

SOLVATION BY ACETONITRILE IN AN  $S_N1$  REACTION

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The effects of solvation by dipolar aprotic solvents on the rate of  $S_N2$  reactions are well-documented.<sup>1</sup> We here report for the first time the acceleration of the rate of an  $S_N1$  reaction due to this cause. The rate of hydrolysis of the anion of *p*-methoxy benzylhydrogen phthalate has been studied in water, 30% (v/v) and 50% (v/v) aqueous acetonitrile in the absence and presence of mercuric chloride (containing sufficient chloride ions to prevent its hydrolysis). If the change in ionizing capacity of the solvent is the major factor determining the rates, it should be expected that the rate of both the normal and catalysed reaction would decrease as the water content of the solvent is reduced. This has been found to be true for the normal and mercuric chloride catalysed solvolysis of alkyl chlorides.<sup>2</sup> However in the present case while rate of the normal hydrolysis decreases, that of the catalysed reaction increases as the water content of the solvent is reduced. The latter observation is most likely due to the capacity of the acetonitrile to solvate the highly polarizable transition-state containing a formal anionic unit charge. A  $B_{AC}2$  mechanism is unlikely because of the ease with which *p*-methoxy benzylhydrogen phthalate undergoes  $S_N1$  solvolysis.<sup>3</sup>

The large difference in the value of the activation parameters for the normal and catalysed reactions in water is presumably due to the reluctance of the polar protic solvent water to solvate highly polarizable transition states. The activation parameters for the reaction in the aqueous acetonitrile solvents refer to the total rate in presence of catalyst and not for the catalysed reaction alone; (however, the rate constants reported for the reaction in presence of catalyst in these solvents refer to those due to the catalyst only). Even then, it can be seen that both the enthalpy and entropy factors are markedly

Table

$$[\text{p-methoxy benzylhydrogen phthalate anion}] = 0.015\text{M}$$

$$[\text{HgCl}_2] = 0.05\text{M}$$

$$[\text{NaCl}] = 0.1\text{M}$$

solvent	$10^4 k_1 \text{sec}^{-1}$ 79.6°C		$\Delta H_{25^\circ\text{C}}^\ddagger$ k.cal/mol		$\Delta S_{25^\circ\text{C}}^\ddagger$ e.u	
	normal	catalsed	normal	catalsed	normal	catalsed
water	1.32	0.160	21.1	31.0	-16.8	-2.0
30% (v/v) acetonitrile	0.079	0.200		17.7		-29.5
50% (v/v) acetonitrile	0.034	0.290		16.2		-33.8

\*Temperature range used 79.6°C to 91.3°C,

probable error.  $\Delta H^\ddagger = \pm 0.02$   $\Delta S^\ddagger = \pm 0.5$

less in these solvents as compared to those for the catalysed reaction in water. We interpret it as due to the peculiar ability of the dipolar aprotic solvent, acetonitrile, to solvate the transition state of the catalysed reaction. The difference in the values of the parameters would have been even more impressive if the values for the catalysed reaction alone had been obtained in the aqueous-organic solvents. This was not done because of the very low rates of the normal reaction in these solvents.

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### References

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