Kinetics of the Base Decomposition of Dodecatungstophosphate(3−) in Weakly Alkaline Solutions

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The kinetics of the decomposition of $[PW_{12}O_{40}]^{3-}$ (1.5×10^{-5} mol dm^{-3}) to $[WO_4]^{2-}$ and $[PO_4]^{3-}$ has been studied in the range pH 7—9 at an ionic strength of 0.1 mol dm^{-3}. The reaction proceeds *via* the intermediates $[PW_{11}O_{39}]^{7-}$ and $[PW_9O_{34}]^{9-}$. Only the final stage, the hydrolysis of $[PW_9O_{34}]^{9-}$, was studied in detail. The $[PW_9O_{34}]^{9-}$ ion exists in rapid equilibrium with $[HPW_9O_{34}]^{8-}$ and $[H_2PW_9O_{34}]^{7-}$ with the unprotonated and monoprotonated ions decomposing *via* first-order kinetics. The pK_a values for $[H_2PW_9O_{34}]^{7-}$ and $[HPW_9O_{34}]^{8-}$ were determined as 7.3 and 9.2 respectively, and the rate constants for decomposition of $[HPW_9O_{34}]^{8-}$ and $[PW_9O_{34}]^{9-}$ as 8.0×10^{-4} and 6.3×10^{-3} s^{-1} respectively at 25.6 °C.

In strongly alkaline solutions ($[OH^-] = 0.002$—0.40 mol dm^{-3}), the rate of base decomposition of 12-tungstophosphate (3−),* $[PW_{12}O_{40}]^{3-}$, to $[PO_4]^{3-}$ and $[WO_4]^{2-}$ occurs *via* a single, short-lived intermediate, $[PW_{12}O_{40}(OH)]^{4-}$.[4] No evidence was found for the existence of 11-tungstophosphate(7−), $[PW_{11}O_{39}]^{7-}$, or 9-tungstophosphate(9−), $[PW_9O_{34}]^{9-}$, as intermediates, although in a similar study of the $[SiW_{12}O_{40}]^{4-}$ ion, the degradation to $[SiO_3]^{2-}$ and $[WO_4]^{2-}$ was found to proceed *via* the 11-tungstosilicate(8−) and 9-tungstosilicate(10−) species.[5] The existence of both $[PW_{11}O_{39}]^{7-}$ and $[PW_9O_{34}]^{9-}$ is now well established. The former ion is obtained by the addition of alkali to $[PW_{12}O_{40}]^{3-}$ (ref. 6) and the latter can be obtained by the further hydrolysis of $[PW_{11}O_{39}]^{7-}$.[7] The structures of different isomers of 11- and 9-tungstoheteropolyanions have been the subject of recent investigations.[1,3]

$[PW_{12}O_{40}]^{3-}$ has the Keggin[8] structure of 12 corner- and edge-sharing WO_6 octahedra grouped around a central tetrahedrally co-ordinated phosphorus atom. The $[PW_{11}O_{39}]^{7-}$ structure is thought to be derived from $[PW_{12}O_{40}]^{3-}$ by the removal of one of the outer WO_6 octahedra, as is found in $K_8[SiW_{11}O_{39}]\cdot 13H_2O$.[9] The $[PW_9O_{34}]^{9-}$ structure is unknown but is thought to be derived from $[PW_{12}O_{40}]^{3-}$ by the removal of either three corner-sharing (A-type) or three edge-sharing (B-type) octahedra.[3] Structural evidence exists for the A-type in $Na_3H_6[PMo_9O_{34}]\cdot nH_2O$ which is formed in acid solutions.[10] The 9-tungstoheteropolyanions existing in basic solutions are thought to have the B-type structure.[3]

In order to investigate further the possibility of $[PW_{11}O_{39}]^{7-}$ and $[PW_9O_{34}]^{9-}$ existing as intermediates in the base decomposition of $[PW_{12}O_{40}]^{3-}$, the kinetic study of the reaction has been extended to weakly alkaline solutions (pH 7—9).

Experimental

Sodium 12-Tungstophosphate(3−).—Analytical grade 12-tungstophosphoric acid was converted into the sodium salt by the method of Pope and Varga[11] (Found: Na, 2.1; P, 1.0; W, 68.9; H_2O, 8.2. Calc. for $H_{30}Na_3O_{55}PW_{12}$: Na, 2.2; P, 1.0; W, 68.6; H_2O, 8.3%).

Potassium 11-Tungstophosphate(7−).—This was prepared by the method of Souchay[6] (Found: K, 8.9; P, 1.0; W, 65.6; H_2O, 4.1. Calc. for $H_{14}K_7O_{46}PW_{11}$: K, 8.9; P, 1.0; W, 65.7; H_2O, 4.1%).

Potassium 9-Tungstophosphate(9−).[7]—Sodium 11-tungstophosphate(7−) (10 g) was dissolved in distilled water (100 cm^3) and the solution evaporated down to 25 cm^3. This solution was then added to a solution of potassium carbonate (2.8 g) in distilled water (20 cm^3). A white salt precipitated immediately. The salt was filtered off, washed with a small amount of cold water, and dried at 100 °C. Yield 6.8 g (Found: K, 11.7; P, 0.9; W, 64.4; H_2O, 4.7. Calc. for $H_{14}K_9O_{41}PW_9$: K, 11.7; P, 1.0; W, 64.0; H_2O, 4.7%).

Sodium 12-tungstophosphate(3−) and potassium 11-tungstophosphate(7−) were identified by i.r. spectroscopy[12,13] and potassium 9-tungstophosphate(9−) by polarography [$E_{\frac{1}{2}} = -0.79$ V ($2e^-$), pH 4.7, acetate buffer].[14]

Buffered Solutions.—Carbonate-hydrogencarbonate buffers were used to maintain pseudo-first-order conditions within the selected pH range. Buffers were prepared from standard solutions of $NaHCO_3$ and Na_2CO_3 or HCl to produce a final ionic strength of 0.10 mol dm^{-3}. The change in absorbance of the resultant solutions at 250 nm, and the pH of the reactant solutions, were monitored as a function of time. Above pH 7, the pH of individual solutions varied by less than 0.05 pH unit during the course of a reaction. Below pH 7, difficulties were encountered in maintaining constant pH and deviations from first-order kinetics occurred.

Unbuffered Solutions.—The kinetics of the decomposition reaction was studied in unbuffered solutions to determine the effect of the buffer on the reaction rate. Sodium hydroxide was added to solutions of $Na_3[PW_{12}O_{40}]$ to give an initial $[OH^-]$ of 5.5×10^{-4} and 8.3×10^{-4} mol dm^{-3}. Ionic strength was maintained at 0.10 mol dm^{-3} with NaCl and precautions were taken to exclude atmospheric CO_2. Changes in pH and absorbance at 250 nm were monitored concurrently as a function of time. Observed rate constants ($k_{exp.}$) were calculated by the method of Corigliano and Di Pasquale.[15]

Ultraviolet spectral and kinetic measurements were carried out on a Varian DMS 90 double-beam spectrophotometer with a constant-temperature cell housing. The pH measurements were performed with a Metrohm AG 9100 combined electrode connected to a Radiometer E 512 pH meter. A constant-temperature water-bath controlled the temperature of reactant solutions to ±0.2 °C. Infrared spectra were recorded as KBr discs on a Perkin-Elmer 457 grating i.r. spectrophotometer, polarograms on a Princeton Applied Research model

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* 12- and 11-tungstoheteropolyanions may exist in two isomeric forms, denoted by either α or β preceding the name of the anion.[1,2] 9-Tungstoheteropolyanions may also exist in various isomeric forms.[2,3] This paper refers only to the more stable α isomers.

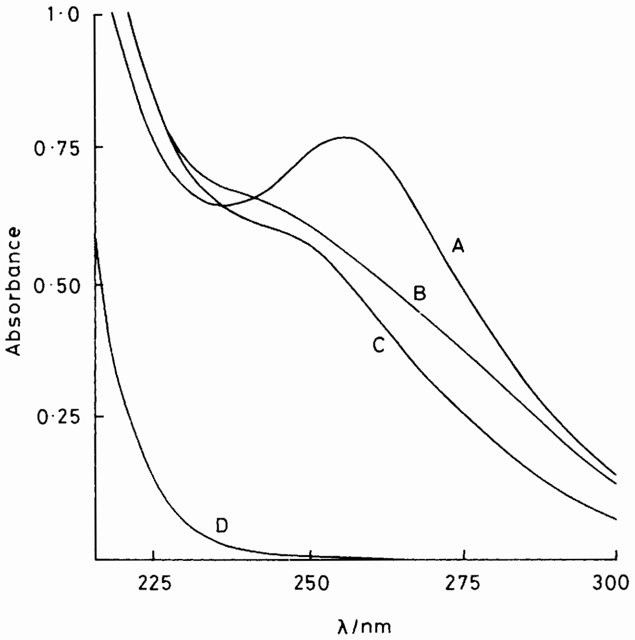

Figure 1. Ultraviolet absorption spectra of $[PW_{12}O_{40}]^{3-}$ (A), the intermediate ions $[PW_{11}O_{39}]^{7-}$ (B) and $[PW_9O_{34}]^{9-}$ (C), and the final products $[PO_4]^{3-}$ and $[WO_4]^{2-}$ (D). The initial concentration of $[PW_{12}O_{40}]^{3-}$ was 1.0×10^{-5} mol dm^{-3}

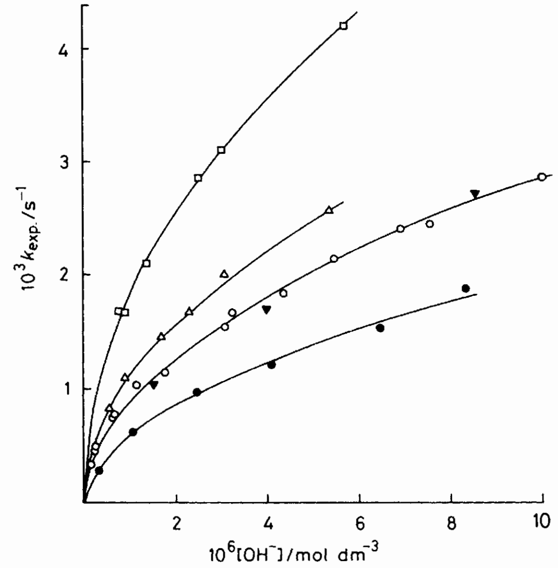

Figure 2. Hydroxide ion dependence of the experimental rate constants at 20.3 (●), 25.6 (○), 30.2 (△), and 35.6 °C (□) for the base hydrolysis of $[PW_9O_{34}]^{9-}$. Total ionic strength = 0.1 mol dm^{-3}. For the points (▼), $K_9[PW_9O_{34}]\cdot 7H_2O$ was used as the source of $[PW_9O_{34}]^{9-}$ ions instead of $Na_3[PW_{12}O_{40}]\cdot 15H_2O$. Theoretical curves are drawn for equation (7) using the values of k_1, k_2, k_3, K_1, and K_2 in the Table

174A polarographic analyzer, and stopped-flow experiments on a modified[16] Durrum–Gibson stopped-flow spectrophotometer.

Results

The base hydrolysis of 12-tungstophosphate(3−) to tungstate(2−) and phosphate(3−)* was found to occur in three stages as shown in (1), the intermediate products being identified as 11-tungstophosphate(7−) and 9-tungstophosphate(9−).

$$[PW_{12}O_{40}]^{3-} \xrightarrow[\text{v. fast}]{6[OH]^-} [PW_{11}O_{39}]^{7-} \xrightarrow[\text{fast}]{6[OH]^-} [PW_9O_{34}]^{9-} \xrightarrow[\text{slow}]{12[OH]^-} [PO_4]^{3-} + [WO_4]^{2-} \quad (1)$$

The intermediate ions $[PW_{11}O_{39}]^{7-}$ and $[PW_9O_{34}]^{9-}$ were prepared as the potassium salts, by known methods, and identified by analysis and i.r. spectroscopy ($[PW_{11}O_{39}]^{7-}$) or polarography ($[PW_9O_{34}]^{9-}$). Ultraviolet spectra of these products agreed with those of the intermediate ions (Figure 1) as did the rate of base hydrolysis of $[PW_9O_{34}]^{9-}$ (Figure 2).

Initial experiments using a stopped-flow spectrophotometer showed that the addition of a solution of $[PW_{12}O_{40}]^{3-}$ to a solution buffered between pH 7 and 9 resulted in an ' instantaneous' (<2 ms) change in spectrum to that of $[PW_{11}O_{39}]^{7-}$. This spectrum then changed over seconds to that of $[PW_9O_{34}]^{9-}$, concurrently with the latter ion decomposing to tungstate(2−) and phosphate(3−), the final reaction occurring over minutes to hours depending on pH and temperature (Figure 1). Consequently, the only reaction that could be examined in detail was the degradation of $[PW_9O_{34}]^{9-}$ to tungstate(2−) and phosphate(3−).

Base Decomposition of 9-Tungstophosphate(9−).—The experimentally observed rate constants ($k_{exp.}$), determined at four different temperatures, for the base decomposition of $[PW_9O_{34}]^{9-}$ to $[WO_4]^{2-}$ and $[PO_4]^{3-}$, are plotted as a function of $[OH^-]$ in Figure 2. Concentrations of OH^- were calculated from pH data using published values of K_w for each of the temperatures at which the reaction was studied.[17] The values of $k_{exp.}$ increase in a non-linear fashion with increasing $[OH^-]$.

The observed rate constants were independent of the initial concentration of $[PW_{12}O_{40}]^{3-}$ and inversely proportional to the concentration of added $[WO_4]^{2-}$. Ionic strength dependence experiments in the region $I = 0.04$—0.10 mol dm^{-3} showed the observed rate constants obeyed the equation $\log k_{exp.} = +2.5I^{\frac{1}{2}}$.

Experiments performed in unbuffered solutions, using NaOH as a source of hydroxide ions and NaCl to maintain ionic strength, demonstrated that the reaction proceeded more slowly than in buffered solutions, but the hydroxide ion dependence of the observed rate constants was similar (Figure 3).

Discussion

The base decomposition of $[PW_{12}O_{40}]^{3-}$ to $[WO_4]^{2-}$ and $[PO_4]^{3-}$ in weakly alkaline solutions has been shown to proceed *via* two intermediates, $[PW_{11}O_{39}]^{7-}$ and $[PW_9O_{34}]^{9-}$, confirming the degradation occurs *via* a similar mechanism to $[SiW_{12}O_{40}]^{4-}$.[5]

The rate of base hydrolysis of $[PW_{12}O_{40}]^{3-}$ to $[PW_{11}O_{39}]^{7-}$ was found to be ' instantaneous ' (on the stopped-flow timescale) in the pH region 7—9. The mixing time of the stopped-flow spectrophotometer is about 2 ms, implying that the minimum value for the second-order rate constant for this reaction (assuming it proceeds by a simple second-order mechanism as does $[SiW_{12}O_{40}]^{4-}$), is about 10^{10} dm^3 mol^{-1} s^{-1}. This is very much faster than that reported for $[SiW_{12}O_{40}]^{4-}$

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* Also includes $[H_2PO_4]^-$ and $[HPO_4]^{2-}$ which are the major species present between pH 7 and 9.

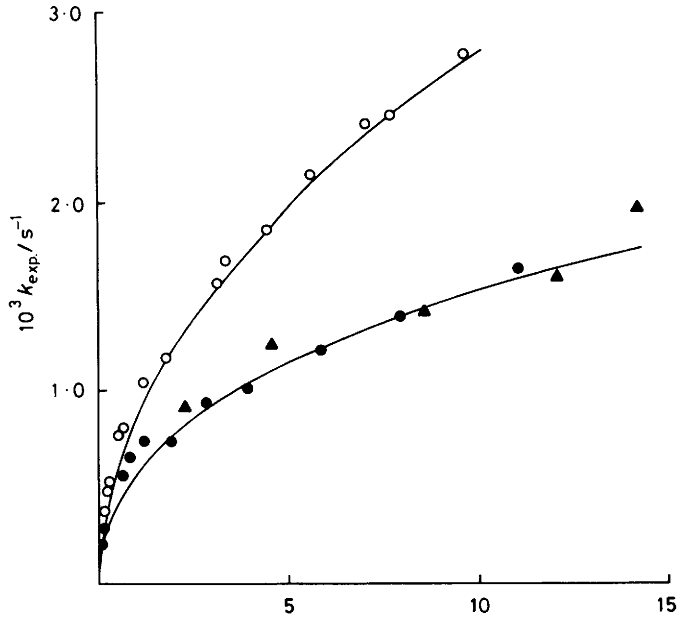

Figure 3. Hydroxide ion dependence of the experimental rate constants obtained at 25.6 °C in buffered (○) and unbuffered (●, ▲) solutions for the base hydrolysis of $[PW_9O_{34}]^{9-}$ at ionic strength 0.1 mol dm^{-3}. Theoretical curves are drawn for equation (7), using $k_2 = 5.5 \times 10^{-4}$ and $k_3 = 3.0 \times 10^{-3}$ s^{-1} for the unbuffered solutions. Values of k_1, K_1, and K_2 are the same as for buffered solutions (Table). Initial [NaOH] were 5.5×10^{-4} (▲) and 8.3×10^{-4} mol dm^{-3} (●)

(160 dm^3 mol^{-1} s^{-1}) and is in the region of diffusion controlled reactions.

The degradation of $[PW_{11}O_{39}]^{7-}$ to $[PW_9O_{34}]^{9-}$ was much slower and occurred over seconds to about one minute at pH 7—9. The reaction could not be studied in detail due to the concurrent, but much slower, decomposition of $[PW_9O_{34}]^{9-}$ to $[WO_4]^{2-}$ and $[PO_4]^{3-}$. Again, this is much faster than the conversion of $[SiW_{11}O_{39}]^{8-}$ to $[SiW_9O_{34}]^{10-}$.[5]

The final step in the decomposition reaction, the splitting up of $[PW_9O_{34}]^{9-}$ into tungstate(2−) and phosphate(3−), was much slower than the initial two steps and could be studied in detail. The most likely explanation of the non-linear hydroxide ion dependence of the observed rate constants is the following mechanism [equations (2)—(6)] in which two protonated 9-tungstophosphate ions exist in rapid equilibrium with $[PW_9O_{34}]^{9-}$ and all three species decompose to $[WO_4]^{2-}$ and $[PO_4]^{3-}$ at different rates.

$$[H_2PW_9O_{34}]^{7-} + OH^- \underset{\text{fast}}{\overset{K_1}{\rightleftharpoons}} [HPW_9O_{34}]^{8-} + H_2O \tag{2}$$

$$[HPW_9O_{34}]^{8-} + OH^- \underset{\text{fast}}{\overset{K_2}{\rightleftharpoons}} [PW_9O_{34}]^{9-} + H_2O \tag{3}$$

$$[H_2PW_9O_{34}]^{7-} \xrightarrow[\text{slow}]{k_1} \text{products} \tag{4}$$

$$[HPW_9O_{34}]^{8-} \xrightarrow[\text{slow}]{k_2} \text{products} \tag{5}$$

$$[PW_9O_{34}]^{9-} \xrightarrow[\text{slow}]{k_3} \text{products} \tag{6}$$

$$k_{\text{exp.}} = \frac{k_1 + k_2K_1[OH^-] + k_3K_1K_2[OH^-]^2}{1 + K_1[OH^-] + K_1K_2[OH^-]^2} \tag{7}$$

Table. Activation parameters * and k_2 and k_3 for the decompositions of $[HPW_9O_{34}]^{8-}$ and $[PW_9O_{34}]^{9-}$, respectively, to tungstate(2−) and phosphate(3−). Ionic strength was maintained at 0.10 mol dm^{-3} with Na_2CO_3, $NaHCO_3$, and HCl

	θ_c/°C	10^4k_2/s^{-1}	10^3k_3/s^{-1}
	20.3	4.6 ± 0.9	4.6 ± 0.3
	25.6	8.0 ± 0.4	6.3 ± 0.1
	30.2	9.2 ± 0.8	8.1 ± 0.5
	35.6	15.5 ± 1.0	12.5 ± 0.6
$\Delta H^‡$/kJ mol^{-1}	25.6	54 ± 14	46 ± 8
$\Delta S^‡$/J K^{-1} mol^{-1}	25.6	120 ± 60	130 ± 30

* Error in k_2 and k_3 ± 2 standard deviations. The value of k_1 was zero at all temperatures; K_1 and K_2 were (5.2 ± 2.6) × 10^6 and (6.0 ± 3.0) × 10^4 dm^3 mol^{-1} respectively at all temperatures.

The rate expression for this reaction scheme is given by equation (7). The values for k_1, k_2, k_3, K_1, and K_2 which give the best fit to the experimental data are listed in the Table. The calculation of values of k_2 and k_3 over a range of temperatures enabled the enthalpies and entropies of activation for reactions (5) and (6) to be determined (Table). The value of zero found for k_1 indicates that the diprotonated ion $[H_2PW_9O_{34}]^{7-}$ is either stable in this pH region or decomposes much more slowly than do $[HPW_9O_{34}]^{8-}$ and $[PW_9O_{34}]^{9-}$.

Little information is available on the possible degree of protonation of the $[PW_9O_{34}]^{9-}$ ion. Analysis of the potassium salt, $K_9[W_9O_{34}]\cdot 7H_2O$, revealed that the precipitated ion was not protonated. This ion is prepared in a potassium carbonate solution at pH *ca.* 9. The 9-molybdophosphate species, which is precipitated in acid solutions, is known to have six protons.[10] It has an acid dissociation constant (pK_a) of 1.01 whilst the penta- and tetra-protonated ions have pK_a values of 3.04 and 4.41 respectively.[18] For $[H_2PW_9O_{34}]^{7-}$ and $[HPW_9O_{34}]^{8-}$ the pK_a values can be calculated from the data of Table 1 as 7.3 and 9.2 respectively. It appears from this evidence that the degree of protonation is probably low in the range pH 7—9. The ions in equations (2)—(5) have therefore been written as mono- and di-protonated ions, although other degrees of protonation cannot be excluded.

The enthalpies and entropies of activation for the first-order decomposition of $[HPW_9O_{34}]^{8-}$ and $[PW_9O_{34}]^{9-}$ are the same within experimental error, indicating that both degrade by similar mechanisms. Very little data are available on the activation parameters for the first-order decomposition of other polyanions, most reacting primarily through a second-order mechanism. For $[V_{10}O_{28}]^{6-}$, where both first- and second-order pathways are observed,[19] the enthalpy (117 kJ mol^{-1}) and entropy (75 J K^{-1} mol^{-1}) of activation for the first-order reaction contrast with the present findings. The instability of $[PW_9O_{34}]^{9-}$ in aqueous solutions [14] compared with decavanadate, which is stable below pH 6,[15] accounts for its much lower enthalpy of activation for decomposition. The large positive entropy of activation observed for $[V_{10}O_{28}]^{6-}$ is indicative of a less solvated and/or less ordered transition state that for the reactant. This is not unusual for a first-order decomposition reaction. For $[HPW_9O_{34}]^{8-}$ and $[PW_9O_{34}]^{9-}$, this is clearly not the case. The large negative values for $\Delta S^‡$ may be due to the increased ordering of water molecules around the complex, including the penetration of some water molecules into the co-ordination sphere of tungsten atoms, as the anion breaks up into a more open structure. The role of water in decomposing the $[PW_9O_{34}]^{9-}$ molecule is probably much more important than in the degradation of $[V_{10}O_{28}]^{6-}$. Counter ion effects have been shown greatly to effect the activation parameters for the base hydrolysis of $[SiW_9O_{34}]^{10-}$

(ref. 5) and possibly have some effect on the present reaction. Further studies in other cationic media would be required to investigate this possibility.

In unbuffered solutions the decomposition reaction proceded *via* the intermediates $[PW_{11}O_{39}]^{7-}$ and $[PW_9O_{34}]^{9-}$ as occurred in buffered solutions. Values of the observed rate constants, $k_{exp.}$, could not be accurately determined due to the constantly changing pH, but estimates could be made from successive readings of absorbance and pH.[15] These data showed a similar dependence of $k_{exp.}$ on hydroxide-ion concentration as was found in buffered solutions, although the actual rate constants were smaller (Figure 3). The decomposition reaction of $[PW_9O_{34}]^{9-}$ appears to occur by the same mechanism in both buffered and unbuffered solutions, but the rate is enhanced in the presence of the $[CO_3]^{2-}$ and/or $[HCO_3]^-$ ions. Le Meur and Souchay[20] have reported a similar catalytic effect for a number of different buffer solutions, including the carbonate–hydrogencarbonate system, in the alkaline decomposition of dihydrogendodecatungstate(6−), $[H_2W_{12}O_{40}]^{6-}$.

Acknowledgements

I thank Mrs. E. Lancanienta for analysis of the tungstophosphate salts. Financial support was provided by the University of Papua New Guinea.

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Received 24*th March* 1983; *Paper* 3/469