

KINETICS OF HYDROXIDE PROMOTED DECOMPOSITION OF TETRAPHENYLPHOSPHONIUM CHLORIDE IN PROTIC-DIPOLAR APROTIC SOLVENT SYSTEMS

M.T. Hanna*, Fayez Y. Khalil* and S.M. Beder**

*Chemistry Department, Faculty of Science,
Alexandria University, Alexandria, Egypt

**Egyptian Petrochemicals Company,
Amrya, Alexandria, Egypt

(Received July 27, 1990; revised April 26, 1991)

ABSTRACT. The effects of varying concentrations of dimethyl sulphoxide in mixture with water on rates and activation parameters for the hydroxide promoted decomposition of tetraphenylphosphonium chloride have been studied. Increasing the DMSO content of the reaction medium up to 50% (v/v) results in a ca. 10^4 -fold rate acceleration at 45°C. This is explained as due to increased desolvation of reactants as well as an opposite effect on the transition-state solvation in DMSO-rich medium. This inverse proportionality of rate to the water concentration of the medium showed that a large number of water molecules should be removed from the solvation sheaths of reactants prior to formation of the activated complex. The specific solvent effects due to the unique properties of DMSO as a solvent were discussed in relation to the different activation energy values as well as the dielectric constant effects.

INTRODUCTION

The hydroxide and alkoxide promoted decomposition of organic phosphonium compounds [1-4], is the point of our interest in the last years from the view point of the kinetics and solvent effects. In the present work alkaline hydrolysis of tetraphenylphosphonium chloride is studied in a relatively wide range of protic-dipolar aprotic solvent mixtures involving aqueous DMSO. The latter has an outstanding ability to desolvate the hydroxide ion, rendering it highly active [5], and is also assumed to solvate transition states strongly, thereby helping more in rate enhancement [6]. For this reason, the present reaction is studied in an extensive series of solvent compositions providing a wide range of dielectric constant, and hence large medium effects will be expected to occur. The latter are important in any trial in order to obtain a deeper insight into the solution phenomena as well as to test the described theoretical treatments of rate-medium correlations.

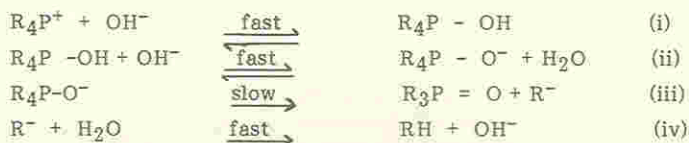
EXPERIMENTAL

Pure tetraphenylphosphonium chloride (Fluka) was obtained after several recrystallisations from chloroform - ether. DMSO (Fluka) was distilled twice under reduced pressure in a nitrogen atmosphere. The middle fraction boiling at 70°C (8 mm Hg) was collected. The purified solvent had a melting point of 18.5°C.

Measurement of the reaction rate was based on determination of the amount of sodium hydroxide consumed during the course of the reaction [4]. The dielectric constant data of DMSO-H₂O mixtures were obtained by interpolation from the findings of Wolford [7].

RESULTS AND DISCUSSION

The reaction, involving hydroxide anions and yielding triphenylphosphonium oxide and benzene, follows a third-order kinetics. The latter includes first and second order dependences on the concentrations of the phosphonium cation and hydroxide anion, respectively [8]. The mechanism of the reaction can be illustrated by the following scheme:



The rate constants at different temperatures and solvent compositions are collected in Table 1, together with the respective activation energies.

Dependence of rate on temperature. The observed isocomposition activation energy E_c decreases as the organic component in the solvent mixture is increased. Thus, the value of E_c which amounts to 92.12 kJ mol⁻¹ in pure water drops to as low a value as 70.11 kJ mol⁻¹ in 60% (v/v) DMSO-water mixture. Addition of DMSO to the aqueous solvent increases the solvation of the transition state [6]. The latter effect, together with the decrease in the solvation of the reactant hydroxide ion [9,10] participates in the large drop in activation energy with increase of the organic solvent content of the medium (Table 1). This drop follows a least square correlation of the activation energy with solvent composition in the form:

$$E = 94.81 - 0.38 [\text{DMSO}]_{\text{vol}\%} \quad \text{Corr. Coeff.} = 0.97$$

Table 1. Observed rate coefficients, activation energies and entropies for the alkaline decomposition of tetraphenylphosphonium chloride in DMSO-water mixtures at different temperatures.

DMSO content			$k, l^2 \text{ mol}^{-2} \text{ min}^{-1}$							E_c	ΔS^\ddagger
Vol%	Wt%	Mol%	30°C	35°C	40°C	45°C	55°C	65°C	75°C	kJ mol ⁻¹	J mol ⁻¹ deg ⁻¹ at 45°C
0	0	0				3.2×10^{-4}	9.3×10^{-4}	2.4×10^{-3}	6.4×10^{-3}	92.1	31.4
20	21.4	5.9				3.2×10^{-3}	9.3×10^{-3}	2.5×10^{-2}	6.1×10^{-2}	89.8	19.4
30	31.7	9.7				2.5×10^{-2}	6.3×10^{-2}	1.8×10^{-1}	3.8×10^{-1}	85.3	17.1
40	41.8	14.1	3.9×10^{-2}	9.2×10^{-2}	1.3×10^{-1}	1.8×10^{-1}				79.7	16.4
50	52.2	20.1	7.4×10^{-1}	1.4	2.3	3.5				75.8	4.6
60	66.9	26.5	39.6	53.4	84.2	1.5×10^2				70.1	-7.1

Isocomposition and isodielectric activation energies. The experimentally determined activation energies have been calculated from velocity constants

in solvents of constant composition, thus including the effect due to changes in the dielectric constant of the solvent with change in temperature. The latter effect can be excluded by calculating the isodielectric activation energies from the corresponding rate constants in isodielectric solutions. The relation between the two activation energies may be formulated in terms of the expression [11,12].

$$\Delta E = (E_D - E_C) = 2.303 b D R T^2 \left(\frac{\log k'}{\log D} \right)_T$$

where E_D and E_C are the isodielectric and isocomposition activation energies, respectively, b is the slope of a plot of $\ln D$ against T , for the temperature range 30–75°C for DMSO-water mixtures, the term $(\partial \log k' / \partial D)_T$ is the slope of a plot of the logarithm of the observed rate constant against D at constant temperature (Fig. 1). The above equation can be tested by calculating the right hand side at different temperatures and dielectric constants, and comparing the results with the observed difference ΔE on the left hand side. This comparison is recorded in Table 2 where it is shown that the calculated ΔE is more or less close to the observed value for the reaction in water, the small difference in ΔE being attributed to an experimental error which doesn't exceed 5%. The situation for the hydrolysis in DMSO medium is quite different where

Table 2. Calculated and observed values of ΔE according to the Svrbely-Warner equation for the alkaline hydrolysis of the phosphonium salt in DMSO-water mixtures.

Temp., °C	35°	40°	55°	75°
D (calculated)	75	70	65	60
DMSO, Wt%	0.00	52.2	52.2	41.6
ΔE (calculated) K J mol ⁻¹	1012	973	996	1044
ΔE (observed) K J mol ⁻¹	964	701	378	128

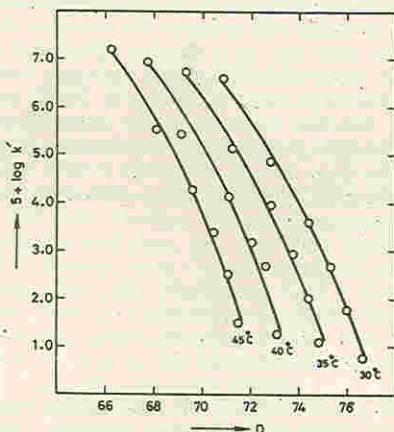


Fig. 1. Dependence of rate constant for the alkaline hydrolysis of the phosphonium salt on the dielectric constant of DMSO-water mixtures.

the calculated ΔE is much higher than that observed. This discrepancy is rationalised in terms of the specific role of DMSO in the medium. The unique properties [9] of this solvent renders impossible the application of the above treatment to give any regular trend in the values of ΔE .

Effect of solvent composition on reaction rate. The reaction rate is largely accelerated as the content of the organic cosolvent in the reaction mixture is increased (Table 1). Thus, at 45°C the rate in 50% DMSO-H₂O (v/v) is 1.1×10^4 times faster than in pure water. The rate enhancement for the reaction is generally accompanied by a large decrease in the energy of activation. Increasing the organic cosolvent will decrease the amount of water necessary for extensive hydration of the HO⁻ anions, and hence the solvating power of the medium will decrease progressively until it reaches a minimum in slightly aqueous or non-aqueous solvents. Consequently, the retarding effect on rate will decrease, and the net result will be a tremendous rate acceleration. Evidence for this argument is provided by the fact that polarizable transition states, formed in bimolecular reactions of anions are more solvated in aprotic solvents than in protic ones [5].

The competition between the DMSO molecules and the hydroxide anions for the water molecules will deprive HO⁻ from their hydration sheaths, thereby increasing their ability to react. At high water concentrations, however, there will be enough water molecules both to solvate the HO⁻ anions and to form a 2:1 association complex [13,14] with DMSO molecules. Therefore, comparatively mild effect of DMSO on rate is to be expected in this range of solvent composition. Further increase of the DMSO content will help in the formation of more of the association complex until most of the water molecules are captured by DMSO molecules and thus prevented from hydrogen bonding with the HO⁻ anions. A pronounced effect of DMSO on rate is then to be felt, and should reach a maximum at a mole fraction of about 0.3 DMSO, corresponding to about 60% (w/w). At this point the 1:2 complex will have been formed in large amounts and the system shows extremum behaviour in many of its physical properties [7,14,15].

Furthermore, it is to be pointed out that the addition of DMSO to aqueous solutions of hydroxide ion has a great effect on the basicity of such solutions. Thus, Dolman and Stewart [16] indicated that acidity function of 0.011M tetramethylammonium hydroxide rises from 12 in water to 26 in 99.5 mole % DMSO. This increase in basicity upon the addition of DMSO to the system must be due to the increases in the activity of the hydroxide ion and to the decreases in the water activity, both of which will enhance the reaction rate. The decreases in the water activity is not only due to a dilution effect but also to the ability of DMSO to complex with water through strong hydrogen bonds [14,15], a fact which is also evidenced by the large heats of mixing of DMSO and water [14].

The dependence of the reaction rate on water concentration of the mixed solvent could be represented by a plot of $\log k'$ against $\log [H_2O]$, where a linear relationship with a negative slope of n in the range 0-50% (v/v) DMSO (or 55-27 mol/l of water) were obtained. The value of n was computed in this way by least square regression:

$\log k' (30^\circ\text{C}) = 19.9 - 13.9 \log [H_2O]$	$r = 0.997$
$\log k' (35^\circ\text{C}) = 20.5 - 14.1 \log [H_2O]$	$r = 0.996$
$\log k' (40^\circ\text{C}) = 20.4 - 13.9 \log [H_2O]$	$r = 0.997$
$\log k' (45^\circ\text{C}) = 20.2 - 13.6 \log [H_2O]$	$r = 0.997$

in which n ranges around 14, confirming the assumption that a large number of water molecules is involved in the activation process. This is not surprising if one considers that the HO⁻ anion is, at least, trihydrated in water [17] and that the solvation sheaths around two hydroxide anions and one phosphonium

cation have to be disrupted before the formation of the activated complex can take place.

Effect of dielectric constant on reaction rate. The reaction rate shows an increase as the dielectric constant of the medium is lowered. The relationship can be expressed in the form of Scatchard's equation [18]

$$\frac{\partial \log k'}{\partial (1/D)} = - \frac{Ne}{2.303 KTr^*}$$

for uni-univalent ionic reactions, where N is Avogadro's number, e the electronic charge, T the absolute temperature, and r^* the distance of closest approach of the reactant ions during the formation of the activated complex. The plot of $\log k'$ against $1/D$ for a reaction between two ions at zero ionic strength should be linear [19,20]. The present results give a straight line which deviates from linearity at compositions higher than 40% (v/v) DMSO-water mixtures. This deviation is well attributable to specific solvation effects [19] in which the reactants and activated complex are differentially solvated by the more polar constituent of the solvent mixture. The slope of the linear portion of the plots gives 0.03 \AA for r^* ; where the least square regressions are:

$\log k' (30^\circ\text{C}) = 7160 (1/D) - 98$	$r = 0.99$
$\log k' (35^\circ\text{C}) = 7948 (1/D) - 110$	$r = 0.98$
$\log k' (40^\circ\text{C}) = 7506 (1/D) - 106$	$r = 0.99$

The value of r^* , calculated according to the above theory is much lower than the sum of radii of the unsolvated HO^- and ph_4P^+ which is about 5.6 \AA [21]. It is to be remembered, however, that the value of the bulk dielectric constant, and not the microscopic one in the immediate vicinity of the reactants, was used in calculating r^* according to the above equation. Furthermore, actual values of k' were used rather than the theoretically preferable values at zero ionic strength to be obtained by extrapolation. The latter factors are partly responsible for the inaccuracy of application of Scatchard's theory to the present reaction in the present solvent system. In other words, treating the solvent as one with a uniform dielectric constant and a zero ionic strength, which is not the case, causes this discrepancy and renders the rates of the present ionic reaction poorly correlatable to the dielectric constant of the medium [22,23].

REFERENCES

1. G. Aksnes, F.Y. Khalil and P.J. Majewski, *Phosphorus and Sulfur*, **3**, 157 (1977).
2. G. Aksnes and A.I. Eide, *Phosphorus*, **4**, 209 (1974).
3. W.E. McEwen and K.O. Berline, "Organophosphorus Stereochemistry", Part I, Dowden, Hutchinson and Ross, Inc. New York (1975).
4. F.Y. Khalil and G. Aksnes, *Acta Chem. Scand.*, **27**, 3832 (1973).
5. A.J. Parker, *Chem. Rev.*, **69**, 1 (1969).
6. R. Fuchs and L.L. Cole, *J. Amer. Chem. Soc.*, **95**, 3194 (1973).
7. R.K. Wolford, *J. Phys. Chem.*, **68**, 3392 (1964).
8. W.E. McEwen, K.F. Kumli, A. Blade-Font, M. Zanger and C.A. Vander Werf, *J. Amer. Chem. Soc.*, **86**, 2387 (1964).
9. H.L. Schäfer and W. Schaffernicht, *Angew. Chem.*, **72**, 618 (1960).
10. C.D. Richie, in "Solute-Solvent Interactions", J.F. Coetzee and C.D. Richie, Eds., Marcel Dekker, New York (1969).
11. W.J. Svrbely and J.C. Warner, *J. Amer. Chem. Soc.*, **57**, 1883 (1935).

12. R.K. Wolford and R.G. Bates, *J. Phys. Chem.*, **66**, 1496 (1962).
13. J.R. Jones, "Ion Association in Proton Transfer Reactions", *Chem. Brit.*, **7**, 336 (1971).
14. J.M.G. Cowie and P.M. Toparowski, *Can. J. Chem.*, **39**, 2240 (1961).
15. J.J. Lindberg and J. Kenttämä, *Suomen Kemistilehti*, **B33**, 104 (1960).
16. D. Dolman and R. Stewart, *Can. J. Chem.*, **45**, 911 (1967).
17. G. Yagil and M. Anbar, *J. Amer. Chem. Soc.*, **85**, 2375 (1963).
18. G. Scatchard, *Chem. Revs.*, **10**, 229 (1932).
19. E.S. Amis, "Solvent Effect on Reaction Rates and Mechanisms". Academic Press, New York (1966), pp. 22-25.
20. H.S. Harned and B.B. Owen, "The Physical Chemistry of Electrolytic Solutions", Third Edition, Reinhold Publishing Corporation, New York (1964) p. 546.
21. E. Grunwald, G. Baughman and G. Kohnstam, *J. Amer. Chem. Soc.*, **82**, 5801 (1960).
22. E.S. Amis and G. Jaffé, *J. Chem. Phys.*, **10**, 598 (1942).
23. J.E. Plotts and E.S. Amis, *J. Amer. Chem. Soc.*, **71**, 2112 (1949).