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# THE ACID CATALYZED HYDROLYSIS OF METHYL DIALKYLPHOSPHINATES

Robert D. Cook* and Khamis Abbas[1]

Department of Chemistry, American University of Beirut, Beirut, Lebanon

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There has been considerable recent work on the alkaline hydrolysis of alkyl dialkylphosphinates[2,3], but there have been no previous reports on the hydrolysis of these compounds in acid medium. We wish to report on our study of the acid-catalyzed hydrolysis of the esters Ia-c. The catalyzing acid was $D_2SO_4$. The rates were studied by monitoring the reactions by

$R_2PO_2CH_3$ Ia R = $CH_3$- Ib R = $CH_3CH_2$- Ic R = $(CH_3)_2CH$-

n.m.r. spectroscopy. The bands in the n.m.r. due to the product, methanol, and the $PO\underline{CH_3}$ group of the ester are well separated and can be easily integrated. The rates were measured at the acid strength at which the individual esters are half protonated, and also at an acid strength of $D_0 = -5.8 \pm 0.05$, where there is a constant activity of water and the esters are approximately 100% protonated. The rate data for our compounds plus comparison data for other ester systems are given in Table I. The pKa data in Table II were determined by n.m.r. in $D_2SO_4$-$D_2O$ by the method of Haake[4]. Table II also gives the activation parameters for the

Table I

Relative Rates for Ester Hydrolyses

| Reaction | R = Methyl | Ethyl | Isopropyl | Conditions |
|---|---|---|---|---|
| $R_2PO_2CH_3 + D^+$[a] | 12 | 3.4 | 1 | 75.8°C in $D_2SO_4$-$D_2O$; $D_0 = -5.8$, this work |
| $R_2PO_2CH_3 + D^+$[b] | 8 | 1.9 | 1 | 75.8°C in $D_2SO_4$-$D_2O$; $D_0$ = pKa, this work |
| $R_2PO_2CH_3 + OH^-$ | 53 | 1 | -[c] | 75°C in 60% dimethoxyethane-water, ref. 2 |
| $RCO_2C_2H_5 + OH^-$ | 7.5 | 3.8 | 1 | 44.7°C in 70% acetone, ref. 8 |
| $RCO_2C_2H_5 + H^+$ | 3.3 | 2.7 | 1 | 44.7°C in 70% acetone, HCl = 0.1 M, ref. 8 |

[a] The $k_{obs}$ for $(CH_3)_2PO_2CH_3 = 2.04 \times 10^{-5}$ $sec^{-1}$.

[b] The $k_{obs}$ for $(CH_3)_2PO_2CH_3 = 3.3 \times 10^{-5}$ $sec^{-1}$.

[c] This ester does not give simple second order kinetics, reference 7.

three esters at 75°C.

It is quite clear from the data in Table I that polar and steric effects do not play as important a part in the acid-catalyzed hydrolysis as in the alkaline hydrolysis of phosphinates. This difference is similar to the well-established result for carboxylic esters[5]. However, the steric and polar effects play a more important part in the hydrolysis of phosphinates than in carboxylates. This observation is consistent with the mechanisms for these reactions; the carboxylate system goes through a tetravalent intermediate[6] while the phosphinate goes through a pentavalent intermediate[2,3,7]. Although at present the study of the phosphinate esters is not complete, it appears as if Ia-c are affected by acid concentration in a similar manner; that is, there is an initial acid catalysis followed by an acid inhibition of the rate of hydrolysis.

Table II

Acidity Constant Data and Activation Parameters for the Acid-Catalyzed Hydrolysis of Methyl Dialkylphosphinates

| Compound | pKa[a] | M[a] | $\Delta G^{*}$[b] Kcal/mole | $\Delta H^{*}$[b] Kcal/mole | $\Delta S^{*}$[b] e.u. |
|---|---|---|---|---|---|
| Ia | -3.14 | 0.486 | 27.7 | 21.6 | -18 |
| Ib | -3.56 | 0.508 | 28.7 | 20.6 | -23 |
| Ic | -3.29 | 0.511 | 29.2 | 21.6 | -22 |

[a] Obtained from the least squares analysis of a plot of log $SD^+/S$ versus $D_0$, where the slope = M and intercept = MpKa. The value M represents the derivation of the substrate from Hammett basicity, see reference 4.

[b] From acid strengths where the esters are half protonated and the values are for 75°C.

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