Base Decomposition of Decavanadate

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The reaction of decavanadate(6−) (1·0 × 10^{-3} mol l^{-1} in $[V_{10}O_{28}]^{6-}$) with excess hydroxide ion at an ionic strength of 1·30 mol l^{-1} proceeds *via* base-independent and base-dependent paths. Both paths are strongly dependent upon the cation chosen to maintain constant ionic strength. The base-independent rate constant increases in the order $K^+ \ll Na^+ \sim Li^+ \ll Me_4N^+ < Et_4N^+$. Extensive measurements in mixed cation media show that this base-independent rate increases as the strength of the cation–decavanadate(6−) ion pair decreases, the importance of ion pairing decreasing in the order $K^+ > Na^+ > Me_4N^+ > Et_4N^+$. In contrast, the base-dependent rate constant shows the reverse trend, decreasing in the order $K^+ \gg Na^+ > Li^+ \gg Me_4N^+ \sim Et_4N^+ \sim 0$. The same mixed-cation studies show that this base-dependent path proceeds *via* reactive alkali-metal decavanadate species.

As part of a programme on the study of the equilibria between, and the rates of reaction of, polymeric hydroxo-bridged cations and oxo-bridged anions, we report a kinetic study of the decomposition of decavanadate(6−), $[V_{10}O_{28}]^{6-}$, with excess base to form $[VO_4]^{3-}$.[1] The rapid decomposition of decavanadate(6−) with excess acid has been studied by stopped-flow techniques,[2] and proceeds by successive protonation through the ions $[H_2V_{10}O_{28}]^{4-}$, $[H_3V_{10}O_{28}]^{3-}$, to $[H_4V_{10}O_{28}]^{2-}$. The rate of decomposition depends markedly on the cation present,[3] the protonated decavanadates forming stable ion pairs with large cations such as tetra-alkylammonium ions which do not react with acid. This effect is greater the larger the size of the onium ion. Alkali-metal cations however do not form ion pairs.

This finding is in contrast to that of Schwarzenbach and Geier [4] who used continuous-flow methods and found that the unprotonated $[V_{10}O_{28}]^{6-}$ and monoprotonated $[HV_{10}O_{28}]^{5-}$ form ion pairs with alkali-metal cations, but not with tetra-alkylammonium ions, the ion-pair association constants decreasing in the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$.

The decomposition of decavanadate(6−) with base is much slower than the decomposition with acid, and can be followed by conventional techniques. During the course of the present work Goddard and Gonas [5] published a similar study and found a base-independent path and a base-dependent path, the latter depending upon the counterion. Their work however did not include our extensive measurements on mixed cations which are necessary to elucidate the nature of the competitive ion-pairing reactions.

EXPERIMENTAL

The stock decavanadate solution was prepared as before,[2] and standardised using the iodide–iodate method.[6] Alkali-metal chlorides and nitrates were analytical reagent grade and were used without further purification. Tetramethylammonium chloride and tetraethylammonium chloride (B.D.H.) solutions were boiled with activated charcoal to remove slight yellow colourations.[7] All stock chloride solutions were standardised against silver nitrate. Tetramethylammonium and tetraethylammonium hydroxide solutions were prepared from the respective bromides and freshly prepared silver oxide,[8] and standardised against nitric acid just prior to use.

Spectral and kinetic measurements were carried out on a Perkin-Elmer 450 double-beam spectrophotometer. The spectra were measured as a function of time over the visible region (750—350 nm), the rate measurements being made at 490 nm. The decavanadate solution (2·0 × 10^{-3} mol l^{-1} in $[V_{10}O_{28}]^{6-}$) was added to a solution containing the base together with the alkali metal or tetra-alkylammonium chloride to maintain the final ionic strength at 1·30 mol l^{-1}. The reaction was followed for three to four half lives. The extrapolated ' zero time ' transmittance was that expected for decavanadate. The transmittance increased to 100% at ' infinite time.' All reactions were cleanly first order. Rate constants were reproducible to ±2%, the error arising mainly from temperature fluctuations (±0·2 °C). All data were computer fitted using standard least-squares programmes.

RESULTS

The dependence of the observed first-order rate constant for the decomposition of decavanadate in a large excess of hydroxide on the hydroxide ion concentration is shown in Figure 1. The rate is dependent upon the choice of cation in the supporting electrolyte, but independent of the anion. For lithium, sodium, and potassium, the observed rate constants increase linearly with increasing hydroxide ion concentration, and the lines have positive intercepts on the rate axis. This corresponds to a rate law of the form $k_{obs} = k_a + k_b[OH^-]$, where k_a is the base-independent, and k_b is the base-dependent, rate constant. For tetramethylammonium ion and tetraethylammonium ion as the supporting electrolytes, the observed first-order rate constants were independent of hydroxide ion concentration, the decomposition occurring exclusively through the base-independent path. Similar results were obtained over a range of temperatures.[9] Least-squares fits on this data yields the rate constants in Table 1, the error in each rate constant being taken as twice the standard error of the intercept and slope respectively.

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[1] D. L. Kepert, 'The Early Transition Metals,' Academic Press, London, 1972.

[2] B. W. Clare, D. L. Kepert, and D. W. Watts, *J.C.S. Dalton*, 1973, 2479.

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

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[5] J. B. Goddard and A. M. Gonas, *Inorg. Chem.*, 1973, **12**, 574.

[6] A. I. Vogel, 'A Text-book of Quantitative Inorganic Analysis,' Longmans, London, 1961, 3rd edn., p. 381.

[7] A. I. Vogel, 'A Text-book of Practical Organic Chemistry,' Longmans, London, 1956, p. 127.

[8] J. E. Prue, A. J. Read, and G. Romeo, *Trans. Faraday Soc.*, 1971, **67**, 420.

[9] A complete listing of all k_{obs} are included in D. M. Druskovich, Ph.D. Thesis, University of Western Australia, 1974.

A more quantitative insight into the relative importance of ion pairing can be gained by studying mixtures of cations, while maintaining the total ionic strength constant at 1·30 mol l^{-1} as before. This procedure is particularly useful for mixtures of alkali-metal ions with tetra-alkylammonium ions, where there are large differences in both k_a and k_b. Experiments on mixtures of potassium ion with sodium, tetramethylammonium, and tetraethylammonium ions could not be carried out at 25·8 °C owing to the precipitation of the mixed salts $K_4Na_2[V_{10}O_{28}]\cdot 11H_2O$, $K_4[Me_4N]_2[V_{10}O_{28}]\cdot 12H_2O$, and a mixture of $K_4[Et_4N]_2[V_{10}O_{28}]\cdot xH_2O$ and $K_5[Et_4N][V_{10}O_{28}]\cdot xH_2O$, respectively. This problem was overcome by working at 38·0 °C, and in the last case, by using 10^{-4} mol l^{-1} decavanadate solutions.

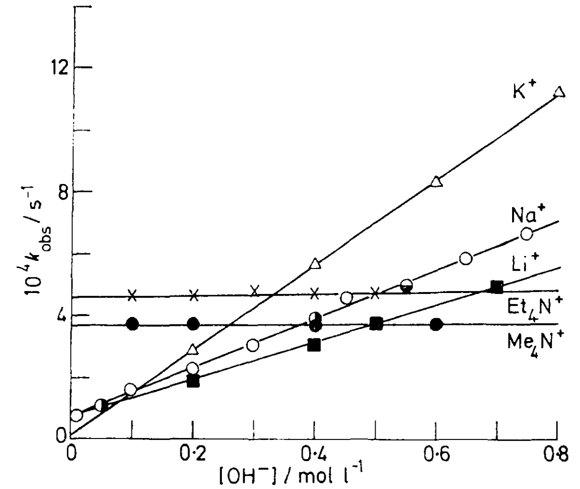

FIGURE 1 Plots of k_{obs} against [OH$^-$] for the base decomposition of $[V_{10}O_{28}]^{6-}$ (1·0 × 10^{-3} mol l^{-1}) at 25·8 °C: I = 1·30 mol l^{-1} MCl, M = K, Na, Li, Me$_4$N, or Et$_4$N (◑; 1·30 mol l^{-1} NaNO$_3$, ◒; 1·30 mol l^{-1} NaClO$_4$)

Mixed cation systems studied were sodium–potassium, sodium–tetramethylammonium, sodium–tetraethylammonium, potassium–tetramethylammonium, and potassium–tetraethylammonium. At each composition the linear plots, containing from four to six experimental rate constants,[9] of k_{obs} against [OH$^-$] yielded base independent (k_a) and base dependent (k_b) rate constants as before. These are shown as a function of composition in Figures 2 and 3 for k_a, and Figures 4—6 for k_b (the low and relatively constant values of k_a for the sodium–potassium mixtures are not shown as they do not warrant further discussion).

DISCUSSION

The decomposition of decavanadate in the presence of sodium hydroxide at 25·8 °C, with the ionic strength maintained at 1·30 mol l^{-1} with sodium chloride, yields a value of 10^4 k_b of 7·9 l mol^{-1} s^{-1} (Table 1). This is almost double the value obtained from the results of Goddard and Gonas [5] interpolated to the same temperature for the same reaction but at the higher ionic strength of 2·50 mol l^{-1}, illustrating the large effect of ionic strength. Goddard and Gonas' values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for this base-dependent path were 17·6 ± 0·5 kcal mol^{-1} and −13 ± 2 cal K^{-1} mol^{-1} (their errors being the standard deviations), which may be compared with our values of 16·0 ± 1·0 kcal mol^{-1} and −19 ± 1 cal K^{-1} mol^{-1} respectively (Table 2). Goddard and Gonas reported no activation parameters for the base-independent rates (k_a), but their $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the decomposition of decavanadate, in carbonate–hydrogencarbonate ion buffers at an ionic strength of 2·50 mol l^{-1} (NaCl), of 28·3 ± 0·5 kcal mol^{-1} and 17 ± 2 cal K^{-1} mol^{-1}, respectively, are in good agreement with our base-independent path parameters of 28·4 ± 3·0 kcal mol^{-1} and 18 ± 3 cal K^{-1} mol^{-1} respectively (Table 2).

TABLE 1

k_a and k_b for the reaction of $[V_{10}O_{28}]^{6-}$ with excess of base. Ionic strength maintained at 1·30 mol l^{-1} with MCl

M	t/°C	$10^4 k_a$/s^{-1}	$10^4 k_b$/l mol^{-1} s^{-1}
Na	25·8	0·8 ± 0·1	7·9 ± 0·3
	29·9	1·3 ± 0·2	12·0 ± 0·4
	36·5	3·5 ± 0·3	21·0 ± 0·6
	40·0	7·0 ± 0·7	28·7 ± 1·5
Li	25·8	0·7 ± 0·2	6·1 ± 0·4
K	25·8	0·1 ± 0·3	13·9 ± 0·5
Me$_4$N	25·8	3·8 ± 0·1	0·1 ± 0·2
	31·2	8·2	*a*
	34·4	14·0	*a*
	39·0	26·2	*a*
Et$_4$N	25·8	4·6 ± 0·1	0·4 ± 0·3
	29·2	7·8	*b*
	34·8	17·7	*a*

[a] Carried out at [OH$^-$] = 0·2 mol l^{-1} only. [b] Carried out at [OH$^-$] = 0·1 mol l^{-1} only.

TABLE 2

Activation parameters for the reaction of $[V_{10}O_{28}]^{6-}$ with excess of base. Ionic strength maintained at 1·30 mol l^{-1} with MCl

	E_a/ kcal mol^{-1}	$\Delta H^\ddagger$/ kcal mol^{-1}	$\Delta S^\ddagger$/ cal K^{-1} mol^{-1}
Base-independent path			
Na	29 ± 3	28 ± 3	+18 ± 3
Me$_4$N	27·3 ± 0·6	26·7 ± 0·6	+15 ± 1
Et$_4$N	27·0 ± 0·4	26·4 ± 0·4	+15 ± 1
Base-dependent path			
Na	16·6 ± 1·0	16·0 ± 1·0	−19 ± 1

Table 1 shows that the value of the base-independent rate constant k_a increases in the order $K^+ \lll Na^+ \sim Li^+ \lll Me_4N^+ < Et_4N^+$. The base-dependent rate constant k_b shows the reverse trend, $K^+ \ggg Na^+ > Li^+ \ggg Me_4N^+ \sim Et_4N^+ \sim 0$. Schwarzenbach and Geier [4] have shown that ion association between alkali-metal cations and decavanadate to form $[MV_{10}O_{28}]^{5-}$ ion pairs and $[M_2V_{10}O_{28}]^{4-}$ ion triplets decreases in the order $K^+ \ggg Na^+ \sim Li^+$. It therefore appears that the greater the ion association, the slower is the reaction with water molecules through the base-independent path, and the faster is the reaction with the negatively charged hydroxide ion through the base-dependent path. Schwarzenbach and Geier assumed that very large cations, such as tetra-alkylammonium ions, did not ion pair with decavanadate, but the different values of k_a obtained here for tetramethylammonium ion and tetraethylammonium ion show that at least one, or more probably both, of these ions associate with decavanadate.

The four sets of mixtures, Na^+–Me_4N^+, Na^+–Et_4N^+, K^+–Me_4N^+, and K^+–Et_4N^+, all show that a small amount of alkali-metal cation has a relatively large effect on the base-independent rate constant, the curves in Figures 2 and 3 being convex downwards. This behaviour confirms the observations of Schwarzenbach and Geier that alkali-metal cations form stronger ion pairs than do tetra-alkylammonium ions. However in no case is it possible to fit these experimental points with curves generated by using the base-independent rate constants obtained from the single cation studies, and assuming the formation of only alkali metal–decavanadate ion pairs. This confirms that both tetramethylammonium and tetraethylammonium ions form ion pairs with decavanadate.

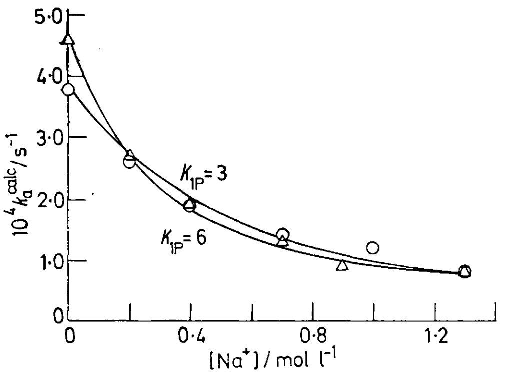

FIGURE 2 Theoretically generated curves for the dependence of k_a on $[Na^+]$ for Na^+/Me_4N^+ (○; $K_{IP} = 3$) and Na^+/Et_4N^+ (△; $K_{IP} = 6$) cation mixtures at 25·8 °C and $I = 1{\cdot}30$ mol l⁻¹ MCl (M = Na or R_4N)

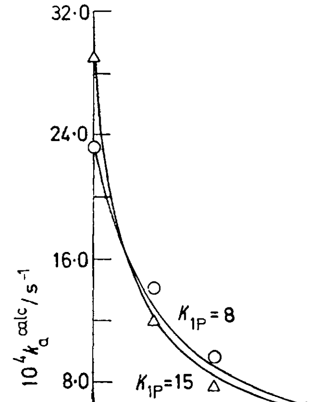

FIGURE 3 Theoretically generated curves for the dependence of k_a on $[K^+]$ for K^+/Me_4N^+ (○; $K_{IP} = 8$) and K^+/Et_4N^+ (△; $K_{IP} = 15$) cation mixtures at 38·0 °C and $I = 1{\cdot}30$ mol l⁻¹ MCl (M = K or R_4N)

The mechanism to be considered therefore is where both cations form ion pairs, which decompose at different rates:

$$[M'V_{10}O_{28}]^{5-} + M^+ \overset{K_{IP}}{\rightleftharpoons} [MV_{10}O_{28}]^{5-} + M'^+$$

$$[M'V_{10}O_{28}]^{5-} \xrightarrow{k_a^{M'}} \text{Products}$$

$$[MV_{10}O_{28}]^{5-} \xrightarrow{k_a^{M}} \text{Products}$$

The base-independent rate law is then:

$$\begin{aligned}\text{Rate} &= k_a[V_{10}O_{28}{}^{6-}]_{\text{Total}}\\ &= k_a^{M'}[M'V_{10}O_{28}{}^{5-}] + k_a^{M}[MV_{10}O_{28}{}^{5-}]\end{aligned}$$

Since $K_{IP} = ([MV_{10}O_{28}{}^{5-}][M'^+])/([M'V_{10}O_{28}{}^{5-}][M^+])$
and
$[V_{10}O_{28}{}^{6-}]_{\text{Total}} = [MV_{10}O_{28}{}^{5-}] + [M'V_{10}O_{28}{}^{5-}]$

Standard algebraic manipulation yields:

$$k_a = \frac{k_a^{M'} + k_a^{M}K_{IP}([M^+]/[M'^+])}{1 + K_{IP}([M^+]/[M'^+])}$$

Using values of k_a^M and $k_a^{M'}$ derived from the single-cation results, sets of curves may be generated with different K_{IP} and compared with experiment. The agreement between the best curves and the experimental results are shown in Figures 2 and 3, the values for the competitive ion-pair association constants being given in Table 3.

To test if these ion-pair association constants are internally consistent, it is possible to derive the competitive ion-pair association constant between $[NaV_{10}O_{28}]^{5-}$ and $[KV_{10}O_{28}]^{5-}$:

$K_{IP} = (3 \pm 1)/(8 \pm 2) = 0{\cdot}4 \pm 0{\cdot}2$ (M = Na, M′ = K)
and
$K_{IP} = (6 \pm 1)/(15 \pm 2) = 0{\cdot}4 \pm 0{\cdot}1$

which agree within experimental error. (Note that in taking these ratios it is assumed that either the competitive ion-pair constants do not vary with temperature over this temperature range, or that the Na^+–Me_4N^+ and K^+–Me_4N^+ competitive ion-pair association constants vary in a parallel manner with temperature, within the wide limits of experimental accuracy.)

The data in Table 3 quantitatively confirms that the importance of ion pairing decreases in the order $K^+ > Na^+ > Me_4N^+ > Et_4N^+$.

TABLE 3

Ion-pair association constants

M	M′	K_{IP}	t/°C
Na	Me_4N	3 ± 1	25·8
Na	Et_4N	6 ± 1	25·8
K	Me_4N	8 ± 2	38·0
K	Et_4N	15 ± 2	38·0

Similar data for the dependence of the base-dependent rate constant, k_b, on supporting electrolyte composition is shown in Figures 4—6. For the Na^+–K^+ mixtures (Figure 4), a small amount of K^+ has a relatively large effect on k_b, again confirming that K^+ forms the stronger ion pair.

The above mechanism incorporating competing ion pairs of both cations with decavanadate is insufficient to explain the results for the base-dependent path.

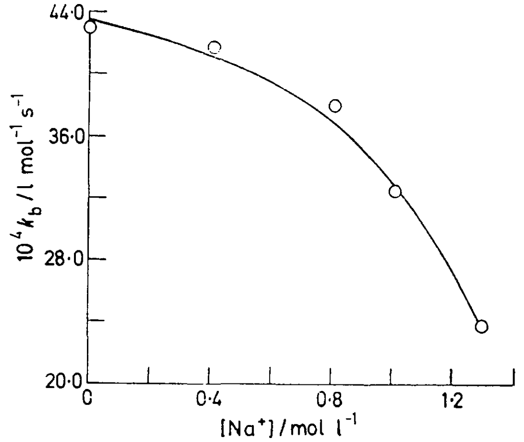

FIGURE 4 The dependence of k_b on $[Na^+]$ for Na^+/K^+ cation mixtures at 38·0 °C and I = 1·30 mol l^{-1} MCl (M = Na or K)

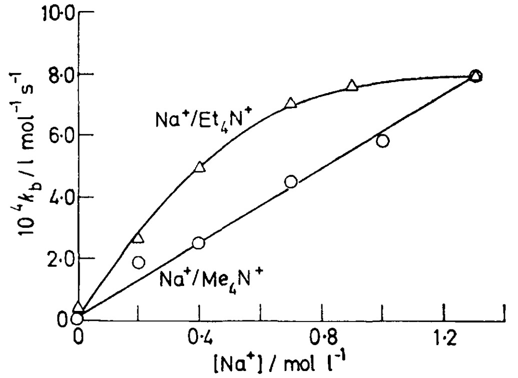

FIGURE 5 Dependence of k_b on $[Na^+]$ for the Na^+/Me_4N^+ (○) and the Na^+/Et_4N^+ (△) cation mixtures at 25·8 °C and I = 1·30 mol l^{-1} MCl (M = Na or R_4N)

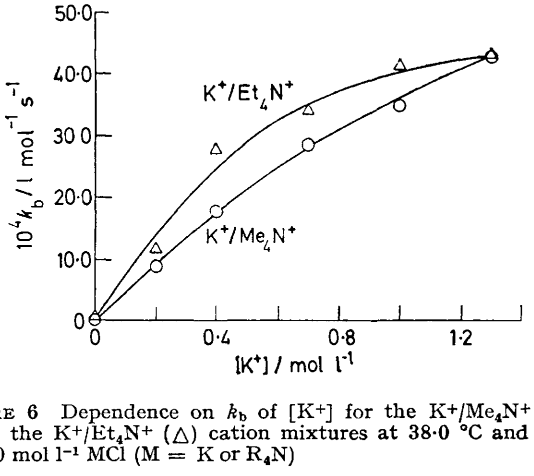

FIGURE 6 Dependence on k_b of $[K^+]$ for the K^+/Me_4N^+ (○) and the K^+/Et_4N^+ (△) cation mixtures at 38·0 °C and I = 1·30 mol l^{-1} MCl (M = K or R_4N)

Using values of K_{IP} derived from the base-independent reaction (Table 3), and values of k_b^M and $k_b^{M'}$ derived from the single-cation work (Table 1), the theoretical curves are always much more convex upwards than found experimentally (Figures 5 and 6). As pointed out by Goddard and Gonas,[5] to explain the first-order dependence of k_b on sodium-ion concentration for the Na^+–Me_4N^+ mixtures (Figure 5), it is necessary to assume that sodium ion forms a higher ionic aggregate with decavanadate, which then reacts with hydroxide ion in the rate-determining step. The model is:

$$[M'V_{10}O_{28}]^{5-} + M^+ \overset{K_{IP}}{\rightleftharpoons} [MV_{10}O_{28}]^{5-} + M'^+$$

$$[MV_{10}O_{28}]^{5-} + M^+ \overset{K'}{\rightleftharpoons} [M_2V_{10}O_{28}]^{4-}$$

$$[M_2V_{10}O_{28}]^{4-} + OH^- \xrightarrow{k_b^M} \text{Products}$$

where M^+ is the alkali-metal cation and M'^+ is the tetra-alkylammonium cation. The base-dependent rate is then:

$$\text{Rate} = k_b[OH^-][V_{10}O_{28}{}^{6-}]_{Total} = k_b^M[M_2V_{10}O_{28}{}^{4-}][OH^-]$$

Since

$$[V_{10}O_{28}{}^{6-}]_{Total} = [M'V_{10}O_{28}{}^{5-}] + [MV_{10}O_{28}{}^{5-}] + [M_2V_{10}O_{28}{}^{4-}]$$

and K_{IP} is the same as before, similar arrangement leads to:

$$k_b = \frac{k_b^M K_{IP} K'[M^+]^2}{[M'^+] + K_{IP}[M^+] + K_{IP}K'[M^+]^2}$$

For the Na^+–Me_4N^+ mixtures, since $K_{IP} = 3$ and $[M^+] + [M'^+] = 1{\cdot}3$:

$$\frac{k_b}{k_b^M K'} = \frac{3[M^+]^2}{1{\cdot}3 + 2[M^+] + 3K'[M^+]^2}$$

Similarly for the Na^+–Et_4N^+ mixtures:

$$\frac{k_b}{k_b^M K'} = \frac{6[M^+]^2}{1{\cdot}3 + 5[M^+] + 6K'[M^+]^2}$$

Since there are two unknowns in each expression (k_b^M and K'), they cannot be solved quantitatively. However since k_b^M and K' will have the same numerical values in both the Na^+–Me_4N^+ and Na^+–Et_4N^+ mixtures, the equations predict that for a given value of $[M^+]$, $k_b/(k_b^M K')$ will be less for the Na^+–Me_4N^+ mixtures than for the Na^+–Et_4N^+ mixtures. This explains, at least qualitatively, why the dependence of k_b on sodium-ion concentration is less convex upwards for the Na^+–Me_4N^+ mixtures than for the Na^+–Et_4N^+ mixtures (Figure 5).

Similar treatment shows that the curve for the K^+–Me_4N^+ mixtures should be less convex upwards than for the K^+–Et_4N^+ mixtures, in agreement with Figure 6.

In conclusion, these results may be contrasted to the decomposition of decavanadate in excess acid[3] to form $[VO_2]^+$, which is complete in a matter of seconds compared with the decomposition in excess base to form $[VO_4]^{3-}$ which takes minutes to hours. The former reaction proceeds through protonated decavanadates, and is not dependent upon the choice of alkali-metal cation. Tetra-alkylammonium ions however markedly decrease the rate, the larger onium ions giving the slower rate. In the base-independent path of the base decomposition however, tetra-alkylammonium ions form the weaker, and more reactive, ion pairs. The base-dependent rate of the base decomposition is *via* a reactive alkali-metal decavanadate species.

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