Indian Journal of Chemistry
Vol. 14A, April 1976, pp. 223-225

Dissociation Constants of Tetraphosphoric Acid

H. C. MALHOTRA & (Miss) S. K. THAREJA
Department of Chemistry, University of Delhi, Delhi 110007

Received 11 *April* 1975; *accepted* 8 *May* 1975

Dissociation constants (pK_3, pK_4, pK_5 and pK_6) of tetraphosphoric acid have been determined at 25°±0·05°, 50°±0·05°, 60°±0·05°, 65°±0·05° and 70°±0·05° and at ionic strengths 0·034, 0·068, 0·11, 0·40, 0·70 and 1·00*M*, from the *p*H titration curves of tetramethylammonium tetraphosphate against HCl. The enthalpies ($\Delta H°$) and entropies ($\Delta S°$) of the dissociation have also been calculated.

NOT much work has been reported on the degradation of tetraphosphates particularly with regard to the kinetics of the reaction[1]. Only the data[2] on dissociation constants are available at 25° and $\mu = 1M$. In the present paper are reported the dissociation constants and the enthalpies and entropies of the dissociation of tetraphosphoric acid at different temperatures and ionic strengths.

Materials and Methods

A water-thermostat was used up to 50°. However, above this temperature the studies were carried out in an oil-thermostat. The *p*H titrations were performed on a *p*H-meter (Radiometer Copenhagen type PHM26) using glass electrode (Radiometer G-202C) in conjunction with a SCE. The *p*H-meter was standardized against potassium dihydrogen phthalate buffers and also against the standard buffer solutions supplied by the manufacturers. The ionic strengths were adjusted by adding the calculated amounts of tetramethylammonium bromide.

Preparation of sodium tetraphosphate — Sodium tetraphosphate was prepared from sodium tetrametaphosphate following the Thilo and Rätz[3] method as modified by Crowther and Westmann[1a]. Sodium tetrametaphosphate in turn was prepared by the method of Bell[4]. The tetrametaphosphate gave satisfactory analyses for phosphorus.

An alkaline solution of sodium tetrametaphosphate (*p*H = 12·0) was heated at 65° for 1 hr. The resultant solution was found to be a mixture of tetra-, tetrameta-, tri-, pyro- and ortho-phosphates. The guanidinium tetraphosphate crystals were obtained from this mixture of phosphates by the method of Quimby[5].

The stock solutions of guanidinium tetraphosphate were converted into tetramethylammonium tetraphosphate using Dowex-50 cation exchange resin presaturated with tetramethylammonium ions. The solution and the resin were kept at nearly 0° since the salt is quite stable at this temperature.

Results and Discussion

Calculation of the dissociation constants — The dissociation constants, determined at 25°±0·05°, 50°±0·05°, 60°±0·05°, 65°±0·05° and 70°±0·05°C and at ionic strengths 0·034, 0·068, 0·11, 0·40, 0·70 and 1·00*M*, were calculated from the *p*H-titration curves of the solutions of 0·0016-0·005*M* tetramethylammonium tetraphosphate against HCl.

Each titration curve showed three inflections. At the first inflection the species $P_4O_{13}^{6-}$ predominates, while at the second and third inflection, the most abundant species are $HP_4O_{13}^{5-}$ and $H_2P_4O_{13}^{4-}$ respectively. The curve differs from those obtained for similar titrations of pyrophosphate[6] and triphosphate[7] in that the inflection at $a = 1$ (*a* being the number of moles of acid added per mole of $P_4O_{13}^{6-}$) is not distinct. This may be due to the fact that the terminal phosphate tetrahedra which are responsible for the strongly bound hydrogen ions are separated by two internal phosphate tetrahedra. This means that the inductive effect due to association or dissociation of a hydrogen ion from one terminal PO_4-tetrahedron will be lowered by the basicity of the other PO_4-tetrahedron.

The average number of hydrogen ions associated with a tetraphosphate anion at any stage in the *p*H-titration is given by Eq. (1).

$$\bar{n} = \frac{C_A - A}{C} \qquad \ldots(1)$$

where $\bar{n}$ = Average number of H^+ ions bound per molecule of the tetraphosphate, C_A = the total concentration of the ligand species (H^+ ions) added to the system, A = free $[H^+]$ at equilibrium, and C = total [tetraphosphate].

In the present study A was calculated from the *p*H value obtained from the titration curve of tetramethylammonium tetraphosphate versus HCl. To obtain C_A, a blank titration of tetramethylammonium bromide was performed against HCl at the corresponding temperature and ionic strength. The value of C_A at any stage of titration of tetramethylammonium tetraphosphate was obtained from the *p*H value which was recorded for the same addition of HCl to the solution of tetramethylammonium bromide.

Bjerrum's[8] formation function ($\bar{n}$) may be written as Eq. (2).

$$\bar{n} = (1-\bar{n})\beta_1[H^+] + (2-\bar{n})\beta_2[H^+]^2 + (3-\bar{n})\beta_3[H^+]^3 + (4-\bar{n})\beta_4[H^+]^4 + (5-\bar{n})\beta_5[H^+]^5 + (6-\bar{n})\beta_6[H^+]^6 \qquad \ldots(2)$$

where $\beta_1 = 1/K_6$, $\beta_2 = 1/K_5 \cdot K_6$, $\beta_3 = 1/K_4 \cdot K_5 \cdot K_6$,

$\beta_4 = 1/K_3 \cdot K_4 \cdot K_5 \cdot K_6$, $\beta_5 = 1/K_2 \cdot K_3 \cdot K_4 \cdot K_5 \cdot K_6$ and $\beta_6 = 1/K_1 \cdot K_2 \cdot K_3 \cdot K_4 \cdot K_5 \cdot K_6$ and in general

$$\beta_n = \frac{[H_nP_4O_{13}]^{(6-n)-}}{[H^+]^n[P_4O_{13}^{6-}]}$$

Calculation of pK_5 and pK_6 is simple, since the two constants are sufficiently different in magnitude as the addition of H^+ ions take place in distinct steps.

The value of $pK_6 = p\text{H} - \log \frac{[P_4O_{13}^{6-}]}{[HP_4O_{13}^{5-}]}$

as $K_6 = \frac{[H^+][P_4O_{13}^{6-}]}{[HP_4O_{13}^{5-}]}$

Thus at half neutralization, i.e. when half an equivalent of the acid has been added,

$$[P_4O_{13}^{6-}] = [HP_4O_{13}^{5-}]$$

and hence

$$pK_6 = pH_{1/2a}$$

Similarly pK_5 is obtained from the titration curve by reading the pH corresponding to the addition of $1\frac{1}{2}$ equivalents of acid.

For evaluating the values of pK_1, pK_2, pK_3 and pK_4, the portion of the titration curve between pH 2·00 and 3·20 was investigated in accordance with Bjerrum's method. Since two hydrogen ions were associated at the pH range 2·00-3·20, Eq. (2) was modified in the actual calculations by defining n^*, as the average number of hydrogen ions combined with $H_2P_4O_{13}^{4-}$, and n^* as the corresponding complexity constant. Thus

$$\beta_n^* = \beta_n/\beta_2$$

and

$$n^* = \bar{n} - 2$$

Hence Eq. (2) takes the form of Eq. (3).

$$n^* = (1-n^*)\beta_3^*[H^+] + (2-n^*)\beta_4^*[H^+]^2 + (3-n^*)\beta_5^*[H^+]^3 + (4-n^*)\beta_6^*[H^+]^4 \quad \ldots(3)$$

Equation (3) can be solved for β_4^*, β_*, β^* and β^*, knowing the values of n^* at four $[H^+]$. In the region where $[H^+]$ is of the order of $10^{-3}M$, the last two terms in Eq. (3) can be neglected as these would be negligibly small. Thus two simultaneous equations in β_3^* and β_4^* are left. Substituting the two sets of values of n^* and H^+ in Eq. (3), the simultaneous equations were solved for β_3^* and β^* to get the values of K_3 and K_4. The values of β^* and β^* (i.e. K_1 and K_2) were not calculated, as the pH titration curve in the lower pH range was almost flat, showing that n^* ($= \bar{n} - 2$) is not a sensitive function of $[H^+]$.

The values of pK_3, pK_4, pK_5 and pK_6 obtained at different temperatures and ionic strengths are given in Table 1. These values are the average of a set of pK values calculated from different points on the titration curve.

The values of the dissociation constants are in good agreement with those reported by Watters[2] at 25° and $\mu = 1$ and 0. pK values $\mu = 0$ were

TABLE 1 — DISSOCIATION CONSTANTS OF TETRAPHOSPHORIC ACID AT DIFFERENT TEMPERATURES ($\mu = 1{\cdot}0M$)

pK_i	μ (M)					
	0·034	0·068	0·11	0·40	0·70	1·00
			TEMP. = 25° ± 0·05°			
pK_3	1·99±0·05	1·94±0·05	1·86±0·04	1·82±0·04	1·63±0·03	1·52±0·04
pK_4	2·64±0·05	2·59±0·04	2·48±0·03	2·44±0·05	2·29±0·03	2·20±0·05
pK_5	6·62±0·03	6·56±0·02	6·50±0·04	6·41±0·04	6·30±0·03	6·23±0·02
pK_6	8· 2±0·02	8·50±0·03	8·39±0·02	8·21±0·03	8·28±0·03	8·16±0·04
			TEMP. = 50° ± 0·05°			
pK_3	1·91±0·04	1·82±0·04	1·73±0·04	1·76±0·04	1·58±0·02	1·44±0·03
pK_4	2·56±0·06	2·47±0·05	2·40±0·05	2·31±0·05	2·22±0·03	2·13±0·03
pK_5	6·75±0·02	6·64±0·02	6·60±0·03	6·44±0·02	6·32±0·02	6·30±0·02
pK_6	8·76±0·03	8·60±0·02	8·48±0·03	8·36±0·02	8·26±0·03	8·18±0·02
			TEMP. = 60° ± 0·05°			
pK_3	—	—	1·79±0·06	1·68±0·04	1·54±0·04	1·43±0·04
pK_4	—	—	2·41±0·05	2·24±0·05	2·19±0·04	2·12±0·05
pK_5	—	—	6·65±0·02	6·42±0·03	6·35±0·03	6·31±0·05
pK_6	—	—	8·51±0·02	8·41±0·03	8·34±0·03	8·23±0·04
			TEMP. = 65° ± 0·05°			
pK_3	—	—	1·69±0·03	1·59±0·01	1·48±0·04	1·40±0·03
pK_4	—	—	2·35±0·03	2·19±0·02	2·16±0·03	2·11±0·03
pK_5	—	—	6·72±0·03	6·50±0·03	6·41±0·02	6·36±0·03
pK_6	—	—	8·53±0·03	8·40±0·02	8·31±0·03	8·26±0·03
			TEMP. = 70° ± 0·05°			
pK_3	1·82±0·04	1·74±0·03	1·66±0·02	1·52±0·03	1·41±0·02	1·36±0·03
pK_4	2·39±0·04	2·35±0·05	2·28±0·04	2·14±0·04	2·11±0·02	2·08±0·04
pK_5	6·92±0·02	6·88±0·03	6·85±0·03	6·63±0·03	6·46±0·01	6·40±0·02
pK_6	8·90±0·02	8·82±0·02	8·59 0·03	8·48±0·03	8·34±0·03	8·28±0·03

TABLE 2 — VALUES OF *Ai*, *Bi* AND *Ci* AT DIFFERENT IONIC STRENGTHS

μ	*Ai*	*Bi*	*Ci*
	$i = 3$		
0·00	−1394·0	−11·58	−0·016
0·11	1394·0	5·58	0·0093
0·40	−7042·0	−47·96	−0·076
0·70	−4768·0	−33·00	−0·052
1·00	−586·9	−6·26	−0·0093
	$i = 4$		
0·00	−3888·0	−28·82	−0·044
0·11	−2044·0	−16·66	−0·025
0·40	−2421·0	−19·61	−0·030
0·70	−1981·0	−15·9	−0·023
1·00	220·1	−1·61	−0·0005
	$i = 5$		
0·00	733·6	−1·55	0·0096
0·11	6236·0	34·92	0·068
0·40	6088·0	33·24	0·0645
0·70	4548·0	23·28	0·048
1·00	1614·0	5·017	0·019
	$i = 6$		
0·00	−1468·0	−16·34	−0·0084
0·11	1394·0	1·67	0·018
0·40	2054·0	5·93	0·025
0·70	2788·0	10·14	0·031
1·00	3081·0	11·96	0·033

obtained by extrapolation of the plots of log K versus $\mu^{1/2}$.

Effect of temperature on dissociation constants — The variation of pK values with temperature conform with the equation[9]:

$$pK_i = \frac{A_i}{T} - B_i + C_i \cdot T \qquad \ldots(4)$$

where A_i, B_i and C_i are the constants. The values (Table 2) of A_i, B_i and C_i were obtained at 25° ± 0·05°, 50° ± 0·05° and 70° ± 0·05° using pK values in Eq. (4). Employing the values of A_i, B_i and C_i, the pK values were evaluated at 60° and 65°. These calculated values have been compared with the values obtained by actual measurements at the corresponding temperatures and ionic strengths in Table 3.

Fairly good agreement can be seen between the observed and calculated pK values. Thus Eq. (4) can be used for calculating dissociation constants of $H_6P_4O_{13}$ in the temperature range 25-70°.

Thermodynamic parameters — Knowing the values of A_i, B_i and C_i in Eq. (4) at $\mu = 0$, the values of $\Delta H°$ and $\Delta S°$ (Table 4) for the dissociation processes:

$$H_nP_4O_{13}{}^{(6-n)-} \longrightarrow [H^+] + H_{n-1}P_4O_{13}{}^{(5-n)-}$$

were calculated with the help of Eqs. (4-7).

$$\frac{dl_nK_i}{dT} = \frac{\Delta H_i}{RT^2} \qquad \ldots(5)$$

$$\Delta H_i = 2{\cdot}303R(A_i - C_i{\cdot}T^2) \qquad \ldots(6)$$

$$\Delta S_i = \frac{\Delta H_i}{T} - 2{\cdot}303R(A_i/T - B_i + C_i{\cdot}T) \qquad \ldots(7)$$

TABLE 3 — COMPARISON OF DISSOCIATION CONSTANTS AT DIFFERENT IONIC STRENGTHS

Temp. °C	pK_3		pK_4		pK_5		pK_6	
	Exptl	Calc.	Exptl	Calc.	Exptl	Calc.	Exptl	Calc.
				$\mu = 0{\cdot}11M$				
60 ± 0·05	1·71	1·69	2·41	2·36	6·65	6·72	8·51	8·56
65 ± 0·05	1·69	1·67	2·35	2·32	6·72	6·79	8·53	8·53
				$\mu = 0{\cdot}40M$				
60 ± 0·05	1·68	1·66	2·24	2·27	6·42	6·51	8·41	8·42
65 ± 0·05	1·59	1·58	2·19	2·23	6·50	6·56	8·40	8·45
				$\mu = 0{\cdot}70M$				
60 ± 0·05	1·54	1·52	2·19	2·17	6·35	6·39	8·34	8·29
65 ± 0·05	1·48	1·47	2·16	2·14	6·41	6·42	8·31	8·31
				$\mu = 1{\cdot}00M$				
60 ± 0·05	1·43	1·40	2·12	2·11	6·31	6·35	8·23	8·22
65 ± 0·05	1·40	1·38	2·11	2·09	6·36	6·37	8·26	8·25

TABLE 4 — THERMODYNAMIC PARAMETERS FOR THE DISSOCIATION OF TETRAPHOSPHORIC ACID

Reaction	$\Delta H°$ kcal mole^{-1}	$\Delta S°$ cal mole^{-1} deg^{-1}
$H_4P_4O_{13}^{2-} \rightarrow H^+ + H_3P_4O_{13}^{3-}$	0·156	−9·4
$H_3P_4O_{13}^{3-} \rightarrow H^+ + H_2P_4O_{13}^{4-}$	−0·078	−13·02
$H_2P_4O_{13}^{4-} \rightarrow H^+ + HP_4O_{13}^{5-}$	−0·819	−34·20
$HP_4O_{13}^{5-} \rightarrow H^+ + P_4O_{13}^{6-}$	−2·402	−48·78

The value of $\Delta S°$ becomes more and more negative as the charge on the tetraphosphate ion increases because the solvent molecules in the neighbourhood of a tetraphosphate ion would be acted upon by strong electrostatic forces which would cause them to have less freedom of motion than they would have otherwise. This results in the loss of entropy, and this loss increases with increasing the charge on the ion. This is what is actually observed. The value of $\Delta H°$ as expected for a dissociation process decreases with the increase in charge on the tetraphosphate ion.

Acknowledgement

One of the authors (S.K.T.) is thankful to the CSIR, New Delhi, for the award of a research fellowship.

References

1. (a) CROWTHER, J. P. & WESTMANN, A. E. R., *Can. J. chem.*, **34** (1956), 969; (b) OTANI, S., MIURA, M. & DOI, T., *Kogyo Kagaku Zasshi*, **66** (1963), 593; (c) GRIFFITH, E. J. & BUXTON, R. L., *J. Am. chem. Soc.*, **89** (1967), 2884.
2. WATTERS, J. I., PETER STURROCK, E. & SIMONAITIS, R. E., *Inorg. Chem.*, **2** (1963), 765.
3. THILO, E. & RATZ, R., *Z. anorg. Chem.*, **260** (1949), 255.
4. BELL, R. N., *Ind. Engng Chem.*, **44** (1952), 568.
5. QUIMBY, O. T., *J. phys. Chem.*, **58** (1954), 603.
6. MITRA, R. P., MALHOTRA, H. C. & JAIN, D. V. S., *Trans. Faraday Soc.*, **62** (1966), 167.
7. MITRA, R. P. & THUKRAL, B. R., *Indian J. Chem.*, 8 (1970), 347.
8. BJERRUM, J., *Chem. Rev.*, **46** (1950), 381.
9. HARNED & OWEN, *Physical chemistry of electrolyte solution*, 665; ROBINSON & STOKES, *Electrolyte solutions*, 1959, 517.