Stepwise Base Decomposition of 12-Tungstosilicate(4−)

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The reaction of $[SiW_{12}O_{40}]^{4-}$ (1.5×10^{-5} mol dm^{-3}) with excess of hydroxide ion at an ionic strength of 1.0 mol dm^{-3} MCl, to form $[SiO_4]^{4-}$ and $[WO_4]^{2-}$, has been studied. The reaction proceeds in three distinct stages, the intermediates being $[SiW_{11}O_{39}]^{8-}$ and $[SiW_9O_{34}]^{10-}$. The first stage proceeds *via* a base-dependent path, the second-order rate constants decreasing in the order $K^+ > Na^+ > Li^+$. The second stage, the hydrolysis of $[SiW_{11}O_{39}]^{8-}$, has been studied in detail only in LiCl, the reaction proceeding *via* both base-independent and -dependent paths directly to $[SiO_4]^{4-}$ and $[WO_4]^{2-}$ in this medium. Comparison of the data obtained for these first two reactions with those obtained for the base hydrolysis of other approximately spherical polyanions indicates that the enthalpy of activation increases as the charge on the polyanion increases. The third stage, the hydrolysis of $[SiW_9O_{34}]^{10-}$, shows a very large dependence on the choice of cation, and studies in mixed-cation media suggest the formation of larger ion aggregates. This final reaction also has exceptional enthalpies and entropies of activation.

As part of a programme on the study of the equilibria between, and rates of reaction of, polymeric hydroxo-bridged cations and oxo-bridged anions, we report a kinetic study of the decomposition of 12-tungstosilicate(4−), $[SiW_{12}O_{40}]^{4-}$, with excess of base to form tungstate(2−), $[WO_4]^{2-}$, and silicate.

Mild hydrolysis [1] of $[SiW_{12}O_{40}]^{4-}$ yields the 11-tungstosilicate(8−) ion, $[SiW_{11}O_{39}]^{8-}$. The structure of $K_8[SiW_{11}O_{39}]\cdot 13H_2O$ shows that the basic Keggin structure of corner- and edge-sharing WO_6 octahedra grouped around a central tetrahedrally co-ordinated heteroatom is retained, but one of the outer octahedra is missing.[2]

$$[SiW_{12}O_{40}]^{4-} + 6[OH]^- \longrightarrow [SiW_{11}O_{39}]^{8-} + [WO_4]^{2-} + 3H_2O \quad (1)$$

Further base hydrolysis of $[SiW_{11}O_{39}]^{8-}$ yields the 9-tungstosilicate(10−) ion, $[SiW_9O_{34}]^{10-}$.[3]

$$[SiW_{11}O_{39}]^{8-} + 6[OH]^- \longrightarrow [SiW_9O_{34}]^{10-} + 2[WO_4]^{2-} + 3H_2O \quad (2)$$

The structure of this ion is unknown, although that of the 9-molybdophosphate analogue $Na_3H_6[PMo_9O_{34}]\cdot nH_2O$ is formed [4] by the removal of three adjacent corner-sharing

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[1] C. Tourne and G. Tourne, *Bull. Soc. chim. France*, 1969, 1124.

[2] K. Y. Matsumoto and Y. Sasaki, *Bull. Chem. Soc. Japan*, 1976, **49**, 156.

[3] R. Contant, J.-M. Fruchart, G. Herve, and A. Teze, *Compt. rend.*, 1974, **C278**, 199.

[4] R. Strandberg, *Acta Chem. Scand.*, 1974, **A28**, 217; H. d'Amour, *Acta Cryst.*, 1976, **B32**, 729.

octahedra from the Keggin structure. Finally, complete hydrolysis to tungstate(2−) and silicate(4−) occurs in alkaline solution.

$$[SiW_9O_{34}]^{10-} + 12[OH]^- \longrightarrow [SiO_4]^{4-} + 9[WO_4]^{2-} + 6H_2O \quad (3)$$

EXPERIMENTAL

Potassium 11-*Tungstosilicate*(8−).—Potassium hydroxide (*ca.* 1.0 mol dm^{-3}) was slowly added to $K_4[SiW_{12}O_{40}]$ (0.1 mol dm^{-3}) until all the latter had been hydrolysed to $[SiW_{11}O_{39}]^{8-}$ as indicated by the u.v. spectrum. The salt $K_7H[SiW_{11}O_{39}]\cdot 8H_2O$ was precipitated by the addition of saturated potassium chloride (Found: K, 9.0; Si, 0.90; W, 64.6; H_2O, 4.6. Calc. for $H_{17}K_7O_{47}SiW_{11}$: K, 8.9; Si, 0.90; W, 65.4; H_2O, 4.7%). The spectrum obtained on redissolving the salt agreed with published spectra [5] of $[SiW_{11}O_{39}]^{8-}$, and the rate of base hydrolysis was the same as that of the first intermediate in the base degradation of $[SiW_{12}O_{40}]^{4-}$.

Potassium 9-*Tungstosilicate*(10−).—Potassium hydroxide (*ca.* 1.0 mol dm^{-3}) was slowly added to $K_4[SiW_{12}O_{40}]$ (0.1 mol dm^{-3}) until all the latter had been hydrolysed to $[SiW_9O_{34}]^{10-}$ as indicated by the u.v. spectrum. The salt $K_9H[SiW_9O_{34}]\cdot 11H_2O$ was precipitated by the addition of saturated KCl (Found: K, 12.8; Si, 1.0; W, 60.9; H_2O, 7.0. Calc. for $H_{23}K_9O_{45}SiW_9$: K, 12.7; Si, 1.0; W, 59.6; H_2O, 7.1%).

12-Tungstosilicic acid [6] and its potassium salt [7] were prepared by standard methods. Tetraethylammonium chloride (B.D.H.) and tetraethylammonium hydroxide (B.D.H.) solutions were boiled with activated charcoal [8] to remove the yellow colour. All the other chemicals were reagent grade. Stock solutions of all the hydroxides were standardised within 24 h of use. Measurements were carried out on a modified [9] Durrum–Gibson stopped-flow spectrophotometer, and a Perkin-Elmer 450 spectrophotometer, rate constants being reproducible to ±5 and ±3% respectively.

RESULTS

The base hydrolysis of $[SiW_{12}O_{40}]^{4-}$ (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).

The hydrolysis to tungstate(2−) and silicate(4−) was found to occur in three distinct stages, the intermediate species being identified as $[SiW_{11}O_{39}]^{8-}$ and $[SiW_9O_{34}]^{10-}$ from their u.v. spectra. The three stages are now described in turn.

Base Decomposition of $[SiW_{12}O_{40}]^{4-}$ *to* $[SiW_{11}O_{39}]^{8-}$.—The addition of base to a solution of $[SiW_{12}O_{40}]^{4-}$ resulted in a rapid decrease in optical density at 260 nm, over several milliseconds. The ' zero-time ' spectrum was that expected for $[SiW_{12}O_{40}]^{4-}$. The spectrum measured after 10 half-lives was that of $[SiW_{11}O_{39}]^{8-}$. All the reactions showed first-order kinetic behaviour for at least four half-lives.

The experimentally observed rate constant (k_{ex}) * increases linearly with increasing hydroxide-ion concentration (Figure 1), the line of best fit passing through the origin. 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 measured (Table 1). Measurements using a wider range of cations, for example tetra-alkylammonium ions, were prevented because of the insolubility of their 12-tungstosilicates.

TABLE 1

k_2 and activation parameters for the reaction of $[SiW_{12}O_{40}]^{4-}$ with excess of base. Ionic strength maintained at 1.0 mol dm^{-3} with MCl

M	θ_c/°C	k_2/dm^3 mol^{-1} s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
K	25.0	203 ± 3	39 ± 2	−71 ± 4
	30.5	268		
	34.9	341		
	39.8	445		
Na	25.0	160 ± 5	33 ± 4	−88 ± 13
	30.4	197		
	35.0	256		
	40.2	317		
Li	25.0	114 ± 6	39 ± 4	−71 ± 13
	30.2	149		
	35.0	186		
	39.8	257		

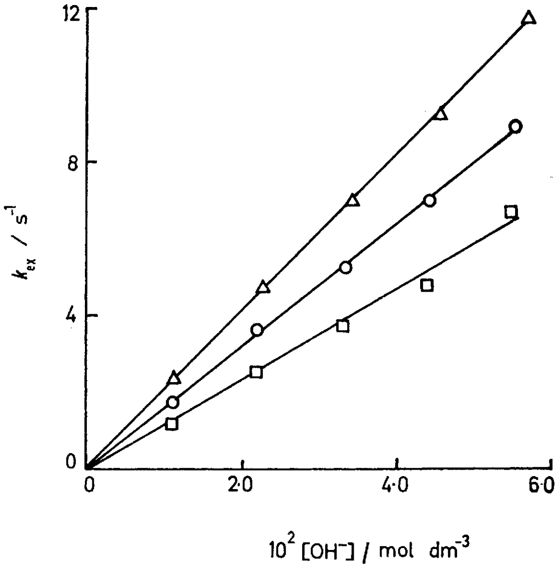

FIGURE 1 Hydroxide-ion dependence of the experimental rate constant at 25 °C for the base hydrolysis of $[SiW_{12}O_{40}]^{4-}$ in 1.0 mol dm^{-3} MCl: M = (△) K, (○) Na, and (□) Li

Additional information on the effect of choice of cation 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 *ca.* 0.1 to 0.9 mol dm^{-3}. The second-order rate constants are listed in Table 2, and a typical series is shown in Figure 2.

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

[5] P. Souchay, A. Teze, and G. Herve, *Compt. rend.*, 1972, **C275**, 1013.

[6] E. O. North, *Inorg. Synth.*, 1939, **1**, 129.

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

[8] A. I. Vogel, ' A Text-book of Practical Organic Chemistry,' Longmans, London, 1956.

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

Base Decomposition of $[SiW_{11}O_{39}]^{8-}$.—The base decomposition of $[SiW_{11}O_{39}]^{8-}$ to $[SiW_9O_{34}]^{10-}$ was examined in less detail due to the concurrent degradation of $[SiW_9O_{34}]^{10-}$ to silicate(4−) and tungstate(2−). Solutions of $[SiW_{12}O_{40}]^{4-}$ (1.5×10^{-5} mol dm^{-3}) were added to potassium, sodium, or lithium hydroxide (10^{-3} mol dm^{-3}), ionic strength being maintained at 1.0 mol dm^{-3} with the appropriate chloride.

TABLE 2

k_2 for the reaction of $[SiW_{12}O_{40}]^{4-}$ with excess of base at 25.0 °C

[M$^+$]/mol dm^{-3}		
K	Li	k_2/dm^3 mol^{-1} s^{-1}
0.10	0.90	122
0.25	0.75	136
0.40	0.60	145
0.55	0.45	157
0.70	0.30	173
0.85	0.15	187
Na	Li	
0.15	0.85	119
0.25	0.75	127
0.30	0.70	125
0.40	0.60	133
0.45	0.55	135
0.60	0.40	142
0.75	0.25	146
0.90	0.10	157
K	Na	
0.15	0.85	167
0.30	0.70	173
0.45	0.55	185
0.60	0.40	185
0.90	0.10	200

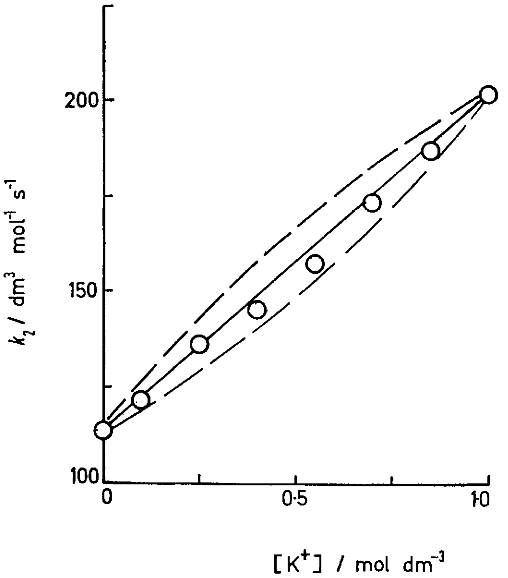

FIGURE 2 Second-order rate constant for the base hydrolysis of $[SiW_{12}O_{40}]^{4-}$ in KCl–LiCl mixtures, total ionic strength = 1.0 mol dm^{-3}. Theoretical curves are given for K_{IP} = 1.5 (upper curve), 1.0, and 0.67 (lower curve)

In potassium and sodium chlorides, the spectrum changed over *ca.* 15—30 min from that of $[SiW_{11}O_{39}]^{8-}$ to that of $[SiW_9O_{34}]^{10-}$. However, the isosbestic point moved during the reaction due to the concurrent hydrolysis of $[SiW_9O_{34}]^{10-}$ to $[SiO_4]^{4-}$ and $[WO_4]^{2-}$, the overlap being more evident at higher [OH$^-$]. These reactions were therefore not fully investigated, although the reaction was clearly faster in the presence of KCl than NaCl.

In LiCl, the spectrum changed directly to that of $[SiO_4]^{4-}$ and $[WO_4]^{2-}$ without any spectral evidence of $[SiW_9O_{34}]^{10-}$, and the reaction could therefore be studied in more detail. The spectrum was measured as a function of time over the range 200—400 nm. All the rate measurements were made at 258 nm where the transmittance increased to 100% over a period of hours. The reactions were followed for four half-lives and the data yielded good first-order rate plots. The experimentally observed rate constant (k_{ex}) was a linear function of [OH$^-$], and the resulting rate constants k_1 and k_2 obtained from a least-squares fit of $k_{ex} = k_1 + k_2[OH^-]$ are shown in Table 3. Similar studies over a range of temperature enabled the enthalpy and entropy of activation to be determined (Table 3).

TABLE 3

k_1, k_2, and activation parameters for the reaction of $[SiW_{11}O_{39}]^{8-}$ with excess of base. Ionic strength maintained at 1.0 mol dm^{-3} with LiCl

	θ_c/°C	10^4k_1/s^{-1}	10^4k_2/dm^3 mol^{-1} s^{-1}
	25.8	1.33 ± 0.04	1.95 ± 0.07
	30.0	2.4 ± 0.1	2.9 ± 0.3
	33.6	3.5 ± 0.4	5.0 ± 0.8
	37.9	6.8 ± 0.2	6.8 ± 0.4
$\Delta H^\ddagger$/kJ mol^{-1}	25.8	101 ± 8	77 ± 12
$\Delta S^\ddagger$/J K^{-1} mol^{-1}	25.8	4 ± 13	−59 ± 9

Base Decomposition of $[SiW_9O_{34}]^{10-}$.—Solutions of $[SiW_{12}O_{40}]^{4-}$ (1.5×10^{-5} mol dm^{-3}) were mixed with a large excess of hydroxide ion, ionic strength being maintained at 1.0 mol dm^{-3} with potassium or sodium chloride. In the case of tetraethylammonium chloride, *ca.* 10^{-3} mol dm^{-3} lithium hydroxide was added to the $[SiW_{12}O_{40}]^{4-}$ solution 5 min before mixing this solution with the tetraethylammonium hydroxide–chloride solution. The $[SiW_{12}O_{40}]^{4-}$, which forms an insoluble tetraethylammonium salt, was thereby converted into $[SiW_{11}O_{39}]^{8-}$ which does not precipitate in the presence of tetraethylammonium ion. The spectra were measured as a function of time over the range 200—400 nm. All the rate measurements were made at 258 nm where the transmittance of the sample increased to 100% over a period of minutes to hours depending on the temperature, [OH$^-$], and supporting electrolyte used. The reactions were followed for four half-lives and the data yielded good first-order rate plots. At the lowest [OH$^-$] used, with potassium as the counter ion, some curvature in the rate plots was evident during the first half-life which was clearly due to the reaction of $[SiW_{11}O_{39}]^{8-}$ to form $[SiW_9O_{34}]^{10-}$.

The experimentally observed rate constant (k_{ex}) is shown as a function of [OH$^-$] in Figure 3. The value of k_{ex} increases linearly with increasing [OH$^-$], and in the case of potassium ion there is a positive intercept on the rate axis. The corresponding rate constants k_1 and k_2, derived from a least-squares fit according to $k_{ex} = k_1 + k_2[OH^-]$, are shown in Table 4. Determinations over a range of temperature enabled resolution into enthalpies and entropies of activation (Table 4). The values of k_1 were not sufficiently accurate to derive activation parameters.

The base hydrolysis of $[SiW_9O_{34}]^{10-}$ in the presence of mixtures of sodium and potassium ions was also studied.

Values of k_1 and k_2 were again obtained by a least-squares fit of k_{ex} obtained at four or more values of [OH$^-$], ranging from 0.01 to 0.1 mol dm^{-3}. The values of k_1 were small and subject to large errors and will not be considered. The values of k_2 are given in Table 5 and in Figure 4.

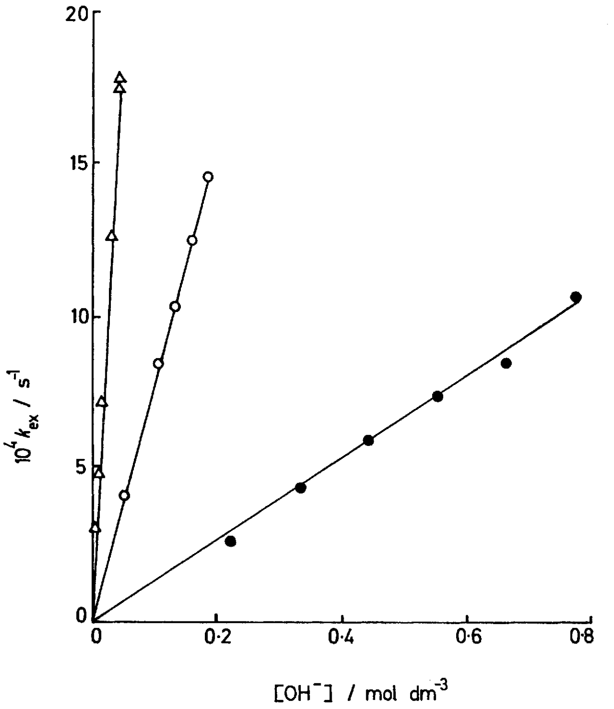

FIGURE 3 Hydroxide-ion dependence of the experimental rate constant at 25.8 °C for the base hydrolysis of $[SiW_9O_{34}]^{10-}$ in 1.0 mol dm^{-3} MCl: M = (△) K, (○) Na, and (●) NEt_4

TABLE 4

k_1, k_2, and activation parameters for the reaction of $[SiW_9O_{34}]^{10-}$ with excess of base. Ionic strength maintained at 1.0 mol dm^{-3} with MCl

	M	θ_c/°C	10^4k_1/s^{-1}	10^4k_2/dm^3 mol^{-1} s^{-1}
	K	21.5	0.94 ± 0.7	220 ± 10
		25.8	0.75 ± 0.4	420 ± 10
		30.5	1.9 ± 0.2	580 ± 10
		35.5	0.12 ± 0.2	1 080 ± 20
$\Delta H^‡$/kJ mol^{-1}		25.8		80 ± 13
$\Delta S^‡$/J K^{-1} mol^{-1}		25.8		−4 ± 14
	Na	20.8	0.1 ± 0.2	49 ± 1
		25.8	0.0 ± 0.3	78 ± 2
		30.3	0.1 ± 0.4	104 ± 4
		34.9	0.4 ± 0.2	141 ± 3
$\Delta H^‡$/kJ mol^{-1}		25.8		51 ± 4
$\Delta S^‡$/J K^{-1} mol^{-1}		25.8		−113 ± 9
	NEt_4	25.8	0.0	13.5 ± 0.5
		30.2	0.0	19.0
		35.2	0.0	29.6
		40.0	0.0	46.5
$\Delta H^‡$/kJ mol^{-1}		25.8		65 ± 4
$\Delta S^‡$/J K^{-1} mol^{-1}		25.8		−84 ± 5

TABLE 5

k_2 for the reaction of $[SiW_9O_{34}]^{10-}$ with excess of base at 25.0 °C

[M$^+$]/mol dm^{-3}		
K	Na	10^4k_2/dm^3 mol^{-1} s^{-1}
0.20	0.80	121 ± 7
0.40	0.60	181 ± 6
0.60	0.40	175 ± 1
0.80	0.20	200 ± 10

DISCUSSION

The base decomposition of $[SiW_{12}O_{40}]^{4-}$ to $[SiO_4]^{4-}$ and $[WO_4]^{2-}$ has been found to proceed *via* two intermediates, $[SiW_{11}O_{39}]^{8-}$ and $[SiW_9O_{34}]^{10-}$, in potassium chloride and sodium chloride solutions, and *via* one intermediate, $[SiW_{11}O_{39}]^{8-}$, in lithium chloride solutions. These findings contrast with those of Glemser *et al.*[10] who reported that the reaction proceeded as a single bimolecular reaction. These workers used conventional spectrophotometric techniques to follow the reaction and would not have detected the first two reactions in the hydrolysis sequence, these being completed within 1 or 2 min under their experimental conditions. Their results therefore refer to the base decomposition of $[SiW_9O_{34}]^{10-}$ rather than $[SiW_{12}O_{40}]^{4-}$, and are compatible with the results obtained in this work.

The rates for the base hydrolysis of $[SiW_{12}O_{40}]^{4-}$ (and $[SiW_{11}O_{39}]^{8-}$) in 1.0 mol dm^{-3} potassium, sodium, and lithium chloride decrease in the order $K^+ > Na^+ > Li^+$, and for the base hydrolysis of $[SiW_9O_{34}]^{10-}$, $K^+ \gg Na^+ \gg [NEt_4]^+$. Similar observations have been made for the base hydrolysis of decavanadate(6−),[11] $[V_{10}O_{28}]^{6-}$ ($K^+ > Na^+ > Li^+ \gg [NMe_4]^+ \sim [NEt_4]^+ \sim 0$), and dichromate,[12] $[Cr_2O_7]^{2-}$ ($K^+ > Na^+ > Li^+ \gg [NMe_4]^+ \gg [NEt_4]^+$). However, the reverse reactivity ($Li^+ >$

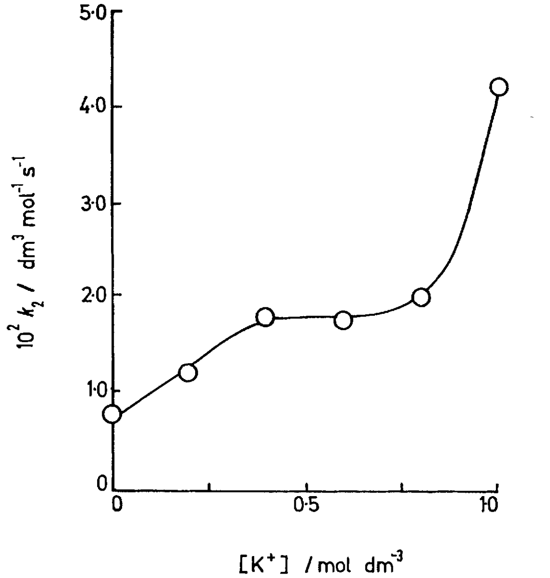

FIGURE 4 Second-order rate constant for the base hydrolysis of $[SiW_9O_{34}]^{10-}$ in KCl–NaCl mixtures, total ionic strength = 1.0 mol dm^{-3}

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

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

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

$Na^+ > K^+$) was found for the base hydrolysis of heptamolybdate(6—),[13] $[Mo_7O_{24}]^{6-}$.

Further information on the effect of counter ions can be obtained using mixtures of cations.[11,13,14] The simplest reaction scheme which can be proposed and is consistent with the above experimental results involves competitive ion pairing between the polyanion and both cations [equations (4)—(6)].

$$[MSiW_{12}O_{40}]^{3-} + M^{*+} \overset{K_{IP}}{\rightleftharpoons} [M^*SiW_{12}O_{40}]^{3-} + M^+ \quad (4)$$

$$[MSiW_{12}O_{40}]^{3-} + [OH]^- \xrightarrow{k_2^M} \text{Products} \quad (5)$$

$$[M^*SiW_{12}O_{40}]^{3-} + [OH]^- \xrightarrow{k_2^{M^*}} \text{Products} \quad (6)$$

$$k_2 = \frac{k_2^M + k_2^{M^*}K_{IP}([M^{*+}]/[M^+])}{1 + K_{IP}([M^{*+}]/[M^+])} \quad (7)$$

The rate expression for this reaction scheme is as in (7). Using values of k_2^M and $k_2^{M^*}$ 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 2 shows curves for $K_{IP} = 0.67$, 1.0, and 1.5, and indicates K_{IP} *ca.* 1.0. Similar results were obtained for each set of mixtures.

The dependence of k_2 for the hydrolysis of $[SiW_9O_{34}]^{10-}$ on the relative concentrations of potassium and sodium ions (Figure 4) shows that in this case the results cannot be explained using a model only involving ion pairs. The point of inflection in the curve near $[K^+] = [Na^+] = 0.5$ mol dm^{-3} suggests that an ion triplet of the form $[NaKSiW_9O_{34}]^{8-}$ is being formed, which may be rationalised as being associated with the very high negative charge on this polyanion, and with the large ' hole ' in its structure which may provide specific cation-binding sites. Any model involving ion triplets requires several unknown parameters, and no quantitative explanation was attempted.

The enthalpies of activation for the base hydrolysis of a series of polyanions increases in the following order ($\Delta H^\ddagger$ in kJ mol^{-1}, Na^+ as cation unless otherwise stated): $[Cr_2O_7]^{2-}$ (20) (ref. 12) < $[SiW_{12}O_{40}]^{4-}$ (33) < $[Mo_7O_{24}]^{6-}$ (56) (ref. 13) < $[V_{10}O_{28}]^{6-}$ (66) (ref. 11) < $[SiW_{11}O_{39}]^{8-}$ (77, Li^+). This is in order of increasing negative charge, and can readily be explained in terms of the increasing electrostatic repulsion between the polyanion and the hydroxide ion. The base hydrolysis of $[SiW_9O_{34}]^{10-}$ in the presence of Na^+ (51 kJ mol^{-1}) compared with K^+ (80 kJ mol^{-1}) is clearly exceptional, suggesting extraordinary interaction between $[SiW_9O_{34}]^{10-}$ and Na^+.

There is also an extraordinarily large difference between the entropies of activation ($\Delta S^\ddagger$ in J K^{-1} mol^{-1}) for the base hydrolysis of $[SiW_9O_{34}]^{10-}$ in the presence of Na^+ (−113) and K^+ (−4). Large negative values (Na^+ as cation unless otherwise stated) have also been found for the base hydrolysis of $[Cr_2O_7]^{2-}$ (−120),[12] $[SiW_{12}O_{40}]^{4-}$ (−88), $[V_{10}O_{28}]^{6-}$ (−79),[11] and $[SiW_{11}O_{39}]^{8-}$ (−59, Li^+), in contrast to the much more positive value found for $[Mo_7O_{24}]^{6-}$ (21).[13] The difference between $[Mo_7O_{24}]^{6-}$ and $[V_{10}O_{28}]^{6-}$, indicating a more solvated reactant and/or a less-ordered activated complex in the molybdenum compound, has been associated with [13] the more open structure of $[Mo_7O_{24}]^{6-}$ compared with the compact $[V_{10}O_{28}]^{6-}$. The same comment can be made when comparing $[SiW_9O_{34}]^{10-}$ (in K^+) with $[SiW_9O_{34}]^{10-}$ (in Na^+), $[SiW_{11}O_{34}]^{8-}$, and $[SiW_{12}O_{40}]^{4-}$.

The entropy of activation for the hydrolysis of $[SiW_{11}O_{39}]^{8-}$ *via* the base-independent path (4 J K^{-1} mol^{-1}) is much more positive than for the base-dependent path (−59 J K^{-1} mol^{-1}). A similar observation was reported for the hydrolysis of $[V_{10}O_{28}]^{6-}$.[11]

[7/953 *Received, 2nd June,* 1977]

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

[14] B. W. Clare, D. L. Kepert, and D. W. Watts, *J.C.S. Dalton*, 1973, 2481.