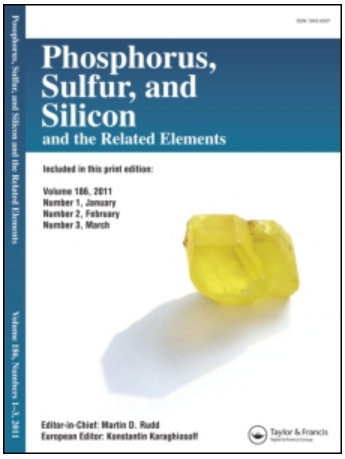

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KINETICS, MEDIUM, AND DEUTERIUM ISOTOPE EFFECTS IN THE ALKALINE DECOMPOSITION OF QUATERNARY PHOSPHONIUM SALTS III[1] Tetraphenylphosphonium Chloride in Dimethylsulphoxide-Water Mixtures

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KINETICS, MEDIUM, AND DEUTERIUM ISOTOPE EFFECTS IN THE ALKALINE DECOMPOSITION OF QUATERNARY PHOSPHONIUM SALTS

III[1] Tetraphenylphosphonium Chloride in Dimethylsulphoxide–Water Mixtures

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The reaction between tetraphenylphosphonium chloride and hydroxide or deuteroxide anions was studied kinetically in a series of dimethylsulphoxide–water mixtures at several temperatures. The rate is first-order in the phosphonium cation and second-order in the hydroxide or deuteroxide anions. The reaction shows a dramatic increase in rate, up to about 10^{10} times, as the DMSO content is increased. The rate enhancement is attributed to a considerable drop in activation energy affected not only through an increased desolvation of reactant anions, but also through an increase in solvation of the transition state, brought about by gradual addition of DMSO. The kinetic solvent deuterium isotope effect in 60% DMSO–40% D_2O is strongly dependent on temperature. The rate constant in the latter solvent mixture is represented by $k' = 11.9\, e^{-12700/RT}\, l^2$ mole^{-2} sec^{-1} as compared to $k' = 19.0\, e^{-22500/RT}\, l^2$ mole^{-2} sec^{-1} in the corresponding 60% DMSO–H_2O mixture. The thermodynamic parameters of activation show strong dependence on solvent composition and are related to structural changes and solvation power of the reaction medium.

INTRODUCTION

In earlier parts of this study[1,2] a kinetic investigation of the alkaline decomposition of tetraphenylphosphonium chloride was made in the two solvent systems dioxane–water and acetone–water. The observed effects on the rate constants of the reaction were interpreted as functions of solvent composition, dielectric constant, and solvation properties of the media studied. The reaction mechanism was discussed and confirmed in terms of the secondary kinetic solvent isotope effect.

Protic-dipolar aprotic solvent mixtures have long been known as suitable media for many reactions. The basicity of a protic solution increases largely by successive addition of increasing amounts of dipolar aprotic solvents, as shown by proton transfer equilibria and the kinetics of different types of reactions. This is accompanied usually by a remarkable enhancement of rates of reactions in such media. It has been emphasized that for bimolecular reactions involving anions the rate enhancements are attributed, among other reasons, to the increased activity of the anion as a result of its desolvation.[3] In this respect, dimethylsulphoxide (DMSO) has received special interest in recent years because of its peculiar properties[4] which make it unique among other solvents. Much work was reported on organic as well as inorganic reactions using DMSO as a medium. The present reaction, however, has yet to be investigated kinetically in this solvent, since a quantitative study of it has not been made before.[5] This is undertaken with the aim to visualize the important role played by the solvent and to compare the data with ours obtained before in other solvents.[1,2]

EXPERIMENTAL

Materials and Procedure

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 DMSO had a melting point of 18.5°C. Tetraphenylphosphonium chloride (Fluka) was pure enough to be used as such. Deuterium oxide (Norsk Hydro) with 99.8% D_2O was employed.

The kinetic procedure involved a titrimetric technique and was described before[2]. The dielectric constant data of DMSO–H_2O mixtures were obtained by interpolation from the findings of Wolford.[6]

RESULTS AND DISCUSSION

Table I includes the third-order rate constants measured in the temperature range 5–65°C and in solvent com-

TABLE I

Third-order rate constants k' and activation energies E for the alkaline decomposition of tetraphenylphosphonium chloride in DMSO–H_2O and DMSO–D_2O mixtures[a,b]

	k', l^2 mole^{-2} min^{-1}										
DMSO, vol %	0.00	10.00	20.00	30.00	40.00	50.00	60.00	60–40D_2O	70.00	$\frac{k'_{DO^-}}{k'_{HO^-}}$	$\frac{k'_{60\%\ DMSO}}{k'_{H_2O}}$
wt %	0.00	11.07	21.56	31.84	41.67	51.30	60.96	58.06	70.26		
mole %	0.00	2.79	5.94	9.73	14.13	19.53	26.44	26.16	35.17		
5°								5882	375000		
10°							2106	7499		3.56	
15°	0.000075[c]	0.00024[d]	0.00102[d]	0.00923[d]	0.1349[d]	6.026[d]	3981	11610	656219	2.92	8.75×10^9
20°							6607	16667		2.50	
25°	0.00053[c]	0.00146[d]	0.00575[d]	0.0489[d]	0.5754[d]	38.90[d]	15560	23684	1778000[d]	1.52	3.36×10^9
30°							26610	33500		1.26	
35°	0.00330[c]	0.00794[d]	0.0277[d]	0.2291[d]	2.138[d]	89.43	47860	48684	3430000[d]	1.02	1.32×10^9
40°	0.00790[c]					153.8					
45°	0.0180[c]	0.03758	0.1288	0.9804	7.272	312.5					
50°	0.0430[c]	0.0805	0.2692	2.083	14.30	562.3					
55°	0.0960[c]	0.1585	0.5420	3.787	25.33	937.5					
60°	0.2000[c]	0.3447	1.096	7.409	41.43						
65°	0.3890[c]	0.6494	2.000	13.90	73.33						
E, kcal/mole	33.50	31.99	29.88	27.66	24.57	23.70	22.52	12.56	16.71		

[a]Equal concentrations of phosphonium and hydroxide or deuteroxide ions of 0.02 M were used.
[b]Total ionic strength amounts to 0.04. No corrections for zero ionic strength or thermal expansion were made.
[c]Taken from our previous measurements (cf. Ref. 2).
[d]Extrapolated.

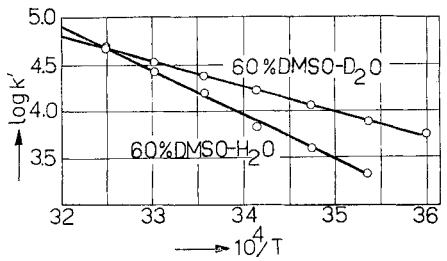

FIGURE 1 Arrhenius plots of log k' against $1/T$ for the reaction in DMSO-H_2O and DMSO-D_2O mixtures.

positions varying from 0 to 70% (v/v) DMSO-H_2O, as well as in 60% DMSO-D_2O mixture at 5-35°C. The activation energies of the reaction in DMSO-H_2O and DMSO-D_2O solvent mixtures were obtained from the corresponding Arrhenius plots, represented in Figure 1, which show clearly that the rate enhancement in D_2O mixtures decreases with increasing temperature. The results obtained confirm the reaction mechanism discussed earlier[2] involving a rate-determining decomposition of a pentacovalent phosphorus anion into a phosphine oxide and a phenyl anion which is protonated to give benzene.

Role of DMSO in Accelerating the Reaction

Examination of Table I shows a dramatic increase in the reaction rate with addition of DMSO to the solvent mixture. Such rate increases can be as high as 9×10^9 times at 15°C in 70% DMSO-H_2O mixture. One reason for this enhancement is the enormous increase in the activity of the hydroxide ion due to its desolvation by DMSO.[4,7] Increasing the DMSO content of the solvent mixture will decrease the amount of water necessary for extensive hydration of the HO^- anions not only through a dilution effect but also by the ability of DMSO to coordinate with water forming a 2: 1 association complex.[8,9] This tendency leads to a strong competition between DMSO and the HO^- anions for the water molecules. On the other hand, the DMSO molecule itself has a very weak ability to solvate the small HO^- anions,[3] and hence there will be no opportunity for the large DMSO molecules to form any closely fitting solvation sheath around them. The activity of HO^- anions will, therefore, be largely promoted. At high water concentrations, however, there will be enough water molecules both to solvate the HO^- anions and to form the 2: 1 association complex with DMSO molecules. Therefore, comparatively mild effect of DMSO on rate is to be expected in this range of solvent composition. Increasing the DMSO content will help in the formation of more of the association complex until most of

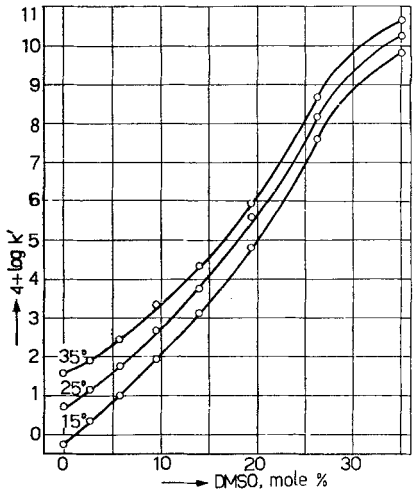

FIGURE 2 Variation of log k' for the reaction with the mole % of DMSO in the solvent mixture.

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. This effect should reach a maximum at a mole fraction of about 0.3 of DMSO, corresponding to the above-mentioned association complex, then decrease again. These predictions are almost fully realized in Figure 2 where the rate increases first relatively slowly until about 10 mole % DMSO then sharply until about 28 mole % and thereafter slowly again. Supporting these arguments is the fact that very close to the latter point the DMSO-H_2O system shows deviations from ideality in many of its physical properties.[6,9,10] Thus, the viscosity and thermodynamic excess functions, including the considerable volume contraction on mixing, all show extremum behaviour which indicates a highly structured solvent mixture involving a compound DMSO · $2H_2O$ at a mole fraction of about 0.3.

Another factor which contributes to the rate enhancement by DMSO is the increased solvation of the transition state.[11-13] When the DMSO content of the solvent predominates, and after almost all the water molecules have been bound to DMSO, the latter proceeds to solvate the transition state. This helps further to decrease the energy gap between the ground and transition states and hence will contribute largely in the rate increase in DMSO-rich solvents.

Solvent Deuterium Isotope Effect

The kinetic factor k'_{DO^-}/k'_{HO^-} decreases considerably with temperature (Table I) and is almost unity at 35°C. Similar, but much less pronounced, effects were

observed in dioxane-water[2] and acetone-water[1] mixtures. The secondary kinetic isotope effect in DMSO is best visualized on comparing the temperature at which k'_{DO^-}/k'_{HO^-} is equal to unity with that for other solvents. This temperature, obtained by extrapolation, is 69°C for 70% dioxane and 52°C for 70% acetone. Moreover, a difference of 9.86 kcal/mole in E found in DMSO-H_2O and DMSO-D_2O mixtures is considerably larger than that in dioxane[2] (3.83 kcal/mole) and acetone[1] (5.63 kcal/mole). The faster rate in DMSO-D_2O compared to DMSO-H_2O at temperatures below 35°C can well be attributed to the greater basicity of DO^- than HO^- anions, respectively, but the large difference in activation energy in the two media and the consequent dependence of k'_{DO^-}/k'_{HO^-} on temperature must be due to a difference in the stabilities of the internal structure of the solvent systems as the temperature is increased. It was found[4] that there is an association decomposition of DMSO between 40 and 60°C. This is the range in which k'_{DO^-}/k'_{HO^-} is lowest and, in fact, less than 1. Furthermore, the hydrogen-bonded DMSO-H_2O complexes are known to break down with increasing temperature[14] and the influence of hydrogen bonding is most pronounced at low temperatures. Consequently, the solvation abilities of the two media, which are dependent on hydrogen or deuterium-bond abilities will vary with temperature. This effect will outweigh that of the increased basicity of DO^- over HO^-, causing a lower rate in D_2O compared to H_2O above 35°C.

The large decrease of E in D_2O compared to H_2O is rather striking but may be rationalized on the following grounds: (a) solvation of reactant HO^- in H_2O is relatively stronger than that of DO^- in D_2O mixtures, i.e., the potential energy of the ground state is lower in the former than in the latter mixture, and (b) solvation of the transition state by DMSO molecules[3] is greater in D_2O than in H_2O mixtures, on account of the weaker deuterium bond compared to hydrogen bond, respectively. Hence, the potential energy of the transition state will be lower in D_2O than in H_2O mixtures. These two factors will cooperate in decreasing the energy gap more effectively in D_2O than in H_2O mixtures.

Rate, Activation Energy and Dielectric Constant

The reaction rate increases as the dielectric constant is lowered. According to the Bronsted-Christiansen-Scatchard equation[15] the plot of log k' against $1/D$ for a reaction between two ions at zero ionic strength should be linear. The present data give a straight line which deviates from linearity at low dielectric constants. The slope of the linear portion is, however, too high to give any reasonable value for r, the distance of closest approach of reactant ions. This is a typical example of specific solvent effects which result in a false dependence of rate on D. Also, if the dielectric constant effect in this solvent system has any significance, it would have given rates which, according to the Hughes-Ingold theory, are much lower than those in dioxane[2] and acetone[1] on account of the much higher dielectric constant of DMSO. In fact, quite the reverse was obtained which implies that the proper dependence of rate on D is pertinent only when electrostatic influences expressed in, e.g. dielectric constant or polarity predominate over specific solvent effects which influence the solvation shell geometry of reactants and transition state.

More interesting is the effect of solvent composition expressed in dielectric constant, on the activation energy of the reaction which is illustrated in Figure 3. Thus, as D decreases, E drops sharply first in the region 0–40% (v/v) DMSO, then gradually between 40 and 60% DMSO and sharply again. There seems to

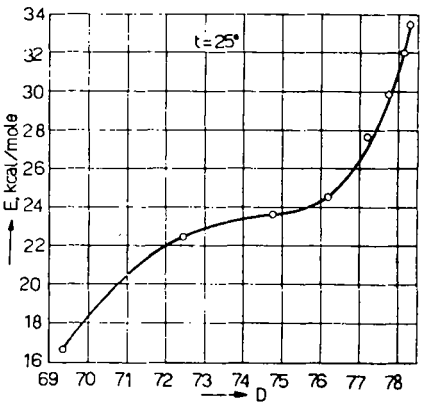

FIGURE 3 Plot of the activation energy E of the reaction against the dielectric constant of the medium.

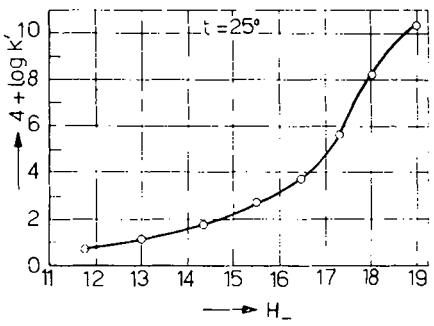

FIGURE 4 Relation between log k' of the reaction and the acidity function H_- of DMSO-H_2O solvent mixture.

be a parallelism between the behaviour of E and the changes in the internal solvent structure. The large decrease in E throughout the whole range of solvent composition as well as the manner in which it varies with DMSO content lend support to the importance of the increased solvation of the transition state.

A better understanding of the solvent effect could perhaps be obtained by comparing the rate with the acidity function H_- of the binary solvent mixture. In Figure 4 the rates in different DMSO-H_2O mixtures are plotted against H_- obtained from literature.[17] It is seen that the rate at the beginning increases more rapidly than proportional to H_-. This indicates that not only the reacting ions are changing their solvation but also the transition state. The latter is better solvated in the organic solvent than in water, thus lowering the activation energy of the reaction.

Rate and Thermodynamic Activation Parameters

The changes of the thermodynamic, as well as Arrhenius parameters, are in fact indicative of the internal structural changes of the medium and their influence on the reaction rate. Increasing the DMSO content of the solvent gradually will help in breaking more of the hydrogen bonds around reactants, and hence the free energy, ΔF^* associated with breaking such bonds will decrease progressively. This is evident in Table II, which also shows that the changes in ΔF^* are reflected in a considerable decrease in the enthalpy ΔH^*. In spite of some compensation by the entropy, appearing in the drop of ΔS^* with increasing DMSO content, it is the decrease in the enthalpy of activation that constitutes the major factor controlling the reaction. The rate enhancement is effected through increased desolvation of anions and increased solvation of the activated complex, both are essentially enthalpy terms. The hydroxide anion, which is at least trihydrated in water,[18] will undergo gradual dehydration as the DMSO is successively added. Therefore, in order to attain the transition-state structure, H_2O molecules must be displaced from hydrated HO^- anions by the phosphonium cations. This process, which takes place with expenditure of energy, will occur more readily with increased dehydration of HO^- anions caused by DMSO molecules. This results in the observed considerable decrease in ΔH^*. Supporting this argument is the determination of enthalpies of transfer of the phosphonium and hydroxide ions from water to aqueous DMSO.[19] These values were calculated to be, respectively, 0.7 and 10.1 kcal/mole for transfer from water to 70% DMSO-H_2O mixture. The sum, 10.8 kcal/mole, justifies the corresponding high enthalpy difference $\Delta\Delta H^*$ of 16.8 kcal/mole calculated from Table II for the reaction in the two media.

The strong lowering of ΔS^*, however, indicates a decrease in the extent of expulsion of solvent molecules in the transition state as the medium becomes enriched in DMSO. The more positive values of ΔS^* in the water-rich solvents presumably show a considerable decrease in order as water molecules bonded to HO^- ions are partially released in attaining the transition-state structure.

There is a more or less general tendency of $\log A$, the frequency factor (Table 2) to decrease in a manner parallel to the decrease of E with adding DMSO. These changes in $\log A$, though considerable, are outweighed by the major changes in E causing a net sharp increase in rate.

Rates in DMSO-H_2O and Acetone-H_2O Mixtures

It is of interest in this stage to compare the effects of DMSO and acetone contents on the reaction under

TABLE II

Thermodynamic parameters of activation and frequency factors at 25°C.

DMSO content vol %	DMSO content mole %	ΔF^*, kcal/mole	ΔH^*, kcal/mole	ΔS^*, cal/mole deg	$\log (A$, l^2 mole^{-2} sec^{-1})
0	0.00	24.3	32.9	29.1	19.6
10	2.79	23.7	31.4	26.0	18.9
20	5.94	22.8	29.3	21.7	18.0
30	9.73	21.6	27.1	18.4	17.3
40	14.13	20.1	24.0	12.9	16.1
50	19.53	17.6	23.1	18.4	17.3
60	26.44	14.1	21.9	26.3	19.0
60–40 D_2O	26.16	13.9	12.1	−6.1	11.9
70	35.17	11.3	16.1	16.1	16.8

investigation. Although DMSO and acetone are similar in structure, yet the DMSO molecule is pyramidal while the acetone molecule is planar.[20] The lone pair of electrons on the sulphur atom in DMSO molecule is lacking in acetone. The dielectric constant[6] of DMSO (46.4) is much higher than that of acetone (20.7) and the polarity of the former molecule (μ = 3.9 debye)[21] is greater than the latter (μ = 2.9 debye). Moreover, as deduced from the heats of mixing,[22] the hydrogen bonding between DMSO and water is much stronger than that between acetone and water.[23,24] The effective hydrogen-bond energy is 4.7 and 3.5 kcal/mole for DMSO-H_2O and acetone-H_2O bonds, respectively.[23b] Rowlinson's classification[25] based on the enthalpies and entropies of mixing of the organic solvents with water, considers DMSO as a typical non-aqueous and acetone as a typical aqueous solvent.

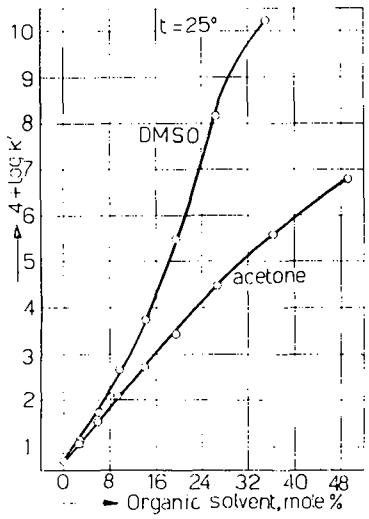

FIGURE 5 Comparative representation of the reaction rate as a function of the mole % of organic solvent in DMSO-H_2O and acetone-water mixtures.

In the light of the above comparative data, Figure 5 illustrates the effect of the organic solvent on the rate in DMSO-H_2O and acetone-H_2O mixtures. It is evident that at equal mole % of the organic solvent, the rate in DMSO is always higher than in acetone. The difference in rate is, however, dependent on the mole % of the organic solvent, being slight in the beginning and increasing sharply as the amount of the organic solvent is increased. This may be attributed to the fact that desolvation of OH^- anions is not great before the concentration of the organic solvent becomes appreciable, and hence the OH^- activity does not increase much in highly aqueous DMSO than in highly aqueous acetone. In addition, solvation of the reactant phosphonium cation with the dipolar aprotic solvent[26-28] will not differ much in the presence of slight amounts of DMSO or acetone. Consequently, the total potential energy of the ground state is almost identical in the water-rich region of the two solvent systems. The slight difference in rate in this range should then be ascribed to a difference in the transition-state solvation. The latter effect increases as the organic solvent is successively added to cause a much higher rate in DMSO than in acetone when the mole % of the organic solvent approaches about 50. The value of E, which is not only lower but also more dependent on solvent composition in DMSO-H_2O than in acetone-H_2O, perhaps indicates that apart from the increased desolvation of reactant HO^- ions, the transition-state solvation in DMSO-H_2O is larger than in acetone-H_2O. This seems to be interesting since the planar acetone molecule should be expected to solvate the transition state better than the pyramidal DMSO molecule does.[29] However, on account of the much higher polarity of the DMSO molecule, the latter effect will probably be outweighed, and larger solvation by DMSO rationalized. This is supported by the fact that although the frequency factor A in DMSO is remarkably lower than in acetone, the rate is still enormously higher, due to a considerable decrease in E. The much lower entropy of activation ΔS^* in DMSO than in acetone mixtures lends evidence also to a stronger solvation of the transition state in the former solvent.

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