Kinetics of Degradation of Tetraphosphates

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The degradation of tetraphosphates between pH 2 and 10 and at $50°\pm0.05°$, $60°\pm0.05°$, $65°\pm0.05°$ and $70°\pm0.05°$ and $\mu = 1M$, is first order in [tetraphosphate]. The H$^+$ ions catalyse and control the equilibria between the various tetraphosphate species. The overall rate constants (k) can be resolved into the individual rate constants using the values of dissociation constants obtained under conditions of the kinetic experiments. The activation parameters for the overall reaction, as also for the stepwise reactions, have been calculated.

THE kinetics of pyrophosphate and triphosphate have been investigated thoroughly by several workers[1-3]. However, no comprehensive study seems to have been done on the degradation of the tetraphosphate. Earlier studies[4-7] on the kinetics of degradation of the tetraphosphate covered rather limited ranges of pH and temperature. The significant observations recorded during these studies were a first order dependence of the rate on [tetraphosphate] and a decrease in rate with increasing pH. No effort was made to estimate the concentrations of various tetraphosphate species with a view to analysing and interpreting the kinetic data in terms of the degradation of various tetraphosphate species present in the solution. The results of such a study are recorded in this paper. In the present study concentrations of different species were calculated from their dissociation constants which were obtained under the conditions of the kinetic experiments. The degradation of tetraphosphate at $\mu = 1m$ was carried out at pH 2, 3, 4, 5, 6, 7, 8, 9 and 10 and temperatures 50°, 60°, 65° and 70° maintained within $\pm0.05°$.

Materials and Methods

As pure tetraphosphate could not be obtained in sufficiently large quantities, a phosphate mixture containing 40% of tetraphosphate was used. It was obtained by heating an alkaline (pH 12.0) solution of sodium tetrametaphosphate (NaPO$_3$)$_4$·4H$_2$O at 65.5° for 1 hr. The resultant solution was analysed for tetraphosphate (P, 40-45%), tetrametaphosphate (P, 25-30%), triphosphate (P, 20-25%), pyrophosphate (P, 5-7%) and orthophosphate (P, 1-2%) concentrations.

NaOH, HCl, ammonium molybdate and NH$_4$OH used were of AR grade. ZnSO$_4$ (99.5% pure) required for pyrophosphate estimation was of May & Baker grade. EDTA disodium salt and the indicator eriochrome black-T were of E. Merck quality. Acetone and gl. acetic acid used were of BDH grade.

The presence of tetrametaphosphate, orthophosphate, pyrophosphate and triphosphate, however, did not interfere with the degradation of tetraphosphate, since the degradations of the phosphates were independent of each other. This was confirmed

by carrying out the degradation of triphosphate in the absence and presence of sodium pyrophosphate at pH 5.0, temperature $65°\pm0.05°$ and $\mu = 1M$. The reaction rate (6.70×10^{-4} min^{-1}) in both the cases was found to be the same as reported by Smith[5].

Sodium tetrametaphosphate — It was obtained by the low temperature hydration of phosphorus pentoxide[8] followed by neutralization of the resultant tetrametaphosphoric acid with Na$_2$CO$_3$. The crystallization of the sodium salt was effected by adding NaCl. It analysed for tetrametaphosphate (P, 98-99%), orthophosphate (P, 0.5-1.0%), pyrophosphate (P, 0.0%) and triphosphate (P, 0.5-1.0%).

Kinetic measurements — The reaction mixture containing sodium tetraphosphate and adjusted to the desired pH value by adding NaOH/HCl was placed in a 250 ml pyrex measuring flask and suspended in a thermostat. Aliquots (10 ml each) of the reaction mixture were taken out at different time intervals and analysed for orthophosphate, pyrophosphate and triphosphate concentrations.

Estimation of various phosphates present in the mixture — Orthophosphate was estimated initially and then at different intervals of time by colorimetric method due to Bernhart and Wreath[9]. A Colemann spectrophotometer was used for this purpose. The amount of orthophosphate was read from a standard linear plot of optical density versus [orthophosphate].

Pyrophosphate and triphosphate were estimated simultaneously by Bell's method[10]. To 10 ml of the reaction mixture (pH 3.8) was added 10 ml of the ZnSO$_4$ solution (5 g of ZnSO$_4$ dissolved in 100 ml distilled water and pH adjusted to 3.80), which resulted in lowering of pH. The pH of the solution was again adjusted to 3.8 by adding standard NaOH. The amount of NaOH (x) used is equivalent to the concentrations of pyrophosphate and triphosphate present in the mixture. Also at this stage pyrophosphate present was completely precipitated as zinc pyrophosphate. The solution was filtered and the precipitate washed with acetic acid (pH, 3.8) solution till the filtrate became free from SO$_4^{2-}$ ions. The precipitate was dissolved in 2N aq. ammonia and a measured excess of EDTA

solution added to it. The excess EDTA was then titrated against standard $ZnSO_4$ using eriochrome black T as indicator. The EDTA needed for zinc obtained from zinc pyrophosphate corresponded to the concentration of pyrophosphate. The titration equivalent of EDTA used was subtracted from x to get the amount of NaOH equivalent to the amount of triphosphate present in the mixture.

The amount of tetraphosphate was determined as follows: Ten ml aliquot of the reaction mixture was taken at different time intervals and the sample analysed for orthophosphate, pyrophosphate and triphosphate concentrations. In order to get the [tetraphosphate] initially present, the reaction mixture (10 ml) was refluxed on a steam-bath for 10-12 hr to convert all the tetraphosphate completely into mixture of orthophosphate, pyrophosphate and triphosphate and the total amount of orthophosphate, pyrophosphate and triphosphate estimated. From this the amount of orthophosphate, pyrophosphate and triphosphate present initially was subtracted, and the difference corresponded to the amount of tetraphosphate present initially. However, the amount of tetraphosphate present at various stages of the reaction was calculated as follows:

If sum of the total P present as orthophosphate, pyrophosphate and triphosphate initially $= A$ g atoms of P/litre. Sum of the total P present as orthophosphate, pyrophosphate and triphosphate at time $t = B$ g atoms of P/litre, and sum of the total P present as orthophosphate, pyrophosphate and triphosphate after refluxing $= C$ g atoms of P/litre. Then initial [tetraphosphate] $=(C-A)$ g atoms of P/litre and [tetraphosphate] at time $t = (C-B)$ g atoms of P/litre.

The presence of tetrametaphosphate in the system, however, did not interfere with the estimations of ortho-, pyro-, tri- and tetra-phosphates at any stage of the reactions which were carried out in the pH range 2-10 since at these pH values tetrametaphosphate is quite stable[4].

Results and Discussion

The results of the kinetic studies are given in Table 1. The degradation rate (k) of tetraphosphate showed a first order dependence on [tetraphosphate]. A linear dependence of log $(a/a-x)$ on time, further supports this point. The activation energy (E_a) and the frequency factor (A) calculated from the linear plots of log k versus $1/T$ for the overall reaction are given in Table 2.

The data in Table 1 show that $k/[H^+]$ values at any given temperature, rapidly increase with increasing pH. The fact that the relation between the $[H^+]$ and pH is not a simple one is illustrated in Fig. 1. An increase in the rate of hydrolysis with decreasing pH (Table 1) may be either due to an increase in the fraction of more reactive species at a lower pH value or to a catalytic effect of H^+ ions on the hydrolysis of one or more of the species, or due to both of these factors.

The amounts of various species, as fractions (F_i) of the total [tetraphosphate] present in the solution, were calculated from the values of dissociation

TABLE 1 — AVERAGE FIRST ORDER RATE CONSTANT (k) AND THE VALUES OF $k/[H^+]$ AT DIFFERENT TEMPERATURES $[\mu = 1.0M]$

Initial $[P_4O_{13}^{6-}]$ $M \times 10^2$	pH	$k \times 10^4$ (min^{-1})	$k/[H^+]$ (litre mole^{-1} min^{-1})
		TEMP. $= 50° \pm 0.05°$	
1·253	2·0	2·34	2.34×10^{-2}
1·264	3·0	1·82	1.82×10^{-1}
1·286	4·0	1·45	1·45
1·212	5·0	1·15	11·50
1·264	6·0	0·89	8.90×10^1
1·251	7·0	0·72	7.20×10^2
1·270	8·0	0·55	5.50×10^3
1·221	9·0	0·44	4.40×10^4
1·246	10·0	0·35	3.50×10^5
		TEMP. $= 60° \pm 0.05°$	
1·296	2·0	8·71	8.71×10^{-2}
1·304	3·0	6·76	6.76×10^{-1}
1·312	4·0	5·25	5·25
1·204	5·0	4·06	40·60
1·216	6·0	3·13	313·00
1·251	7·0	2·43	2.43×10^3
1·298	8·0	1·91	1.91×10^4
1·210	9·0	1·45	1.45×10^5
1·267	10·0	1·12	1.12×10^6
		TEMP. $= 65° \pm 0.05°$	
1·259	2·0	20·89	20.89×10^{-2}
1·246	3·0	15·85	15.85×10^{-1}
1·267	4·0	12·16	12·16
1·22	5·0	9·23	92·30
1·216	6·0	7·00	700·00
1·263	7·0	5·37	5.37×10^3
1·210	8·0	4·07	4.07×10^4
1·202	9·0	3·09	3.09×10^5
1·259	10·0	2·40	2.40×10^6
		TEMP. $= 70° \pm 0.05°$	
1·211	2·0	30·20	30.20×10^{-2}
1·304	3·0	22·91	22.91×10^{-1}
1·296	4·0	17·38	17·38
1·261	5·0	13·18	131·80
1·322	6·0	10·23	10.23×10^2
1·242	7·0	7·41	7.41×10^3
1·205	8·0	5·89	5.89×10^4
1·211	9·0	4·47	4.47×10^5
1·206	10·0	3·47	3.47×10^6

TABLE 2 — ACTIVATION ENERGY (E_a) AND THE FREQUENCY FACTOR (A) FOR THE OVERALL REACTION

pH	E_a (kcal/mole)	log A* (min^{-1})
2·0	27·14	14·76
3·0	27·29	14·74
4·0	27·46	14·68
5·0	27·10	14·41
6·0	27·07	14·29
7·0	25·03	12·79
8·0	25·84	13·25
9·0	24·93	12·51
10·0	25·90	13·05

*A, corresponds to a pseudo first order reaction, i.e. [water] is taken as constant.

constants[11] of tetraphosphoric acid using Eqs. (1-7)

$$F_{H_6P_4O_{13}} = \frac{H_6P_4O_{13}}{\sum\limits_{n=0}^{6} H_nP_4O_{13}}$$

$$= \frac{1}{\left(1 + \dfrac{K_1}{[H^+]} + \dfrac{K_1K_2}{[H^+]^2} + \dfrac{K_1K_2K_3}{[H^+]^3} + \dfrac{K_1K_2K_3K_4}{[H^+]^4} \right.}$$
$$\left. + \dfrac{K_1K_2K_3K_4K_5}{[H^+]^5} + \dfrac{K_1K_2K_3K_4K_5K_6}{[H^+]^6}\right)$$

...(1)

$$F_{H_5P_4O_{13}^{1-}} = \frac{H_5P_4O_{13}^{1-}}{\sum\limits_{n=0}^{6} H_nP_4O_{13}}$$

$$= \frac{1}{\left(\dfrac{[H^+]}{K_1} + 1 + \dfrac{K_2}{[H^+]} + \dfrac{K_2K_3}{[H^+]^2} + \dfrac{K_2K_3K_4}{[H^+]^3} \right.}$$
$$\left. + \dfrac{K_2K_3K_4K_5}{[H^+]^4} + \dfrac{K_2K_3K_4K_5K_6}{[H^+]^5}\right)$$

...(2)

$$F_{H_4P_4O_{13}^{2-}} = \frac{H_4P_4O_{13}^{2-}}{\sum\limits_{n=0}^{6} H_nP_4O_{13}}$$

$$= \frac{1}{\left(\dfrac{[H^+]^2}{K_1K_2} + \dfrac{[H^+]}{K_2} + 1 + \dfrac{K_3}{[H^+]} + \dfrac{K_3K_4}{[H^+]^2} \right.}$$
$$\left. + \dfrac{K_3K_4K_5}{[H^+]^3} + \dfrac{K_3K_4K_5K_6}{[H^+]^4}\right)$$

...(3)

$$F_{H_3P_4O_{13}^{3-}} = \frac{H_3P_4O_{13}^{3-}}{\sum\limits_{n=0}^{6} H_nP_4O_{13}}$$

$$= \frac{1}{\left(\dfrac{[H^+]^3}{K_1K_2K_3} + \dfrac{[H^+]^2}{K_2K_3} + \dfrac{[H^+]}{K_3} + 1 + \dfrac{K_4}{[H^+]} \right.}$$
$$\left. + \dfrac{K_4K_5}{[H^+]^2} + \dfrac{K_4K_5K_6}{[H^+]^3}\right)$$

...(4)

$$F_{H_2P_4O_{13}^{4-}} = \frac{H_2P_4O_{13}^{4-}}{\sum\limits_{n=0}^{6} H_nP_4O_{13}}$$

$$= \frac{1}{\left(\dfrac{[H^+]^4}{K_1K_2K_3K_4} + \dfrac{[H^+]^3}{K_2K_3K_4} + \dfrac{[H^+]^2}{K_3K_4} + \dfrac{[H^+]}{K_4} \right.}$$
$$\left. + 1 + \dfrac{K_5}{[H^+]} + \dfrac{K_5K_6}{[H^+]^2}\right)$$

...(5)

$$F_{HP_4O_{13}^{5-}} = \frac{HP_4O_{13}^{5-}}{\sum\limits_{n=0}^{6} H_nP_4O_{13}}$$

$$= \frac{1}{\left(\dfrac{[H^+]^5}{K_1K_2K_3K_4K_5} + \dfrac{[H^+]^4}{K_2K_3K_4K_5} + \dfrac{[H^+]^3}{K_3K_4K_5} \right.}$$
$$\left. + \dfrac{[H^+]^2}{K_4K_5} + \dfrac{[H^+]}{K_5} + 1 + \dfrac{K_6}{[H^+]}\right)$$

...(6)

$$F_{P_4O_{13}^{6-}} = \frac{P_4O_{13}^{6-}}{\sum\limits_{n=0}^{6} H_nP_4O_{13}}$$

$$= \frac{1}{\left(\dfrac{[H^+]^6}{K_1K_2K_3K_4K_5K_6} + \dfrac{[H^+]^5}{K_2K_3K_4K_5K_6} \right.}$$
$$\left. + \dfrac{[H^+]^4}{K_3K_4K_5K_6} + \dfrac{[H^+]^3}{K_4K_5K_6} + \dfrac{[H^+]^2}{K_5K_6} + \dfrac{[H^+]}{K_6} + 1\right)$$

...(7)

The plots of log F_i versus pH at 70°C and $\mu = 1 \cdot 0 M$ are shown in Fig. 2. Similar plots were obtained at other temperatures also. Dissociation constants used in the calculations were obtained under conditions of the kinetic experiments.

Calculation of the individual rate constants — The rate constants characteristic of the various species were calculated using Eqs. (8) and (9).

Rate = $k_1[H_6P_4O_{13}] + k_2[H_5P_4O_{13}^{1-}] + k_3[H_4P_4O_{13}^{2-}]$
$+ k_4[H_3P_4O_{13}^{3-}] + k_5[H_2P_4O_{13}^{4-}] + k_6[HP_4O_{13}^{5-}]$
$+ k_7[P_4O_{13}^{6-}] + k_1'[H^+][H_6P_4O_{13}]$
$+ k_2'[H^+][H_5P_4O_{13}^{1-}] + k_3'[H^+][H_4P_4O_{13}^{2-}]$
$+ k_4'[H^+][H_3P_4O_{13}^{3-}] + k_5'[H^+][H_2P_4O_{13}^{4-}]$
$+ k_6'[H^+][HP_4O_{13}^{5-}] + k_7'[H^+][P_4O_{13}^{6-}]$ ...(8)

where k_i is the rate constant for the uncatalysed process and k_i' refers to the same process catalysed by H^+ ions. Equation (8) may be written as Eq. (9).

Rate = $(k_1 + K_1k_2')[H_6P_4O_{13}] + (k_2 + K_2k_3)[H_5P_4O_{13}^{1-}]$
$+ (k_3 + K_3k_4')[H_4P_4O_{13}^{2-}] + (k_4 + K_4k_5')$
$\times [H_3P_4O_{13}^{3-}] + (k_5 + K_5k_6')[H_2P_4O_{13}^{4-}]$
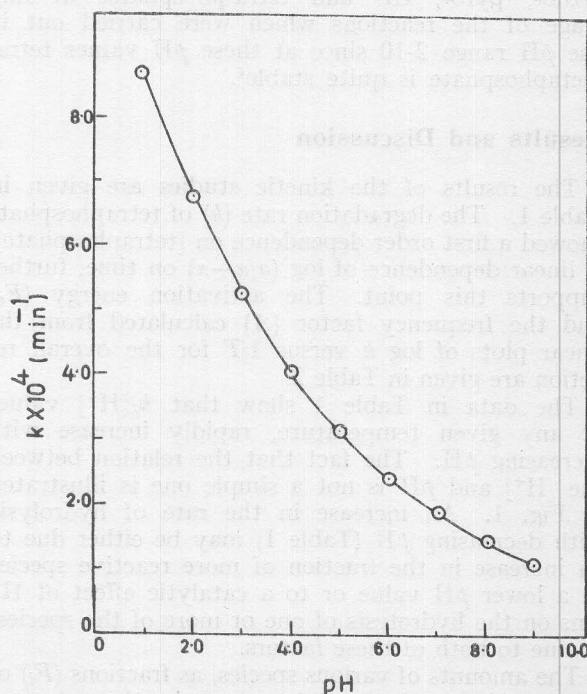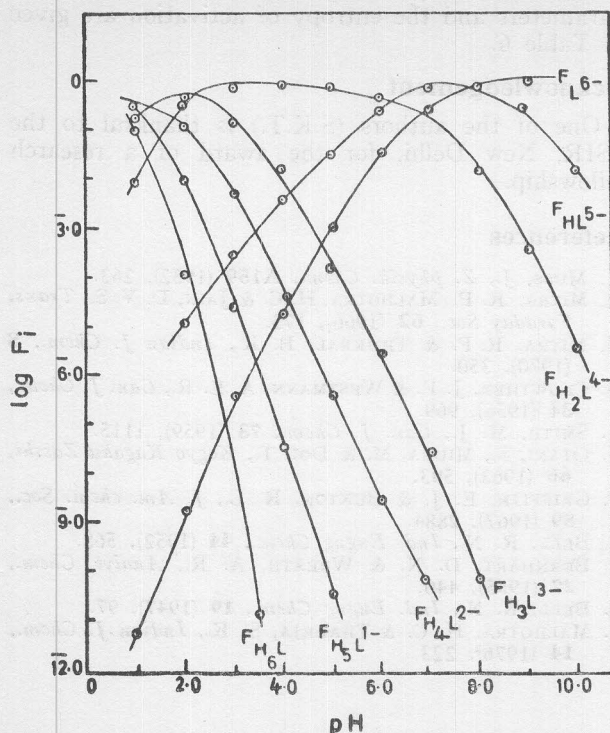$+ (k_6 + K_6k_7')]HP_4O_{13}^{5-}] + k_7[P_4O_{13}^{6-}]$
$+ k_1'[H_6P_4O_{13}][H^+]$ ...(9)

Fig. 1 — Plot of k against pH at 60°

Fig. 2 — Plots of log F_i versus pH at 70° $\{L = P_4O_{13}^{-6}\}$

TABLE 3 — OVERALL RATE CONSTANT OF THE VARIOUS SPECIES

Coefficient	Overall rate constant $\times 10^4$ at			
	50°	60°	65°	70°
$k_3 + K_3 k_4'$	5·51	14·82	26·52	44·89
$k_4 + K_4 k_5'$	4·43	11·95	24·40	42·5
$k_5 + K_5 k_6'$	1·46	4·22	9·27	13·91
$k_6 + K_6 k_7'$	0·81	2·40	4·08	6·10
k_7	0·40	1·19	2·28	3·25

TABLE 4 — VALUES OF THE INDIVIDUAL RATE CONSTANTS OF THE VARIOUS SPECIES

Reaction		$k \times 10^4$ (min^{-1})			
		50°	60°	65°	70°
(a) $H_4P_4O_{13}^{2-} + H_2O \xrightarrow{k_3}$ product		2·91	6·31	13·34	20·90
(b) $H_3P_4O_{13}^{3-} + H_2O \xrightarrow{k_4}$ product		2·31	5·52	9·89	17·08
(c) $H_2P_4O_{13}^{4-} + H_2O \xrightarrow{k_5}$ product		1·40	4·17	9·23	13·50
(d) $HP_4O_{13}^{5-} + H_2O \xrightarrow{k_6}$ product		0·81	2·40	4·08	6·10
(e) $P_4O_{13}^{6-} + H_2O \xrightarrow{k_7}$ product		0·40	1·19	2·28	3·25

Reaction		$k \times 10^4$ (litre mole^{-1} min^{-1})			
		50°	60°	65°	70°
(f) $H_4P_4O_{13}^{2-} + H_3O^+ \xrightarrow{k_3'}$ product		2·11 $\times 10^{-4}$	4·17 $\times 10^{-4}$	6·85 $\times 10^{-4}$	9·11 $\times 10^{-4}$
(g) $H_3P_4O_{13}^{3-} + H_3O^+ \xrightarrow{k_4'}$ product		7·16 $\times 10^{-3}$	22·91 $\times 10^{-3}$	33·11 $\times 10^{-3}$	54·96 $\times 10^{-3}$
(h) $H_2P_4O_{13}^{4-} + H_3O^+ \xrightarrow{k_5'}$ product		4·53 $\times 10^{-2}$	13·44 $\times 10^{-2}$	28·96 $\times 10^{-2}$	48·43 $\times 10^{-2}$
(i) $HP_4O_{13}^{5-} + H_3O^+ \xrightarrow{k_6'}$ product		59·85	87·80	116·9	150·8

TABLE 5 — COMPARISON OF OVERALL RATE CONSTANTS

pH	$k \times 10^4$ (min^{-1})	
	Calc.	Reported
	TEMP. = 65°	
2·55	17·09	18·0[a]
5·35	8·79	8·30[a]
9·80	2·33	2·50[a]
	TEMP. = 60°	
4·0	4·36	4·60[b]
7·0	2·90	2·0[b]
11·0	1·20	0·88[b]

(a) Ref. 4, (b) Ref. 7.

The fraction of the tetraphosphate species existing as $P_4O_{13}^{6-}$ is negligible below pH 7 where as above pH 2·0 the fractions of $H_6P_4O_{13}$ and $H_5P_4O_{13}^{1-}$ can also be neglected. In the pH region 2·0-7·0, the fractions of the species $H_4P_4O_{13}^{2-}$, $H_3P_4O_{13}^{3-}$, $H_2P_4O_{13}^{4-}$ and $HP_4O_{13}^{5-}$ are significant. Thus the first two and last two terms in Eq. (9) can be deleted. The values of $(k_3 + K_3 k_4')$, $(k_4 + K_4 k_5)$, $(k_5 + K_5 k_6')$ and $(k_6 + K_6 k_7')$ were calculated by substituting in Eq. (9) the fraction of each species at four different pH values and then solving the four simultaneous equations thus obtained.

Calculation of k_6 and k_7 — Since at pH 7·0, the significant species are $H_2P_4O_{13}^{4-}$, $HP_4O_{13}^{5-}$ and $P_4O_{13}^{6-}$. The 1st, 2nd, 3rd, 4th and last term in Eq. (9) can be neglected. Thus knowing the values of 5th and 6th term, k_7 was calculated. The rate constant k_7' is of little importance as the H$^+$ ions would not be present in a significant amount along with $P_4O_{13}^{6-}$. The value of K_6 being very small, the product $k_7' K_6$ can be neglected in comparison to k_6 i.e. $k_6 + K_6 k_7'$ may be taken equal to k_6. The values of the coefficients of $H_4P_4O_{13}^{2-}$, $H_3P_4O_{13}^{3-}$, $H_2P_4O_{13}^{4-}$, $HP_4O_{13}^{5-}$, $P_4O_{13}^{6-}$ calculated as above at different temperatures are given in Table 3.

Calculation of k_3, k_3', k_4, k_4', k_5, k_5' and k_6' — The over all rate constants (Table 1) between pH 2·0 and 7·0 were used for the determination of these constants. The amounts of the significant species which are present in this pH range and [H*] were substituted in Eq. (8) and by successive elimination the values of the above individual rate constants were calculated at 50°, 60°, 65° and 70° except k_3' whose value was approximate due to non-availability of an accurate value of dissociation constant K_2. The individual rate constants are given in Table 4.

Employing the individual rate constants, the overall rate constants at 65° and pH 2·55, 5·35 and 9·80, and at 60° and pH 4, 7 and 11 were calculated. The calculated values (Table 5) compared well with those reported by Crowther and Westmann[4] and Griffith and Buxton[7].

TABLE 6 — ACTIVATION ENERGY, FREQUENCY FACTOR AND
ENTROPY OF ACTIVATION

Reaction*	E_a (kcal/mole)	Log A	ΔS^* (e.u.)
(a)	17·10	8·13	−21·62
(b)	19·43	9·25	−16·50
(c)	22·14	9·82	−13·89
(d)	18·14	8·15	−21·53
(e)	18·72	8·18	−21·39
(f)	16·62	7·59	−24·08
(g)	19·63	10·60	−10·31
(h)	18·33	9·43	−15·67
(i)	9·75	8·29	−20·84

*The reactions (a), (b), (c), (d), etc. correspond to those given in Table 4.

Energy and entropy of activation — The activation energy and the frequency factor (A) for each reaction were calculated from the linear plots of log k_i or log k_i' versus $1/T$ where $i = 3, 4, 5, 6$ and 7. These parameters and the entropy of activation are given in Table 6.

Acknowledgement

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