VISCOSITIES of tetraethylammonium bromide and iodide have been measured in acetone-water mixtures and the results analysed in terms of Jones-Dole equation[1].

Tetraethylammonium bromide (TEAB) (BDH) was purified according to the procedure recommended by Harkness and Doggett[2]. Tetraethylammonium iodide (TEAI) was a Merck's extrapure sample. Acetone and water used were purified by standard methods and their specific conductances were within the range reported in literature. All viscosity measurements were carried out in a water-bath maintained at $35° \pm 0.01°$. Tuan-Fuoss[3] viscometer with flow time for water of 1225 sec at 35° was employed in all the measurements. The densities of the solutions were determined using a pyknometer of 25 ml capacity.

The viscosity data are represented graphically in Fig. 1 as a plot of $(\eta/\eta° - 1)/C^{1/2}$ vs $C^{1/2}$. The two coefficients A and B of Jones-Dole equation (Eq. 1) are given in Table 1 for different concentrations of acetone in water.

$$\eta/\eta° = 1 + AC^{1/2} + BC \qquad \ldots(1)$$

The different A values (Table 1) for the two salts indicate the dependence of ionic interactions on the nature of the electrolyte. Iodide ion being larger as compared to the bromide ion, usually remains unsolvated and consequently is expected to have stronger interactions with its counterpart in comparison to the solvated bromide ion. The values of A for tetraethylammonium iodide are of higher magnitude in different acetone-water systems supporting this viewpoint. The variation in A values with the change in acetone content in the mixture can be attributed to the change in the mobility of the ions with a change in the dielectric constant of the medium[4]. Large and positive A values suggest strong ion-ion interactions, possibly due to unusual cation-cation and cation-anion penetrations as suggested by earlier workers[5,6]. The negative A coefficients are without any significance[7].

The positive B values in the case of tetraethylammonium bromide indicate strong alignment of the solvent molecules with the small bromide ion which undoubtedly promotes the formation of structure of the solvent molecules in its immediate vicinity. On the other hand, the large iodide ion with the small charge density has a weak alignment effect and appears to be a great acetone-phobic. This acetone-phobic character of the iodide ion is responsible for the high negative B values in the case of tetraethylammonium iodide in the various acetone-water systems.

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TABLE 1 — VALUES OF COEFFICIENTS A AND B AT 35°

Acetone (w/w, %)	Tetraethylammonium bromide		Tetraethylammonium iodide	
	A	B	A	B
0.0	0.0250	0.1000	−0.0240	0.3850
10.0	0.0378	0.1140	0.5070	−0.6000
30.0	0.0120	0.2800	0.4780	−1.0000
50.0	−0.1520	0.8000	0.3650	−1.6000
80.0	0.0083	0.5710	1.0099	−2.6600

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Fig. 1 — Plot of $(\eta - \eta°)/\eta°C^{1/2}$ against $C^{1/2}$ for tetraethylammonium iodide (TEAI) and tetraethylammonium bromide (TEAB) in acetone-water mixtures

Hydrolysis of Organic Phosphates:
Part IX — Hydrolysis of 1-Nitro-2-naphthyl- & 4-Nitro-1-naphthyl-phosphate Monoesters

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Kinetics of the hydrolysis of 1-nitro-2-naphthyl and 4-nitro-1-naphthyl phosphate monoesters have been investigated in acid medium (0.01-6.0M HCl) at 98°. The esters are reactive through their neutral and conjugate acid species in this region. Arrhenius parameters, concept of molecularity and kinetic data support a bimolecular nucleophilic attack of water on phosphorus atom of the conjugate acid species of nitro-naphthyl phosphate monoesters.
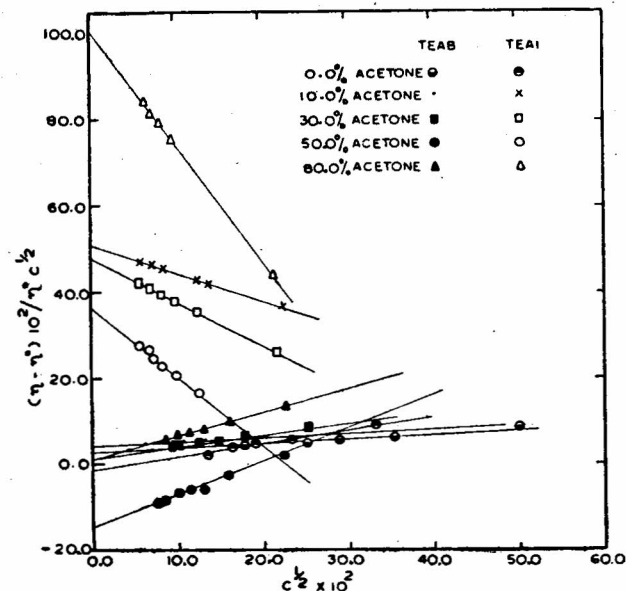
ARYL phosphate esters having electron-attracting substituents in the aryl moiety exhibit abnormal

acid catalysis[1]. Later on electron-repelling groups ($-OCH_3$) were also shown to exhibit such a phenomenon by virtue of their ability to get protonated and acting as electron-attracting substituents[2]. Although nitronaphthyl phosphate esters[3] are important insecticides, they have not been studied kinetically so far. Hence a detailed study of the kinetics of hydrolysis of nitro-naphthylphosphate esters has been undertaken, the results of which are presented in this paper.

1-Nitro-2-naphthylphosphate monoester was prepared by the standard method[4]. 4-Nitro-1-naphthylphosphate monoester was prepared by the slow addition of dry pyridine (4·2 g) to a mixture of 4-nitro-1-naphthol (10 g) in dry benzene (250 ml) and phosphorus oxychloride (8·12 g) under reflux. The reaction mixture was cooled, filtered and benzene was removed under vacuum. The residue was treated with 5% sodium hydroxide solution and filtered. The filtrate was acidified and again filtered. The aqueous solvent was evaporated yielding the crude product which on recrystallization from acetone gave light yellow coloured solid, m.p. 178° (Found: C, 45·02; H, 3·53; P, 11·08. $C_{10}H_8NO_6P$ requires C, 44·61; H, 2·97; P, 11·52%).

Hydrolysis of 1-nitro-2-naphthyl- and 4-nitro-1-naphthyl-phosphate monoesters (0·0005M) was studied in distilled water, unless otherwise specified, and the inorganic phosphate formed during the hydrolysis was estimated colorimetrically using Allen's method[5].

Pseudo-first-order rate constants of hydrolysis of 1-nitro-2-naphthyl- and 4-nitro-1-naphthyl-phosphate monoesters are summarized in Tables 1 and 2. The overall rate of hydrolysis is represented by the Eq.[6] (unpublished data).

$$k_e = k_\Psi + k_N \qquad \qquad \text{...(i)}$$

The kinetics of hydrolysis of (a) 1-nitro-2-naphthyl- and (b) 4-nitro-1-naphthylphosphate monoesters via their conjugate acid species may be described by Eqs. (ii) and (iii) respectively.

(a) $k_\Psi = 0.51 \times 10^{-3} C_{H^+}. \exp.0.021 C_{H^+}.(a_{H_2O})^n$ ...(ii)

where $n = 0$ for 1 to 4M HCl and $n = 1$ and 3 respectively for 5·0 and 6·0M HCl and

(b) $k_\Psi = 16.0 \times 10^{-3} C_{H^+}.(a_{H_2O})^n$ ...(iii)

where $n = 0$ for 1·0 to 3M HCl and $n = \frac{1}{2}$, 1 and 3 respectively for 4, 5 and 6M HCl.

The reactivity differences of specific acid rates may be attributed to the steric hindrance of *peri*-hydrogen atom[7], which precludes the nitro group to enforce its electromeric effect favourable for hydrolysis of 1-nitro-2-naphthylphosphate.

Effects of aqueous-dioxane media are in accord with the transition state formed from the conjugate acid species of monoesters[8]. A changeover of solvent from water to 90% deuterium oxide enhances the rate[9,10] (1-nitro-2-naphthylphosphate: k_{D_2O}/k_{H_2O} =1·9; 4-nitro-1-naphthylphosphate: k_{D_2O}/k_{H_2O}=1·20). Therefore, catalysis is of specific nature for the reason as in the case of *p*-nitrophenylphosphate[1]. The unit slopes of plots of Zücker-Hammett hypothesis[11] and activation parameters[12-14] for reactions in 3M HCl (1-nitro-2-naphthylphosphate: ΔE

TABLE 1 — THE FIRST-ORDER RATE COEFFICIENTS OF HYDROLYSIS IN AQUEOUS SOLUTION AT 98°C

[HCl] M	$k_e \times 10^3$ min^{-1}		$k_e \times 10^3$ min^{-1}	
	Obs.	Calc.	Obs.	Calc.
	1-Nitro-2-naphthyl-phosphate monoester		4-Nitro-1-naphthyl-phosphate monoester	
0·01	27·66	—	—	—
0·05	19·49	—	19·96	—
0·10	16·33	—	15·59	—
0·50	10·73	—	13·56	—
1·00	8·45	10·20	31·04	33·38
	16·06*		36·63*	
1·50	11·30	11·00	39·57	41·72
2·00	11·58	11·85	56·31	54·39
2·50	12·41	12·73	67·05	65·39
3·00	13·17	13·67	76·23	76·84
	7·48 (90°)		52·52 (90°)	
	4·15 (80°)		33·11 (80°)	
4·00	14·16	15·73	82·88	78·00†
	10·03‡		62·66‡	
5·00	9·50	8·76†	69·47	62·64†
6·00	1·34	1·07†	12·57	13·69†

*In deuterium oxide.
†From Eq. (i).
‡In 30% dioxane.

TABLE 2 — THE RATE COEFFICIENTS OF ACID HYDROLYSIS AT CONSTANT IONIC STRENGTHS (μ) AT 98°

[HCl] M	$k_e \times 10^3$ min^{-1}	$k_e \times 10^3$ min^{-1}
	1-Nitro-2-naphthyl-phosphate monoester	4-Nitro-1-naphthyl-phosphate monoester
	$\mu = 2$	
0·4	11·45	30·05
0·8	11·98	38·74
1·2	12·50	46·41
1·6	12·40	52·37
	$\mu = 3$	
0·5	12·28	27·58
1·0	12·88	46·30
1·5	13·14	55·62
2·0	13·30	63·81
	$\mu = 4$	
1·0	13·56	51·19
1·5	14·57	68·69
2·0	14·53	80·32
3·0	15·29	83·80

= 10·40 kcal mole^{-1}, $A = 1.25 \times 10^3$ sec^{-1}, $\Delta S\ddagger$ = −46·80 e.u.; 4-nitro-1-naphthyl phosphate: ΔE = 8·21 kcal mole^{-1}, $A = 1.0 \times 10^2$ sec^{-1}, $\Delta S\ddagger$ = −51·99 e.u.) are indicative of bimolecular nature of hydrolytic reactions. Bunnett and Olsen[15] have suggested that the kinetic dependence of an acid hydrolysis upon acidity can usefully be characterized by the value of ϕ, which is the slope of a plot of $\log k + H_0$ against $H_0 + \log C_{H^+}$. The values of ϕ for both the monoesters are ca. 1·30, which is quite similar to those for *o*-nitrophenyl[16], *p*-nitrophenyl[1] and dinitrophenyl phosphates[17]. A comparative kinetic rate data of other monoesters supports P—O bond fission[18].

Acid hydrolysis of these monoesters may therefore be suggested to involve bimolecular attack of

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water on phosphorus of conjugate acid species formed by fast pre-equilibrium proton transfer.

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Participation of Cr₂O₇²⁻ in the Oxidation of p-Methoxyacetophenone by Cr(VI)

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The oxidation of p-methoxyacetophenone by Cr(IV) under acid condition reveals for the first time participation of Cr₂O₇²⁻ as the active oxidizing species.

PARTICIPATION of both $HCrO_4$ and $Cr_2O_7^{2-}$ species has been demonstrated by Mason and Kowalak[1] in Cr(VI)-As(III) and by Espenson[2] in Cr(VI)-V(IV) oxidations. However, in oxidation of organic compounds by Cr(VI) under acid conditions, no such participation of $Cr_2O_7^{2-}$ as an active oxidant has been demonstrated, the main oxidant being either $HCrO_4^-$ or any of its protonated species. We are, therefore, prompted to put on record the preliminary results which provide a kinetic evidence for the participation of both $HCrO_4^-$ and $Cr_2O_7^{2-}$ in the oxidation of p-methoxyacetophenone (I), by Cr(VI) under acid conditions.

Chemicals used were either chemically pure or were purified using conventional procedures. Since I is sparingly soluble in water, 50% acetic acid-water mixture (v/v) was used as the solvent. The reaction was followed by quenching thermostated ($\pm 0.02°$)

aliquots of the reacting solutions in known excess of ferrous ammonium sulphate solution. Unreacted ferrous ions were estimated using standard sodium dichromate solution and barium diphenyl amine sulphonate as indicator.

Under pseudo first order conditions $\{[Cr(VI)] \times 10 > [I]\}$ the rate of disappearance of Cr(VI) follows first order rate law up to at least 70% conversion. The observed rate of oxidation changes with the changing initial [Cr(VI)]. (cf Table 1) in accordance with the following expression:

$$-d[Cr(VI)]/dt = a[HCrO_4^-] + b[HCrO_4^-]^2$$

where $a(= 1 \times 10^{-4})$ and $b(= 0.1)$ have been evaluated from the linear plot of $-d[Cr(VI)]/dt \times 1/[HCrO_4^-]$ against $[HCrO_4^-]$. This indicates that both $HCrO_4^-$ and $Cr_2O_7^{2-}$ are the active oxidizing species. The contribution of the path involving $HCrO_4^-$ to the observed rate is small and significant only at lower [Cr(VI)]. At higher initial [Cr(VI)] the oxidation is practically due to $Cr_2O_7^{2-}$ (cf. Table 1).

This observation is radically different from chromic acid oxidation of acetophenone and nuclear substituted acetophenones[3] under acid conditions where there is a strict first order dependence on $[HCrO_4^-]$.

Order with respect to hydrogen ions is two (cf. Table 2). Dependence on [I] follows the rate expression as revealed by the linear plot between $([ketone]/k_1) \times 10^{-2}$ and [ketone]

$$k_1 = 5.26 \times 10^{-4}.[ketone]/(1.84 \times 10^{-1} + [ketone])$$

which suggests a rapid complex formation between the substrate and the oxidant. Since ketone variation has been carried out at relatively higher concentration of Cr(VI) (Table 3) where $HCrO_4^-$ contribution

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TABLE 1 — VARIATION OF RATE WITH INITIAL [Cr(VI)]

$\{[Ketone] = 0.10M; [HClO_4] = 3.15M; temp. = 30°\}$

[Cr(VI)] $\times 10^3(M)$	[HCrO₄⁻] $\times 10^3(M^*)$	$(-d[Cr(VI)]/dt)†$ $\times 10^7$	$\left\{\dfrac{1}{[HCrO_4^-]^2}\right\} \times \left\{\dfrac{-d[Cr(VI)]}{dt}\right\}$
2·40	2·04	6·12	0·147
4·80	3·65	17·42	0·134
7·20	5·17	31·00	0·116
9·60	6·23	45·40	0·117
12·00	7·33	61·40	0·114

*Calculated using K_h for the reaction $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^-$ (ref. 4 & 5) = $2·3 \times 10^{-2}$ at 30°.
†Values within ± 5·0%.

TABLE 2 — VARIATION OF RATE WITH INITIAL [H⁺]

$\{[Cr(VI)] = 6 \times 10^{-3}M; [Ketone] = 0.10M; [ClO_4^-] = 4.05M; temp. = 30°\}$

[H⁺] $\times M$	$\left(\dfrac{-d[Cr(VI)]}{dt}\right) \times 10^6$	$\left[\dfrac{-d[Cr(VI)]}{dt}\right] \times \dfrac{10^7}{[H^+]^2}$
1·80	2·67	8·24
2·25	3·84	7·58
2·70	5·47	7·50
3·15	7·34	7·40
3·60	10·80	8·33
4·05	13·20	8·05