*, **14**, 237 1985.
- [4] J.G. Dawber, J. Ward and R.A. Williams, *J. Chem. Soc.*, **84(3)**, 713 1988.
- [5] R.W. Taft, J.L.M. Abboud and M.J. Kamlet, *J. Org. Chem.*, **49**, 2001 1984.
- [6] C.G. Swain, *J. Org. Chem.*, **49**, 2005 1984.
- [7] M.T. Hanna, F.Y. Khalil and M. El-Batouti, *Ber. Bunsenges. Phys. Chem.*, **95(1)**, 76 1991.
- [8] M.T. Hanna, F.Y. Khalil and S.M. Beder, *Bull. Chem. Soc. Ethiop.*, **5(1)**, 21 1991.
- [9] M.T. Hanna, F.Y. Khalil and S.M. Beder, *Bull. Soc. Chem. Belg.* **96(1)**, 27 1987.
- [10] A.J. Parker., *Chem. Rev.*, **69**, 1 1969.
- [11] J. Miller and A.J. Parker, *J. Amer. Chem. Soc.*, **83**, 117 1961.
- [12] C.A. Kingsbury, *J. Org. Chem.*, **29**, 3262 1964.
- [13] P. Haberfield, L. Clayman and J.S. Cooper, *J. Amer. Chem. Soc.*, **91**, 787 1969.
- [14] G. Aksnes, F.Y. Khalil and P.J. Majewski, *Phosphorus and Sulfur*, **3**, 157 1977.
- [15] P.S. Danniell and T.H. Holdebrand, *J. Amer. Chem. Soc.*, **44**, 2824 1922.
- [16] H. Lund and A. Bjerrum, *Chem. Ber.*, **64B**, 210 1931.
- [17] M. Cocivera, *J. Amer. Chem. Soc.*, **88**, 672 1966.
- [18] F.Y. Khalil and G. Aksnes, *Acta Chem. Scand.*, **27**, 3832 1973.
- [19] G. Åkerlof, *J. Amer. Chem. Soc.*, **54**, 4125 1932.
- [20] S. Glasstone, K.J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York 1941.
- [21] R.A. Robinson and R.H. Stokes, "Electrolyte Solutions", Butter Worths, London 1968.
- [22] K.J. Laidler and H. Eyring, *Ann. N.Y. Acad. Sci.*, **39**, 303 1940.
- [23] A.J. Parker, *Quart Rev.*, **16**, 163 1962.
- [24] C.S. Marvel, *Organic Syntheses Vol. 5*, Wiley, New York 1925.
- [25] A.L. McClellan, "Tables of Experimental Dipole moment", Freeman, San Francisco 1963.
- [26] C.D. Richie and W.F. Sager, *Prog. Phys. Org. Chem.*, **2**, 323 1964.
- [27] E. Buncl and J.P. Millington, *Can. J. Chem.*, **43**, 556 1965.