

Effect of Aqueous Dipolar Aprotic Solvents on Kinetics of Saponification of Some Acid Phthalic Esters

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Rates of alkaline hydrolyses of acid phthalic esters of 1-(*p*-R-phenyl)ethanol (where R = H, Me, *t*-Bu, MeO, Cl and Br) have been measured in water-DMSO, water-acetonitrile and water-acetone solvent systems. The observed rate enhancements in these aqueous dipolar aprotic solvent systems, in comparison to water-ethanol are in accordance with the extent of solvation of the transition state and its structure in relation to solvation.

Rates of ester saponification reactions, like those of S_N2 type processes are enhanced, though to a lesser extent, when the medium is changed from protic to dipolar aprotic or aqueous dipolar aprotic solvent, and the acceleration in rates is more for the aromatic esters than that for the aliphatic ones¹⁻⁶. The present investigation deals with the kinetics of alkaline hydrolyses of the acid phthalic esters of 1-(*p*-R-phenyl)ethanol (where R = H, Me, *t*-Bu, MeO, Cl and Br) in water-ethanol mixtures and aqueous dipolar aprotic solvents, such as water-dimethyl sulphoxide, water-acetonitrile and water-acetone. The structural features of the present esters are such that there are carbonium ion stabilizing factors at C- α and that electronic effects of substituents at the *para*-position of the phenyl group of the alcohol moiety have only smaller effects at the reaction site.

The acid phthalic esters were prepared and purified by known methods⁷. Solvents used were purified by standard procedures. The reaction was followed by titration technique and the specific rate values were calculated using the equation

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

where *a* and *b* are the initial concentrations of alkali and ester (as anion) respectively. The other symbols have their usual significance. All kinetic measurements were made at least in duplicate and the rate constants are reproducible within $\pm 1.5\%$.

The rate constants in the aqueous dipolar aprotic solvents, particularly those in water-DMSO mixtures are larger than those in water-ethanol mixtures of similar compositions (Table 1). This becomes more so as the percentage of the organic co-solvent is above

Table 1—Effect of Aqueous Organic Solvents on Rates of Saponification of 1-(*p*-R-phenyl)ethyl Hydrogenphthalate

[Ester] = 0.02 mol dm⁻³; [NaOH] = 0.05 mol dm⁻³; temp. = 38.85°

R $k \times 10^3$ (dm³ mol⁻¹ s⁻¹) in aq. organic solvent containing organic component, % (v/v)

| R | Ethanol | | | | DMSO | | | |
|--------------|---------|------|------|------|-------|-------|-------|-------|
| | 20 | 40 | 60 | 80 | 20 | 40 | 60 | 80 |
| H | 1.14 | 1.02 | 0.93 | 0.81 | 2.67 | 4.71 | 5.65 | 21.65 |
| Me | 0.89 | 0.77 | — | 0.48 | 2.30 | 3.41 | — | 10.29 |
| <i>t</i> -Bu | — | — | — | 0.59 | — | — | — | 6.85 |
| MeO | 0.28 | 0.26 | — | 0.22 | 1.91 | 1.10 | — | 2.65 |
| Cl | 3.97 | 2.88 | 2.52 | 2.13 | 10.29 | 15.36 | 21.28 | 34.26 |
| Br | 3.06 | 2.58 | 2.17 | 1.98 | 8.75 | 13.15 | 17.72 | 31.07 |

| R | Acetonitrile | | | | Acetone | | | |
|--------------|--------------|------|------|-------|---------|------|------|-------|
| | 20 | 40 | 60 | 80 | 20 | 40 | 60 | 80 |
| H | 1.33 | 1.06 | 3.00 | 12.20 | 1.24 | 1.04 | 2.81 | 10.22 |
| Me | 0.95 | 0.87 | — | 9.83 | 0.94 | 0.86 | — | 8.140 |
| <i>t</i> -Bu | — | — | — | — | — | — | — | — |
| MeO | 0.34 | 0.27 | — | 1.45 | 0.29 | — | — | 1.32 |
| Cl | 3.49 | 3.38 | 4.71 | 21.80 | 3.46 | 3.09 | 4.70 | 20.46 |
| Br | 3.29 | 2.87 | 4.45 | 17.77 | 3.17 | 2.63 | 4.33 | 17.29 |

50%. The specific rates continuously decrease as the percentage of ethanol in water-ethanol mixtures increases, while in water-DMSO mixtures, the *k* values continuously increase with increase in the percentage of DMSO. In water-acetone and water-acetonitrile mixtures, however, there is a rate minimum between 30 and 40% (v/v) of the organic co-solvents. But the minimum value in either case is higher than that in water-ethanol mixture of the same composition (Table 1 and Fig. 1).

The relative magnitudes of specific rates for these esters are in conformity with the requirements of the electronic effects of the substituents. But contrary to the theory based on solvent polarity and rates of ionic reactions, there is considerable enhancement in rates for the hydrolyses of these esters in the aqueous dipolar aprotic solvents employed. The observed rate enhancement in such circumstances has been attributed to greater solvation of the transition state, though arguments were based exclusively on the effect of hydroxyl ion desolvation in dipolar aprotic media⁵. Although desolvation helps formation of very active hydroxyl ions, working with different aliphatic and aromatic esters under identical experimental conditions, it has been shown that solvation and hence stabilization of the transition state plays a major role in the catalysis by the dipolar aprotic solvents.

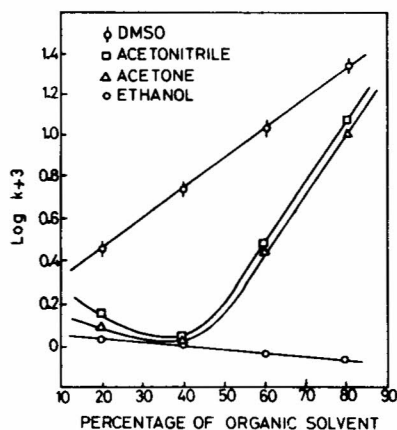


Fig. 1—Variation of rate constant with percentage of organic solvent in aqueous organic solvent for the saponification of 1-phenylethyl hydrogenphthalate at 38.85°C

Table 2— k^s/k^o Values in 80% (v/v) Aqueous Dipolar Aprotic Solvents for Saponification of 1-(*p*-R-Phenyl) ethyl Hydrogenphthalates

Reference solvent: 80% (v/v) Ethanol-water; temp. 38.85°C

| R | k^s/k^o values in | | |
|--------------|---------------------|--------------------|---------------|
| | DMSO-water | Acetonitrile-water | Acetone-water |
| H | 26.6 | 20.6 | 17.7 |
| Me | 21.6 | 15.2 | 12.7 |
| <i>t</i> -Bu | 11.7 | — | — |
| MeO | 12.7 | 7.4 | 6.8 |
| Cl | 15.7 | 10.2 | 9.6 |
| Br | 9.8 | 9.0 | 8.7 |

The above conclusion is based on the equation¹,

$$\log \frac{k^s}{k^o} = \log {}^o\gamma^s Y^- + \log {}^o\gamma^s RS - \log {}^o\gamma^s YRX^\ddagger^-$$

which correlates the ratio of the specific rate in the dipolar aprotic solvent (k^s) to that in the protic solvent (k^o) and the solvent transfer activity coefficients of the reactants (${}^o\gamma^s Y^-$ and ${}^o\gamma^s RX$) and the transition state (${}^o\gamma^s YRX^\ddagger^-$).

The k^s/k^o values for the 80% (v/v) aqueous dipolar aprotic solvents are given in Table 2. These values vary from 9.8 to 26.6 in the case of water-DMSO mixtures of different compositions. Similar trend is observed in other aqueous dipolar aprotic solvent systems but to a lesser extent. These rate ratios are, however, not very high as compared to those observed for some aromatic esters⁸. The reactant ester entities in the present case are large anionic species and hence their stabilization by solvation in dipolar aprotic media can be appreciable compared to that of the hydroxyl ions. Also the transition state in this case has greater hydrogen bond acceptor capacity for effecting a relatively better solvation in protic media. These two

factors tend to operate in such a way as to diminish the magnitudes of the k^s/k^o ratios. Moreover, because of the lesser polarisability of the B_{AC} transition state, it is stabilised by aqueous dipolar aprotic solvents only to a smaller extent, causing a decreased relative value of k^s .

It is interesting to note that the rate coefficients in water-acetonitrile and water-acetone solvent systems also show a minimum (Fig. 1). Such behaviour may be due to the extreme in the various properties of these liquid mixtures and is still subject to speculation^{9,10}.

The present case is worth examining on the basis of the concept of 'tight' and 'loose' transition states, and generalisations made for such transition states in these types of solvents^{11,12}. The structural factors favour 'looseness' for all the transition states in this case in general, and among these the 'tighter' of the transition states happens to be that formed from 1-phenylethyl hydrogenphthalate. Accordingly this substrate shows the largest value for the ratio k^s/k^o (Table 2) in aqueous dipolar aprotic solvents, because, 'tighter' transition states are better solvated and stabilised by dipolar aprotic solvents.

The activation parameters, ΔH^\ddagger and ΔS^\ddagger in the case of 1-(*p*-methylphenyl)ethyl hydrogenphthalate have been calculated and found to be 69.9, 64.0, 63.3, 64.8 kJ mol⁻¹ and -54.6, -89.9, -72.1, -68.9 JK⁻¹ mol⁻¹ in 80% (v/v) ethanol-water, DMSO-water, acetonitrile-water and acetone-water systems respectively. The standard deviation is calculated to be $\pm 5\%$. The values of both ΔH^\ddagger and ΔS^\ddagger decrease when the medium is changed from water-ethanol to aqueous dipolar aprotic solvents. Their magnitudes vary in such a way as to cause practically no change in the ΔF^\ddagger values. Their relative values also support the view that these transition states are stabilised better in the aqueous dipolar aprotic media.

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