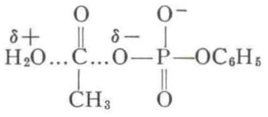
mechanisms, as the following considerations show. A unimolecular decomposition to give acylium ion:

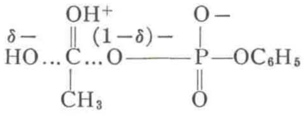
$$CH_3COOPO_3C_6H_5^- \rightarrow CH_3CO^+ + C_6H_5OPO_3^{2-}, \qquad [3]$$

is consistent with the volume and entropy of activation, because the polarity is greatly increased in the transition state. However, the relatively large effect of solvent deuterium oxide, which seems to require that at least one O—H (O—D in deuterium oxide) bond be strongly modified in the transition state, and the great stability of benzoyl phenyl phosphate (9) are difficult to explain by this mechanism. A bimolecular reaction involving solvent could proceed through transition states I, II, III, or IV, which differ in the position



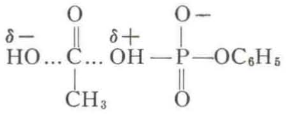
$$\overset{\delta+}{H_2O}\ldots\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\ldots\overset{\delta-}{O}-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}-OC_6H_5$$

I



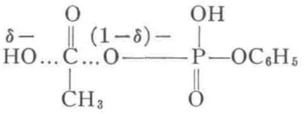
$$\overset{\delta-}{HO}\ldots\overset{\overset{\displaystyle OH^+}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\ldots\overset{(1-\delta)-}{O\!-\!-\!-\!-}\overset{\overset{\displaystyle O-}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}-OC_6H_5$$

II



$$\overset{\delta-}{HO}\ldots\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\ldots\overset{\delta+}{OH}-\overset{\overset{\displaystyle O-}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}-OC_6H_5$$

III



$$\overset{\delta-}{HO}\ldots\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\ldots\overset{(1-\delta)-}{O\!-\!-\!-\!-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}-OC_6H_5$$

IV

of a proton. Each has, of course, resonating forms. The structures might be further modified if the incoming group adds rather than substitutes, as has been suggested (10) for some carboxyl reactions, and if several water molecules are incorporated into the transition state to aid in proton transfer (1, 11). All of these mechanisms appear to be consistent with the volume of activation and other (1) data. It is interesting to compare the experimental data with calculated values for a special case of mechanism IV, according to reactions [4] and [5]:

$$CH_3COOPO_3C_6H_5^- + H_2O \overset{\text{fast}}{\rightleftharpoons} CH_3COOPO_3HC_6H_5 + OH^- \qquad [4]$$

$$CH_3COOPO_3HC_6H_5 + OH^- \xrightarrow{\text{slow}} CH_3COOH + C_6H_5PO_4H^-. \qquad [5]$$

It seems likely that the volume and entropy change and the deuterium isotope effect of reaction [4] will be similar to those for the reaction

$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-, \qquad [6]$$

and those for reaction [5] will be similar to those for the alkaline hydrolysis of esters, in which a hydroxide ion also attacks an acetate group:

$$CH_3COOR + OH^- \rightarrow CH_3COOH + OR^-. \qquad [7]$$

The thermodynamic parameters for reaction [6] can be obtained from those for the reactions

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \qquad [8]$$

and

$$H_2O \rightleftharpoons H^+ + OH^-. \qquad [9]$$

The data are given in Table II. They are mostly for temperatures near 25° C but this should not affect the conclusions in any important way. It is clear that the volume and entropy of activation and the deuterium isotope effect are quantitatively consistent with the mechanism given in reactions [4] and [5].

TABLE II

Reaction No.	ΔV/cm^3 mole^{-1}	ΔS/cal deg^{-1} mole^{-1}	K_H/K_D or k_H/k_D
8 equil.	−15.1 (12)	−15.6 (15, p. 758)	1.61 (17)
9 equil.	−23.4 (13)	−18.7 (15, p. 667)	5.43 (17–19)
6 equil.	−7.9	−3.0	3.37
7 rate	−9 (14)	−27 (16)	0.75 (20)
4 and 5 rate, expected value	−17	−30	2.53
Exptl. value	$-19\pm\sim2$ (this work)	−28.8 (1)	2.5 (1)

NOTE: K_H/K_D and k_H/k_D are the ratio of equilibrium and rate constants in H_2O and D_2O.

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