A Comparison of the Base Decomposition of 12-Tungstophosphate(3−), 12-Tungstosilicate(4−), 12-Tungstoborate(5−), and Dihydrogendodecatungstate(6−)

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The reaction of $[PW_{12}O_{40}]^{3-}$, $[BW_{12}O_{40}]^{5-}$, and $[H_2W_{12}O_{40}]^{6-}$ (1.5×10^{-5} mol dm^{-3}) with excess of hydroxide ion at an ionic strength of 1.0 mol dm^{-3} MCl (M = K, Na, or Li), to form $[WO_4]^{2-}$, phosphate, and borate, has been studied. The rate, and in some instances the mechanism, of the reactions is dependent on the cation chosen to maintain the ionic strength. For simple second-order reactions the rate decreases in the order $[SiW_{12}O_{40}]^{4-} > [BW_{12}O_{40}]^{5-} \sim [H_2W_{12}O_{40}]^{6-}$. Other mechanisms involve a pre-equilibrium with partially hydrolysed species. Rate constants are in the order $K^+ > Na^+ > Li^+$. Measurements in mixed K^+–Na^+ media show that $[BW_{12}O_{40}]^{5-}$ preferentially forms ion pairs with the sodium ion.

THE kinetic behaviour for the base decomposition of the heteropolyanions 12-tungstosilicate(4−), $[SiW_{12}O_{40}]^{4-}$,[1] and its partially degraded products 11-tungstosilicate(8−), $[SiW_{11}O_{39}]^{8-}$, and 9-tungstosilicate(10−), $[SiW_9O_{34}]^{10-}$, and the isopolyanions decavanadate(6−), $[V_{10}O_{28}]^{6-}$,[2] heptamolybdate(6−), $[Mo_7O_{24}]^{6-}$,[3] and dichromate(2−), $[Cr_2O_7]^{2-}$,[4] have been interpreted in terms of ion-pair formation between these highly charged anions and the cations in solution. The results depend on both the choice of cation and the structure and charge of the polyanion.

In this work the base hydrolysis of 12-tungstophosphate(3−), $[PW_{12}O_{40}]^{3-}$, 12-tungstosilicate(4−), 12-tungstoborate(5−), $[BW_{12}O_{40}]^{5-}$, and dihydrogendodecatungstate(6−), $[H_2W_{12}O_{40}]^{6-}$, are compared. These ions are isostructural but of progressively increasing negative charge, and the effect of varying the charge on the ion was expected to be more clearly shown. The differing charges arise merely from the choice of heteroatom (or $2H^+$) embedded in a tetrahedral cavity in the centre of the tungsten–oxygen framework.

EXPERIMENTAL

Sodium 12-Tungstophosphate(3−).—12-Tungstophosphoric acid was prepared by the method of Bailar,[5] and

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[1] D. L. Kepert and J. H. Kyle, *J.C.S. Dalton*, 1978, 137.

[2] D. M. Druskovich and D. L. Kepert, *J.C.S. Dalton*, 1975, 947.

[3] D. M. Druskovich and D. L. Kepert, *Austral. J. Chem.*, 1975, **28**, 2365.

[4] B. W. Clare, D. M. Druskovich, D. L. Kepert, and J. H. Kyle, *Austral. J. Chem.*, 1977, **30**, 211.

[5] J. C. Bailar, *Inorg. Synth.*, 1939, **1**, 132.

converted into the sodium salt[6] (Found: Na, 2.1; P, 1.0; W, 71.9; H_2O, 4.6. Calc. for $H_{14}Na_3O_{47}PW_{12}$: Na, 2.2; P, 1.0; W, 71.4; H_2O, 4.1%).

Sodium Dihydrogendodecatungstate.—This salt was prepared by the method of Freedman[7] (Found: Na, 4.1; W, 65.7; H_2O, 10.7. Calc. for $H_{42}Na_6O_{60}W_{12}$: Na, 4.1; W, 65.9; H_2O, 10.8%).

12-Tungstoboric acid was supplied as a solution from K and K Laboratories, Inc., and was used without further purification. All the other chemicals were analytical grade. Stock solutions of all the hydroxides were standardised within 24 h of use. Measurements were carried out on a modified[8] Durrum–Gibson stopped-flow spectrophotometer, rate constants being reproducible to ±5%.

RESULTS

The base hydrolysis of all the polyanions (1.5×10^{-5} mol dm^{-3}) was studied under pseudo-first-order conditions with hydroxide ion in excess. Ionic strength was maintained at 1.0 mol dm^{-3} with potassium, sodium, or lithium chloride. Preliminary experiments indicated that the rate was independent of the anion (chloride, nitrate, or perchlorate). All the measurements were made at the absorbance peak of the polyanion, at 250 nm for $[PW_{12}O_{40}]^{3-}$ and $[BW_{12}O_{40}]^{5-}$, and at 260 nm for $[H_2W_{12}O_{40}]^{6-}$.

The addition of hydroxide ion to a solution of the polyanion resulted in a rapid decrease in optical density, occurring over several seconds or minutes depending on the polyanion and the concentration of hydroxide ion. The 'zero-time' spectra were those expected for $[PW_{12}O_{40}]^{3-}$, $[BW_{12}O_{40}]^{5-}$, and $[H_2W_{12}O_{40}]^{6-}$, and the spectra measured after ten half-lives was that of $[WO_4]^{2-}$ with phosphate or borate as appropriate. All the reactions showed first-order kinetic behaviour for at least four half-lives. The hydrolysis of each of these ions therefore occurs in a single observed reaction, in contrast to the sequence of three distinct reactions observed for the hydrolysis of $[SiW_{12}O_{40}]^{4-}$.[1]

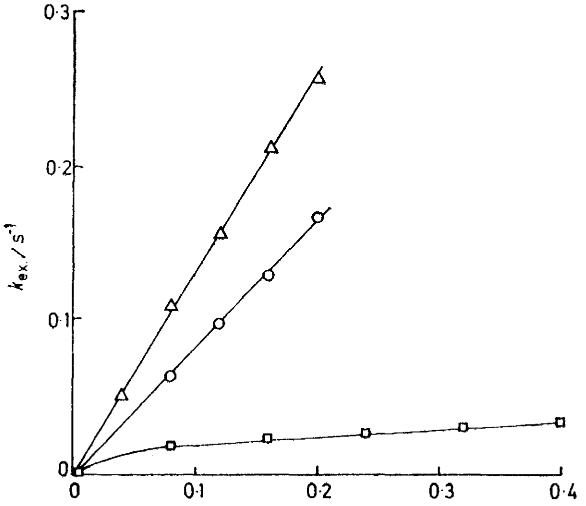

FIGURE 1 Hydroxide-ion dependence of the experimental rate constant at 25.0 °C for the base hydrolysis of $[BW_{12}O_{40}]^{5-}$ in 1.0 mol dm^{-3} MCl: M = K (△), Na (○), and Li (□)

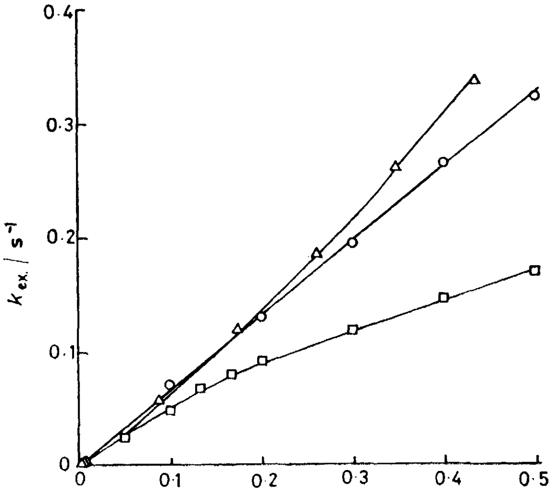

FIGURE 2 Hydroxide-ion dependence of the experimental rate constant at 25.0 °C for the base hydrolysis of $[H_2W_{12}O_{40}]^{6-}$ in 1.0 mol dm^{-3} MCl: as in Figure 1

The dependence of the experimentally observed rate constant ($k_{ex.}$) * on hydroxide-ion concentration is shown in Figures 1—3. The kinetic behaviour is complex, and depends on both the cation and anion.

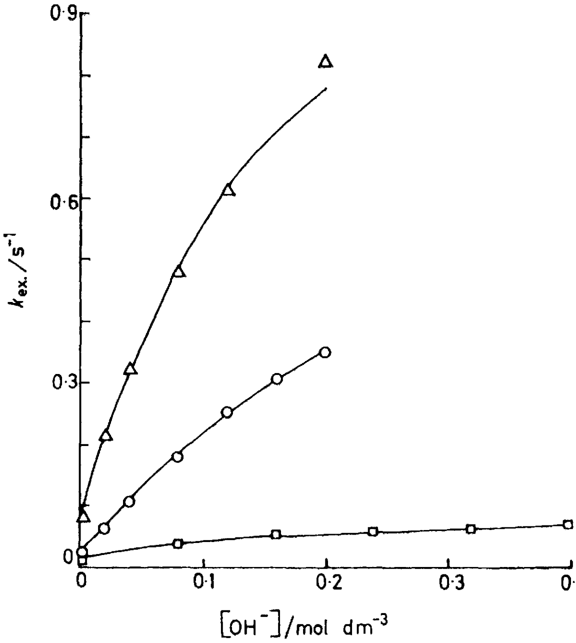

FIGURE 3 Hydroxide-ion dependence of the experimental rate constant at 25.0 °C for the base hydrolysis of $[PW_{12}O_{40}]^{3-}$ in 1.0 mol dm^{-3} MCl: as in Figure 1

The experimentally observed rate constant for the hydrolysis of $[BW_{12}O_{40}]^{5-}$ in the presence of K^+ and Na^+

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* A complete list of the $k_{ex.}$ values is included in J. H. Kyle, Ph.D. Thesis, University of Western Australia, 1976.

[6] M. T. Pope and G. M. Varga, *Chem. Comm.*, 1966, 653.

[7] M. L. Freedman, *J. Amer. Chem. Soc.*, 1959, **81**, 3834.

[8] B. W. Clare, D. L. Kepert, and D. W. Watts, *J.C.S. Dalton*, 1973, 2476.

(Figure 1), and for the hydrolysis of $[H_2W_{12}O_{40}]^{6-}$ in the presence of Na^+ (Figure 2), increases linearly with increasing $[OH^-]$, the line of best fit passing through the origin. This behaviour is the same as that observed for the hydrolysis of $[SiW_{12}O_{40}]^{4-}$ to $[SiW_{11}O_{39}]^{8-}$. The corresponding second-order rate constants $k_2 = k_{ex.}/[OH^-]$ are given in Table 1, the errors quoted being twice the standard error of the gradient. The temperature dependence of the second-order rate constant enabled the enthalpies and entropies of activation to be obtained (Table 3).

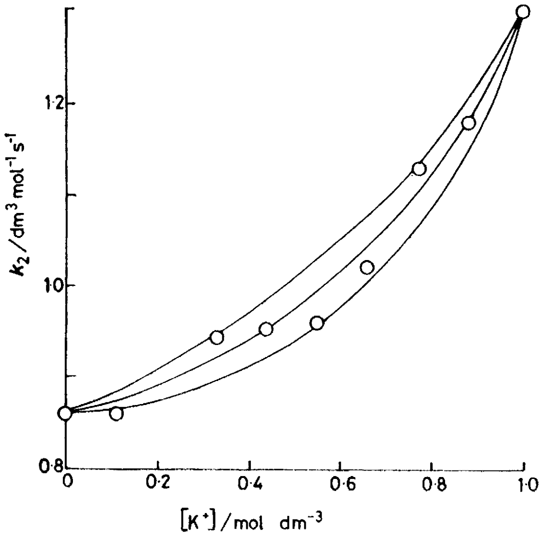

FIGURE 4 Second-order rate constants at 25.0 °C for the base hydrolysis of $[BW_{12}O_{40}]^{5-}$ in NaCl–KCl mixtures; total ionic strength = 1.0 mol dm^{-3}. Theoretical curves are given for K_{IP} = 2.0 (upper), 3.0, and 4.0 (lower)

Glemser *et al.*[9] have also studied the base decomposition of $Na_6[H_2W_{12}O_{40}]$ in sodium hydroxide solutions, no ionic-strength control being reported. They obtained a second-order rate constant of 0.21 dm^3 mol^{-1} s^{-1} at 26 °C.

TABLE 1

Second-order rate constants for the reaction of polyanions with excess of base. Ionic strength maintained at 1.0 mol dm^{-3} with MCl

Polyanion	M	θ_c/°C	$[OH^-]$/ mol dm^{-3}	k_2/dm^3 mol^{-1} s^{-1}
$[BW_{12}O_{40}]^{5-}$	K	25.0	0.04—	1.30
			0.20	±0.06
		30.4	0.20	1.81
		34.7	0.20	2.35
		39.9	0.20	3.21
	Na	25.0	0.08—	0.86
			0.20	±0.05
		30.7	0.08	1.19
		35.0	0.08	1.49
		39.9	0.08	2.08
$[H_2W_{12}O_{40}]^{6-}$	Na	25.0	0.10—	0.64
			0.50	±0.02
		30.2	0.50	0.84
		34.9	0.50	1.11
		40.2	0.50	1.53

Additional information on the effect of choice of cation on the hydrolysis of $[BW_{12}O_{40}]^{5-}$ was obtained by using mixtures of cations in the supporting electrolyte. The total ionic strength was again maintained at 1.0 mol dm^{-3} and the concentration of each cation varied from 0.1 to 0.9 mol dm^{-3}. The second-order rate constants are shown in Figure 4. The simplest reaction scheme which can be proposed and is consistent with these experimental results involves competitive ion pairing between the polyanion and both cations [equations (1)—(3)]. The rate expression

$$[KBW_{12}O_{40}]^{4-} + Na^+ \underset{}{\overset{K_{IP}}{\rightleftharpoons}} [NaBW_{12}O_{40}]^{4-} + K^+ \quad (1)$$

$$[KBW_{12}O_{40}]^{4-} + [OH]^- \xrightarrow{k_2^{K}} \text{Products} \quad (2)$$

$$[NaBW_{12}O_{40}]^{4-} + [OH]^- \xrightarrow{k_2^{Na}} \text{Products} \quad (3)$$

$$k_2 = \frac{k_2^{K} + k_2^{Na}K_{IP}([Na^+]/[K^+])}{1 + K_{IP}([Na^+]/[K^+])} \quad (4)$$

for this reaction scheme is as in (4). Using values of k_2^{K} and k_2^{Na} obtained from the single-cation studies, various values can be assigned to K_{IP} to generate theoretical curves showing the dependence of k_2 on the concentrations of the two cations. Figure 4 shows curves for K_{IP} = 2.0, 3.0, and 4.0, and indicates K_{IP} *ca.* 3.

The dependence of the experimentally observed rate constant for the hydrolysis of $[BW_{12}O_{40}]^{5-}$ in the presence of Li^+ (Figure 1), and of $[H_2W_{12}O_{40}]^{6-}$ in the presence of K^+ or Li^+ (Figure 2), is non-linear, with the curves passing through the origin. This behaviour requires a reaction scheme in which a rapid pre-equilibrium precedes the hydrolysis step, for example equations (5) and (6). In

$$[H_2W_{12}O_{40}]^{6-} + [OH]^- \overset{K}{\rightleftharpoons} [H_2W_{12}O_{40}(OH)]^{7-} \quad (5)$$

$$[H_2W_{12}O_{40}(OH)]^{7-} \xrightarrow{k_1} \text{Products} \quad (6)$$

acid solutions the reverse reaction (5) prevents decomposition of the tungstate ion, but in alkaline solution this reverse reaction is insignificant leading to the rate expression (7). A plot of $1/k_{ex.}$ against $1/[OH^-]$ should be

$$k_{ex.} = k_1K[OH^-]/(1 + K[OH^-]) \quad (7)$$

linear with a gradient of $1/k_1K$ and an intercept of $1/k_1$. This is observed for the decomposition of $[H_2W_{12}O_{40}]^{6-}$ in the presence of Li^+. A least-squares fit of the data gives the constants in Table 2. These data were used to generate the appropriate curve in Figure 2. However, the results for the hydrolysis of $[BW_{12}O_{40}]^{5-}$ in the presence of Li^+, and of $[H_2W_{12}O_{40}]^{6-}$ in the presence of K^+, cannot be fitted to this mechanism and it is necessary to introduce an

TABLE 2

Base-independent, base-dependent, and pre-equilibrium constants for the reaction of polyanions with excess of base at 25.0 °C. Ionic strength maintained at 1.0 mol dm^{-3} with MCl

Polyanion	M	$[OH^-]$/ mol dm^{-3}	k_0/s^{-1}	k_1/s^{-1}	K/dm^3 mol^{-1}
$[H_2W_{12}O_{40}]^{6-}$	Li	0.05—0.50	0.0	0.7	0.8
				±0.4	±0.4
$[PW_{12}O_{40}]^{3-}$	K	0.002—0.20	0.070	1.2	7
				±0.2	±1
	Na	0.002—0.20	0.020	1.4	1.6
				±0.2	±0.2
	Li	0.002—0.40	0.012	0.081	6
				±0.008	±1

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[9] O. Glemser, W. Holznagel, and W. Holtje, *Z. anorg. Chem.*, 1966, **342**, 75.

additional hydrolysis step such as a second-order reaction between $[H_2W_{12}O_{40}(OH)]^{7-}$ and $[OH]^-$, but a unique set of rate and equilibrium constants cannot be obtained from the existing data.

The dependences of the experimentally observed rate constants for the hydrolysis of $[PW_{12}O_{40}]^{3-}$ on $[OH^-]$ (Figure 3) are also non-linear, but in addition the curves have positive intercepts on the rate axis. This indicates that hydrolysis occurs through an additional base-independent path, for example equations (8) and (9). In

$$[PW_{12}O_{40}]^{3-} + 3H_2O \xrightleftharpoons{k_0} [PW_{11}O_{39}]^{7-} + [WO_4]^{2-} + 6H^+ \qquad (8)$$

acid solution the reverse reaction (8) prevents decomposition of the tungstophosphate anion, but in alkaline solution this

$$[PW_{11}O_{39}]^{7-} \xrightarrow{\text{fast}} \text{Products} \qquad (9)$$

reverse reaction becomes insignificant. This scheme accounts for a base-independent reaction even though $[PW_{12}O_{40}]^{3-}$ is stable in aqueous solution. The value of k_0 can be estimated from the data at low hydroxide concentration. Combination of equations of type (5), (6), (8), and (9) leads to (10). A plot of $1/(k_{ex.} - k_0)$ against

$$k_{ex.} = k_0 + \frac{k_1K[OH^-]}{1 + K[OH^-]} \qquad (10)$$

$1/[OH^-]$ is linear with a gradient of $1/k_1K$ and an intercept of $1/k_1$. Least-squares fits of the data give the constants in Table 2. These data were used to generate the curves in Figure 3.

The temperature dependence of the experimentally observed rate constants, determined at four different temperatures over the range 25.0—40.0 °C, enabled the enthalpies and entropies of activation to be determined (Table 3). These were determined at a single hydroxide-ion concentration, and only apply to a single chemical reaction (k_2) for the decomposition of $[BW_{12}O_{40}]^{5-}$ in the presence of K^+ and Na^+, and of $[H_2W_{12}O_{40}]^{6-}$ in the presence of Na^+. For the other systems, the temperature dependence of the experimentally observed rate constants necessarily includes the temperature dependence of the rate constants k_0 and/or k_1 and the equilibrium constant K.

TABLE 3

Activation parameters at 25.0 °C for the reaction of polyanions with excess of base. Ionic strength maintained at 1.0 mol dm⁻³ with MCl

Polyanion	M	$[OH^-]$/ mol dm^{-3}	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/ J K^{-1} mol^{-1}
$[PW_{12}O_{40}]^{3-}$	K	0.20	54 ± 2	−63 ± 3
	Na	0.08	46 ± 2	−88 ± 4
	Li	0.24	56 ± 4	−79 ± 13
$[BW_{12}O_{40}]^{5-}$	K	0.20	45 ± 1	−92 ± 2
	Na	0.08	48 ± 4	−84 ± 3
	Li	0.40	47 ± 4	
$[H_2W_{12}O_{40}]^{6-}$	K	0.43	40 ± 3	
	Na	0.50	41 ± 4	−109 ± 20
	Li	0.50	50 ± 3	−79 ± 8

DISCUSSION

These studies of the isostructural anions $[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$, $[BW_{12}O_{40}]^{5-}$, and $[H_2W_{12}O_{40}]^{6-}$ show that not only the rate but also the mechanism of decomposition is dependent on both the choice of anion and the choice of cation. Only limited comparison between the polyanions can therefore be made.

The base-dependent hydrolysis of $[PW_{12}O_{40}]^{3-}$ proceeds *via* a pre-equilibrium with hydroxide ion. This cannot be to produce species such as $[PW_{11}O_{39}]^{7-}$ or $[PW_9O_{34}]^{9-}$ which are analogous to the intermediates formed in the base hydrolysis of $[SiW_{12}O_{40}]^{4-}$, since to be consistent with equation (10) the equilibrium must involve only one hydroxide ion. It is therefore necessary to postulate a new species, $[PW_{12}O_{40}(OH)]^{4-}$, as the intermediate. Similarly the base hydrolysis of $[H_2W_{12}O_{40}]^{6-}$ in K^+ and Li^+ proceeds *via* a rapid pre-equilibrium with an intermediate $[H_2W_{12}O_{40}(OH)]^{7-}$. This species cannot be $[HW_{12}O_{40}]^{7-}$ formed by the direct removal of one of the protons from the central cavity of the tungstate structure since the rate of exchange between these protons and solvent water is too slow [6] for this rapid pre-equilibrium.

The second-order rate constants for the reaction between $[H_2W_{12}O_{40}]^{6-}$ and hydroxide ion (k_2 0.64 dm^3 mol^{-1} s^{-1} at 25.0 °C with Na^+ as counter ion), and between $[BW_{12}O_{40}]^{5-}$ and hydroxide ion (k_2 0.86 dm^3 mol^{-1} s^{-1}), are much less than for the reaction between $[SiW_{12}O_{40}]^{4-}$ and hydroxide ion (k_2 160 dm^3 mol^{-1} s^{-1}).[1] The rate of hydroxide-ion attack on $[PW_{12}O_{40}]^{3-}$ to form $[PW_{12}O_{40}(OH)]^{4-}$ was not obtained, but it must be greater than the rate of decomposition of $[PW_{12}O_{40}(OH)]^{4-}$ (k_1, Table 2). The enthalpies of activation for the base hydrolysis of a series of polyanions generally increases with increasing charge on the polyanion ($\Delta H^\ddagger$ in kJ mol^{-1}, Na^+ as cation unless otherwise stated): $[Cr_2O_7]^{2-}$ (20),[4] $[SiW_{12}O_{40}]^{4-}$ (33),[1] $[BW_{12}O_{40}]^{5-}$ (48) (this work), $[H_2W_{12}O_{40}]^{6-}$ (41) (this work), $[Mo_7O_{24}]^{6-}$ (56),[3] $[V_{10}O_{28}]^{6-}$ (66),[2] $[SiW_{11}O_{39}]^{8-}$ (77, Li^+),[1] and $[SiW_9O_{34}]^{10-}$ (80, K^+; 51, Na^+).[1] This is readily explained in terms of electrostatic repulsion between the polyanion and the hydroxide ion. On the other hand, the base-independent rate constant for the decomposition of $[H_2W_{12}O_{40}(OH)]^{7-}$ (k_1 0.7 s^{-1} at 25.0 °C with Li^+ as counter ion) is greater than that for the decomposition of $[PW_{12}O_{40}(OH)]^{4-}$ (k_1 0.08 s^{-1}). The entropies of activation (Table 3) are similar to those obtained for the hydrolysis of other polyions, and have been discussed elsewhere.[1]

The rate constants obtained in this work are in the order $K^+ > Na^+ > Li^+$. A similar trend was observed for the base decomposition of $[Cr_2O_7]^{2-}$,[4] $[V_{10}O_{28}]^{6-}$,[2] $[SiW_{12}O_{40}]^{4-}$, $[SiW_{11}O_{39}]^{8-}$, and $[SiW_9O_{34}]^{10-}$,[1] but the reverse was observed for $[Mo_7O_{24}]^{6-}$.[3] In this work mixed-cation studies were restricted to $[BW_{12}O_{40}]^{5-}$ in K^+ and Na^+, which is the only pair exhibiting simple kinetic behaviour. The equilibrium constant between the potassium ion pair and the sodium ion pair [equation (1)] has a value of 3, in contrast to values of 1.0 for $[SiW_{12}O_{40}]^{4-}$, 0.4 for $[V_{10}O_{28}]^{6-}$, and 0.1 for $[Mo_7O_{24}]^{6-}$, suggesting the existence of specific interactions between each polyanion and each cation.

[8/638 *Received, 7th April,* 1978]