Acid Decomposition of Decavanadate: Specific Salt Effects

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The reaction of decavanadate(V), $V_{10}O_{28}^{6-}$, and also the reduced decavanadate $V^{IV}_7V^{V}_3O_{28}^{13-}$, with acid in the presence of a number of supporting electrolytes has been studied. Large cations such as tetra-alkylammonium ions and trialkylsulphonium ions markedly decrease the rate of reaction. This is shown to be due to the formation of stable ion pairs with decavanadate which do not react with acid. The effect is greater the larger the size of the onium ion. Such ion pairs do not form with the alkali-metal cations.

DURING a study of the acid-induced degradation of decavanadate, $V_{10}O_{28}^{6-}$,[1] it was observed that the use of tetramethylammonium nitrate instead of sodium nitrate as the supporting electrolyte drastically reduced the rate of the reaction. In this work this effect has been studied by use of three approaches: (*a*) A study of the hydrogen-ion dependence of the reaction in the presence of tetramethylammonium nitrate, in a similar manner to the previous study for the reaction in the presence of sodium nitrate; (*b*) a study of the rate of the reaction at constant hydrogen-ion concentration in the presence of mixtures of tetramethylammonium nitrate and sodium nitrate. These experiments were extended to cover a wide range of univalent nitrates; and (*c*) a study of the reduced decavanadate, $V^{V}_3V^{IV}_7O_{28}^{13-}$, where the increase in negative charge on the anion has a very large effect on the protonation and ion-pair association constants.

RESULTS

Decavanadate (5×10^{-4} mol dm^{-3}) was allowed to react with a large excess of nitric acid–tetramethylammonium nitrate at ionic strength 1·3 mol dm^{-3} at 25 °C as described earlier.[1] Figure 1 shows the dependence of the pseudo-first-order rate constant (k_{ex}) [1] on the hydrogen-ion concentration. The effect of the nature of the supporting electrolyte was examined by selecting a particular acid concentration (0·5 mol dm^{-3}) and a particular ionic strength (1·3 mol dm^{-3}) while varying the relative amounts of sodium nitrate and tetramethylammonium nitrate in the supporting electrolyte. The decavanadate concentration used was $0{\cdot}5 \times 10^{-3}$ mol dm^{-3} throughout. The resulting rate constants are plotted against electrolyte composition in Figure 2. Similar results were obtained with other onium cations, and other alkali-metal ions. The particular mixtures studied are shown in Table 2. In all cases the rate constants decrease with increasing onium ion concentration, or alternatively, increase with increasing alkali-metal cation concentration. Plots of k_{ex} against metal-ion concentration were always convex downwards.

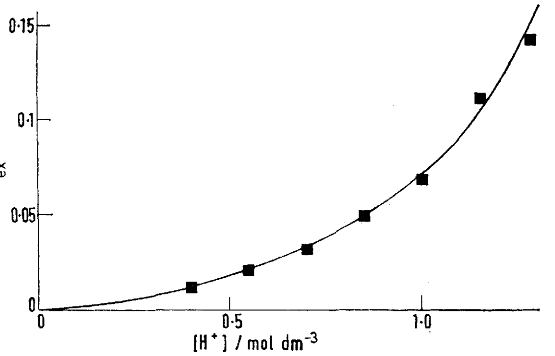

FIGURE 1 The acid concentration-dependence of the rate constant for the decomposition of decavanadate, with tetramethylammonium nitrate as supporting electrolyte. The continuous line represents a fit of the data to equation (5), with the values K_{VT} = 10·0 mol^{-1} dm^3, K^{V}_1 = 10·0 mol^{-1} dm^3, $K^{V}_2k_V$ = 0·132 sec^{-1} mol^{-1} dm^3, K^{T}_1 = 2·25 mol^{-1} dm^3, and $K^{T}_1K^{T}_2k_T$ = 0·05 sec^{-1} mol^{-2} dm^6

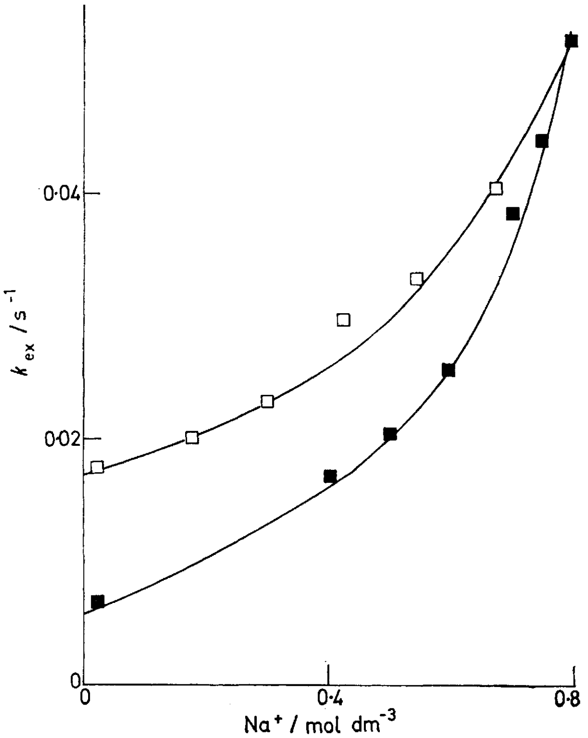

FIGURE 2 The rate constants for decomposition of decavanadate in a mixed electrolyte containing 0·5 mol dm^{-3} nitric acid, and mixtures of sodium and tetra-alkylammonium nitrates, with the ionic strength maintained at 1·3 mol dm^{-3}; □, tetramethylammonium nitrate; ■, tetraethylammonium nitrate

Acidification of the reduced decavanadate anion $V^{V}_3V^{IV}_7O_{28}^{13-}$ leads to the formation of a mixture of the unreduced decavanadate anion and the vanadyl cation, $V^{IV}O^{2+}$, in those pH regions where decavanadate is stable.

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[1] B. W. Clare, D. L. Kepert, and D. W. Watts, preceding paper.

This reaction occurs even in the absence of added acid. Measurements of the rate of decomposition of the reduced anion must therefore be made on freshly prepared solutions.

DISCUSSION

Figure 1 shows that the plot of the pseudo-first-order rate constant against hydrogen-ion concentration with tetramethylammonium nitrate as supporting electrolyte does not reach a limiting slope at high acid concentrations, but continues to curve upward, approaching a rate constant equal to that obtained with sodium nitrate as supporting electrolyte.[1] This behaviour is incompatible with the previous simple mechanism [1] involving successive equilibrium of $V_{10}O_{28}^{6-}$, and decomposition of $H_4V_{10}O_{28}^{2-}$, and suggests that it is necessary to consider the formation of the tetramethylammonium decavanadate ion pair in addition to the free decavanadate and/or the sodium–decavanadate ion pair.

Figure 2 shows that a small concentration of tetramethylammonium ion has a disproportionately large effect on the rate of reaction, showing that it must be the tetramethylammonium ion which pairs preferentially with the decavanadate. This is in contrast to Schwarzenbach and Geier [2] who state that tetra-alkylammonium cations do not form ion pairs with the decavanadate anion.

Preliminary attempts to fit the data of Figure 2 to reaction schemes involving the existence of free decavanadate and/or tetramethylammonium–decavanadate ion pair and/or sodium–decavanadate ion pair, which then decompose with acid, were unsuccessful because either (*a*) it was not possible to fit a particular set of mixed cation data with any choice of equilibrium constants and rate constants, or (*b*) values of the constants obtained from one set of data were not consistent with those obtained from other sets of data involving systems with ions in common. For example, the rate constant deduced for the decomposition of free decavanadate deduced from the mixed sodium–tetramethylammonium data, was different from that deduced from the mixed sodium–tetraethylammonium data.

When a fresh solution of the reduced compound was mixed with a large excess of acid in the stopped-flow apparatus, and the reaction observed at 500 nm, traces were obtained which yielded good first-order rate plots, the rate constant being *ca.* 100 times greater than for the reaction with the unreduced decavanadate. The dependence of the rate constant on hydrogen-ion concentration showed very different behaviour from the unreduced decavanadate. At low acid concentration, the reaction was of the first order in hydrogen ion. At higher acid concentration, the acid concentration dependence was of greater than the first order (Figure 3).

A more general mechanism is therefore postulated which for the case of a mixture of alkali-metal cation M^+ and onium cation T^+ allows the existence of free decavanadate, $H_2V_{10}O_{28}^{4-}$ or A^{n-}, as well as cation–decavanadate ion pairs with both cations. All three species can be protonated and diprotonated, and all three diprotonated species decompose at different rates. The model may be represented as in Scheme 1.

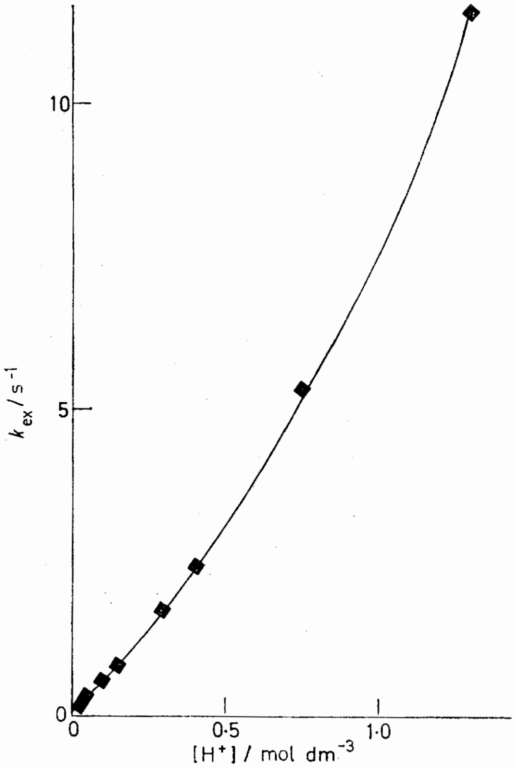

Figure 3 The acid-dependence of the pseudo-first-order rate constant for the decomposition of the salt $Na_4H_9V^V{}_3V^{IV}{}_7O_{28}$,-$15H_2O$ in a sodium nitrate–nitric acid electrolyte of ionic strength 1·3, fitted to equation (11) with *A* = 5·4, *B* = 0·0, and *C* = 0·30

$$\begin{array}{rclcl}
A^{n-} + M^+ & \xrightleftharpoons{K_{VM}} & MA^{(n-1)-} & & K_{VM} = \dfrac{[MA^{(n-1)-}]}{[M^+][A^{n-}]} \\
A^{n-} + T^+ & \xrightleftharpoons{K_{VT}} & TA^{(n-1)-} & & K_{VT} = \dfrac{[TA^{(n-1)-}]}{[T^+][A^{n-}]} \\
A^{n-} + H^+ & \xrightleftharpoons{K^V{}_1} & HA^{(n-1)-} & & K^V{}_1 = \dfrac{[HA^{(n-1)-}]}{[H^+][A^{n-}]} \\
HA^{(n-1)-} + H^+ & \xrightleftharpoons{K^V{}_2} & H_2A^{(n-2)-} & & K^V{}_2 = \dfrac{[H_2A^{(n-2)-}]}{[H^+][HA^{(n-1)-}]} \\
MA^{(n-1)-} + H^+ & \xrightleftharpoons{K^M{}_1} & MHA^{(n-2)-} & & K^M{}_1 = \dfrac{[MHA^{(n-2)-}]}{[H^+][MA^{(n-1)-}]} \\
MHA^{(n-2)-} + H^+ & \xrightleftharpoons{K^M{}_2} & MH_2A^{(n-3)-} & & K^M{}_2 = \dfrac{[MH_2A^{(n-3)-}]}{[H^+][MHA^{(n-2)-}]} \\
TA^{(n-1)-} + H^+ & \xrightleftharpoons{K^T{}_1} & THA^{(n-2)-} & & K^T{}_1 = \dfrac{[THA^{(n-2)-}]}{[H^+][TA^{(n-1)-}]} \\
THA^{(n-2)-} + H^+ & \xrightleftharpoons{K^T{}_2} & TH_2A^{(n-3)-} & & K^T{}_2 = \dfrac{[TH_2A^{(n-3)-}]}{[H^+][THA^{(n-2)-}]} \\
H_2A^{(n-2)-} & \xrightarrow{k_V} & \text{Products} & & \\
MH_2A^{(n-3)-} & \xrightarrow{k_M} & \text{Products} & & \\
TH_2A^{(n-3)-} & \xrightarrow{k_T} & \text{Products} & &
\end{array}$$

Scheme 1

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[2] G. Schwarzenbach and G. Geier, *Helv. Chim. Acta*, 1963, **46**, 906.

Ion pairing involving nitrate of the supporting electrolyte has been ignored.

Under the conditions used, $[M^+]$, $[H^+]$, and $[T^+]$ are all greatly in excess of the decavanadate concentration, and $K^V{}_2$, $K^M{}_2$, and $K^T{}_2$ are much less than $K^V{}_1$, $K^M{}_1$, and $K^T{}_1$ respectively. The experimental rate constant k_{ex} is then given by equation (1).[3]

$$k_{ex} = \frac{K^V{}_1K^V{}_2k_V[H^+]^2 + K^M{}_1K^M{}_2k_M[H^+]^2K_{VM}[M^+] + K^T{}_1K^T{}_2k_T[H^+]^2K_{VT}[T^+]}{(1 + K^V{}_1[H^+]) + (1 + K^M{}_1[H^+])K_{VM}[M^+] + (1 + K^T{}_1[H^+])K_{VT}[T^+]} \qquad (1)$$

Hydrogen-ion Dependence.—In the absence of onium ions, $[T^+] = 0$ and the remaining equation must be reducible to an equation of the form (2) to conform to

$$k_{ex} = \frac{K_1K_2k[H^+]^2}{1 + K_1[H^+]} \qquad (2)$$

the previous work.[1] This can occur in three ways.

Case 1.—K_{VM} is much greater than unity: this leads to equation (3). This would lead to the conclusion that

$$k_{ex} = \frac{K^M{}_1K^M{}_2k_M[H^+]^2}{1 + K^M{}_1[H^+]} \qquad (3)$$

the decavanadate is totally combined as pairs. This has been rejected already.

Case 2.—$K^V{}_1 = K^M{}_1$ and $K^V{}_2k_V = K^M{}_2k_M$.

This would lead to the conclusion that the presence or absence of a pairing metal ion on the decavanadate does not affect its pK_a, or the rate of decomposition of the protonated species. This seems unlikely, as the reduction of charge of the polyanion caused by the pairing alkali-metal cation would make it less easily protonated, by a purely electrostatic effect. This is confirmed later.

Case 3.—K_{VM} is zero. No appreciable ion-pair formation occurs with the alkali metals. On this assumption, equation (1) reduces to (4) which can be simplified to (5),

$$k_{ex} = \frac{K^V{}_1K^V{}_2k_V[H^+]^2 + K^T{}_1K^T{}_2k_T[H^+]^2K_{VT}[T^+]}{(1 + K^V{}_1[H^+]) + (1 + K^T{}_1[H^+])K_{VT}[T^+]} \qquad (4)$$

$$k_{ex} = \frac{D[H^+]^2 + E[H^+]^2[T^+]}{1 + A[H^+] + B[T^+] + C[H^+][T^+]} \qquad (5)$$

where $A = K^V{}_1 = 10$ from ref. 1; $B = K_{VT}$; $C = K^T{}_1K_{VT}$; $D = K^V{}_1K^V{}_2k_V = 1.32$ from ref. 1; and $E = K^T{}_1K^T{}_2k_TK_{VT}$.

When the fraction is cleared, there remains a set of linear equations in three unknowns. There are as many equations as there are points taken on the acid concentration–rate constant plot. These may be reduced to three equations by a computer-fitted least-squares technique.[3] It was found that the equations were very nearly linearly dependent, which resulted in a wide range of values of the three constants which gave almost equally good agreement with the experiment (Table 1). The single-cation studies allow no closer definition of the constants involved. A typical theoretical fit to the rate data is shown in Figure 1.

TABLE 1

Values postulated for the constants in equation (5) together with the resulting standard deviations of the experimental rate constants about the postulated curve, for the decomposition of decavanadate in a nitric acid–sodium nitrate electrolyte of ionic strength 1·3 mol dm^{-3}

K_{VT}	$K^T{}_1K^T{}_2k_TK_{VT}$	$K^T{}_1$	Std. devn.
1·0	0·0	25·06	0·0048
1·5	0·0	16·31	0·0045
2·0	0·0	11·94	0·0045
6·0	0·0	3·21	0·0042
10·0	0·0	1·48	0·0040
20·0	0·0	0·21	0·0042
1·0	0·1	26·66	0·0048
2·0	0·1	12·73	0·0048
6·0	0·1	3·47	0·0042
10·0	0·1	1·64	0·0040
20·0	0·1	0·28	0·0042
1·0	0·5	32·98	0·0055
2·0	0·5	15·88	0·0052
4·0	0·5	7·34	0·0050
6·0	0·5	4·51	0·0048
10·0	0·5	2·25	0·0045
1·0	1·0	40·78	0·0063
2·0	1·0	19·78	0·0063
4·0	1·0	9·28	0·0058
6·0	1·0	5·79	0·0055
10·0	1·0	3·01	0·0051
20·0	1·0	0·21	0·0042
40·0	1·0	0·01	0·0045
1·0	2·0	56·10	0·0080
2·0	2·0	27·42	0·0077
4·0	2·0	13·09	0·0074
6·0	2·0	8·32	0·0066
10·0	2·0	4·52	0·0052
20·0	2·0	1·69	0·0048
30·0	2·0	0·76	0·0048
1·0	5·0	100·12	0·0105
2·0	5·0	49·67	0·0103
4·0	5·0	24·21	0·0100
6·0	5·0	15·72	0·0098
10·0	5·0	8·94	0·0095
20·0	5·0	3·87	0·0085

Mixed-cation Results.—The mixed-cation results are now considered in the light of the simplified model, in which there is no M^+ ion pair. For these systems, equation (1) can be written as (6) where the values

$$k_{ex} = \frac{0.33 + K^T{}_1K^T{}_2[H^+]^2K_{VT}[T^+]}{6.0 + K_{VT}(1 + K^T{}_1[H^+])[T^+]} \qquad (6)$$

$K_{VM} = 0$; $K^V{}_1 = 10.0$ mol^{-1} dm^3, $K^V{}_2k_V = 0.132$ mol^{-1} dm^3 s^{-1}, and $[H^+] = 0.5$ mol dm^{-3} have been inserted. This is of the form (7) where A and B are positive constants.

$$k_{ex} = \frac{0.33 + A[T^+]}{6.0 + B[T^+]} \qquad (7)$$

Curves of k_{ex} against composition, of the type shown in Figure 2, can be calculated for trial values of A and B. These can be varied systematically by the computer to find a minimum standard deviation for the experimental

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[3] B. W. Clare, Ph.D. Thesis, University of Western Australia.

points from the calculated curve.[3] All the mixed-cation results were treated in this way, and it was found that, without exception, changing A from zero gave a higher standard deviation.

The alternative assumption (Case 2) leads to the equation (8) where $A = 0{\cdot}25K^{T}_{1}K^{T}_{2}k_{T}K_{VT}$; $B = K_{VT}(1 + 0{\cdot}5K^{T}_{1})$; and $C = K_{VM}$.

$$k_{ex} = \frac{0{\cdot}33 + A[T^{+}]\left(\dfrac{1}{1 + C(0{\cdot}8 - [T^{+}])}\right)}{6{\cdot}0 + B[T^{+}]\left(\dfrac{1}{1 + C(0{\cdot}8 - [T^{+}])}\right)} \quad (8)$$

Curves of k_{ex} against composition can again be calculated as before for trial values of the constants A, B, and C, and the standard deviation of the experimental k_{ex} from the curves described by the three constants calculated. The constants are varied systematically by the computer as before, to give a minimum standard deviation. Values of K_{VM} greater than 0·02 did not significantly improve the standard deviation. This negligible value confirms that no significant ion pairing occurs with the sodium ion.

The fact that the constant A is always zero gives the result that $K^{T}_{1}K^{T}_{2}k_{T}[H^{+}]^{2}K_{VT} = 0$. Since the constant B is non-zero, K_{VT} is also non-zero. The acid concentration is positive, so $K^{T}_{1}K^{T}_{2}k_{T}$ must be zero. This means that either the onium ion pair is not protonated, or that the protonated species does not decompose. The only effect of the onium ion seems to be to remove some of the reactive free decavanadate from solution, and so reduce the overall rate of the reaction.

The rate of the reaction is given by an expression containing a single disposable constant, $B = K_{VT}(1 + K^{T}_{1}[H^{+}])$. Values for B are obtained by adjusting B to give a minimum standard deviation in the rate constant. The values so obtained are in Table 2.

TABLE 2

Mixed cation rate data for the equation $k_{ex} = \dfrac{0{\cdot}33}{6{\cdot}0 + B[T^{+}]}$

System	$B = K_{VT}(1 + 0{\cdot}5K^{T}_{1})$	Std. devn.
Na^{+}, Me_3S^{+}	19·0	0·0013
Na^{+}, Et_3S^{+}	35·4	0·00093
Na^{+}, Me_3Se^{+}	22·4	0·00094
Na^{+}, Et_3NH^{+}	19·1	0·0014
Na^{+}, $PyMe^{+}$	19·4	0·0034
Na^{+}, Me_4N^{+}	15·8	0·0013
Na^{+}, Et_4N^{+}	32·4	0·0024
K^{+}, Et_4N^{+}	40·0	0·0019
Rb^{+}, Et_4N^{+}	32·5	0·0028
NH_4^{+}, Et_4N^{+}	40·0	0·0035
Na^{+}, $Bu^{n}Me_3N^{+}$	30·0	0·0004
Na^{+}, $PhMe_3N^{+}$	32·3	0·0028

$PyMe^{+}$ is N-methylpyridinium.

Figure 4 shows the accuracy of the fit obtained in three cases. The final mechanism is then as shown in Scheme 2.

As a test for consistency, it can be seen that the value of $K_{VT}(1 + 0{\cdot}5K^{T}_{1})$ for the sodium–tetramethylammonium system is 15·8. This may be compared with one of the sets of constants for the tetramethylammonium–acid system, 15·7 for $K_{VT} = 6{\cdot}0$, $K^{T}_{1} = 3{\cdot}21$, and $E = 0$ from Table 1.

Table 2 shows that the final model is in excellent agreement with experiment (standard deviation in $k_{ex} \leqslant 0{\cdot}001$) for sodium with trimethylsulphonium, trimethylselenonium, triethylsulphonium, triethylammonium, butyltrimethylammonium, and tetramethylammonium. There seems to be a discrepancy (standard deviations 0·002—0·004) with three onium cations, namely tetraethylammonium, N-methylpyridinium, and phenyltrimethylammonium.

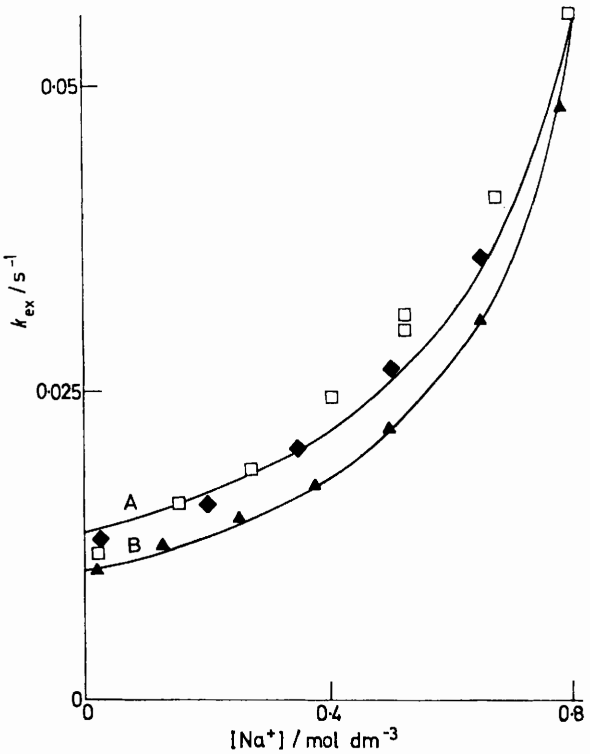
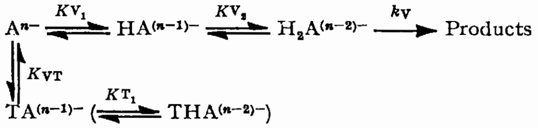


FIGURE 4 Three sets of mixed cation rate data fitted to the equation given in Table 2 where $[T^{+}]$ is the concentration of: ▲, $BuMe_3N^{+}$; ◆, Me_3Se^{+}; and ☐, $PyMe^{+}$. The acid concentration is 0·5 mol dm^{-3} and the ionic strength 1·3 mol dm^{3}



SCHEME 2

These discrepancies, if they are not experimental error, cannot be explained without varying the model. One way in which the model can be slightly modified to improve this agreement is to assume that the decavanadate–onium ion pair can accommodate another onium ion, to form an ionic triplet with stability constant K_{VTT}. The modified model thus includes Scheme 3.

Under the conditions of excess of T^+, excess of H^+, small $K^V{}_2$ and $K^T{}_2$, and with $[H^+] = 0{\cdot}5$ mol dm^{-3},

$$TA^{(n-1)-} + T^+ \xrightleftharpoons{K_{VTT}} T_2A^{(n-2)-} \quad K_{VTT} = \frac{[T_2A^{(n-2)-}]}{[TA^{(n-1)-}]\,[T^+]}$$

SCHEME 3

$K^V = 10{\cdot}0$ mol^{-1} dm^3, and $K^V{}_2k_V = 0{\cdot}132$ mol^{-1} dm^3 s^{-1}, the experimental rate constant is given by [3] equation (9)

$$k_{ex} = \frac{0{\cdot}33}{6{\cdot}0 + B[T^+](1 + A[T^+])} \qquad (9)$$

where $B = K_{VT}(1 + 0{\cdot}5K^T{}_1)$ and $A = K_{VTT}/(1 + 0{\cdot}5K^T{}_1)$. Equation (9), computer-fitted to the data, results in a much improved agreement with experiment (Table 3). Figure 5 shows a typical result, and can be compared with Figure 4.

TABLE 3

Mixed-cation rate data for sodium with phenyltrimethylammonium, N-methylpyridinium, and tetraethylammonium, fitted to equation (9), which allows for ion triplet formation. The acid concentration is 0·5 mol dm^{-3}, the ionic strength is 1·3 mol dm^{-3}

$$A = \frac{K_{VTT}}{1 + 0{\cdot}5K^T{}_1}$$

$$B = K_{VT}(1 + 0{\cdot}5K^T{}_1)$$

$[M^+]$	$[T^+]$	A	B	Std. devn.
Na^+	$PhMe_3N^+$	2·0	17·0	0·00087
Na^+	$PyMe^+$	0·9	14·0	0·00063
Na^+	Et_4N^+	1·4	24·0	0·00105

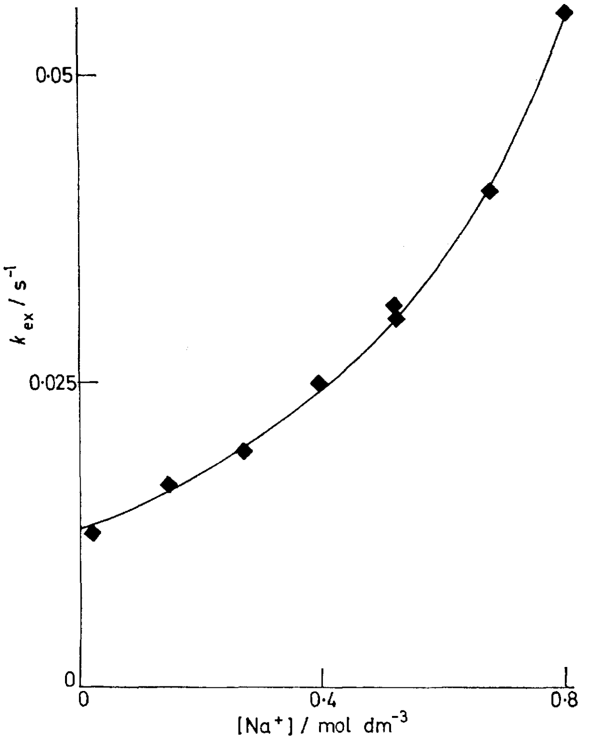


FIGURE 5 Mixed-cation rate data for sodium N-methylpyridinium nitrates, fitted to equation (9), which allows for ion-triplet formation. See Table 2

It may be thought that the constants A and B may be separated into K_{VT}, $K^T{}_1$, and K_{VTT} by repetition of the experiments at another value of the acid concentration. However, the available range of acid concentration is limited on the one hand by the necessity to use fairly large values of the onium salt concentration while maintaining an ionic strength of 1·3, and on the other by the necessity to retain a reasonably fast reaction rate. The constant B is not sufficiently dependent on $K^T{}_1$, and not available with sufficient accuracy, to make this work feasible.

The Reduced Decavanadates.—The general equation [1] for the rate of the reaction of unreduced decavanadate with acid, in the absence of onium ions, can be reduced to (10) which can show first-order dependence on

$$k_{ex} = \frac{K^V{}_1K^V{}_2k_V[H^+]^2 + K^M{}_1K^M{}_2k_M[H^+]^2K_{VM}[M^+]}{(1 + K^V{}_1[H^+]) + (1 + K^M{}_1[H^+])K_{VM}[M^+]} \quad (10)$$

hydrogen-ion concentration at low acid concentration only if $K^V{}_1$ and $K^V{}_2$ are both large, so that the two terms in the denominator become $K^V{}_1[H^+]$ and $K^M{}_1[H^+]K_{VM}[M^+]$ respectively. The equation then becomes (11), with (12)—(14). I is the sum of the sodium nitrate and nitric acid concentration, which is kept constant.

$$k_{ex} = A[H^+]\,\frac{1 - B[H^+]}{1 - C[H^+]} \qquad (11)$$

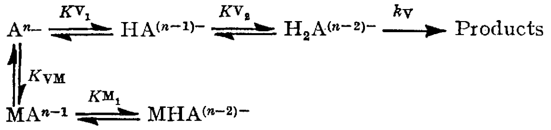
$$A = \frac{K^V{}_1K^V{}_2k_V + K^M{}_1K^M{}_2k_MK_{VM}I}{K^V{}_1 + K^M{}_1K_{VM}I} \qquad (12)$$

$$B = \frac{K^M{}_1K^M{}_2k_MK_{VM}}{K^V{}_1K^V{}_2k_V + K^M{}_1K^M{}_2k_MK_{VM}I} \qquad (13)$$

$$C = \frac{K^M{}_1K_{VM}}{K^V{}_1 + K^M{}_1K_{VM}I} \qquad (14)$$

Using the above equations and the experimental rate constants obtained for the reduced decavandate as a function of acid concentration, we obtained a set of simultaneous linear equations in A, B, and C, one equation for each observed rate constant. These were reduced to three equations as before. Figure 3 shows the resulting fit of the data to the equation. The values of the constants were found to be $A = 5{\cdot}4$, $B = 0{\cdot}0$, $C = 0{\cdot}30$. The fact that B is zero and C is positive suggests that $K^M{}_2k_M$ is very small; that is, the ion pair with sodium decomposes much less readily than the free anion.

The solid 3 : 7 compound has the formula $Na_4H_9V^V{}_3V^{IV}{}_7O_{28},15H_2O$. There is no clear evidence, however, that the ion has charge −4 in solution. The reaction scheme considered is thus Scheme 4. There is no



$$\begin{tikzcd}
A^{n-} \arrow[r, shift left, "K^V{}_1"] \arrow[d, shift left, "K_{VM}"] & HA^{(n-1)-} \arrow[l, shift left] \arrow[r, shift left, "K^V{}_2"] & H_2A^{(n-2)-} \arrow[l, shift left] \arrow[r, "k_V"] & \text{Products} \\
MA^{n-1} \arrow[u, shift left] \arrow[r, shift left, "K^M{}_1"] & MHA^{(n-2)-} \arrow[l, shift left] & &
\end{tikzcd}$$

SCHEME 4

definite evidence on the degree of protonation of A^{n-} except that it probably has a higher negative charge than 4, the charge of the unreduced decavanadate. This higher charge is consistent with its forming a more stable ion pair with the sodium ion.

The experiments described above for sodium nitrate were repeated with tetramethylammonium nitrate, butyltrimethylammonium nitrate, and trimethylsulphonium nitrate.

For tetramethylammonium nitrate, the data can be fitted to the equation used for sodium nitrate (Figure 6) with $A = 1{\cdot}7$, $B = 0{\cdot}6$, and $C = 0{\cdot}61$. The butyltrimethylammonium results gave a poorer fit to the equation, with $A = 1{\cdot}47$, $B = 0{\cdot}0$, and $C = 0{\cdot}068$, and also, gave poor first-order rate plots in the low acid region. The trimethylsulphonium results gave poor rate plots over the almost entire acid concentration range. The standard deviations of the rate plot was as much as 70×10^{-3}.

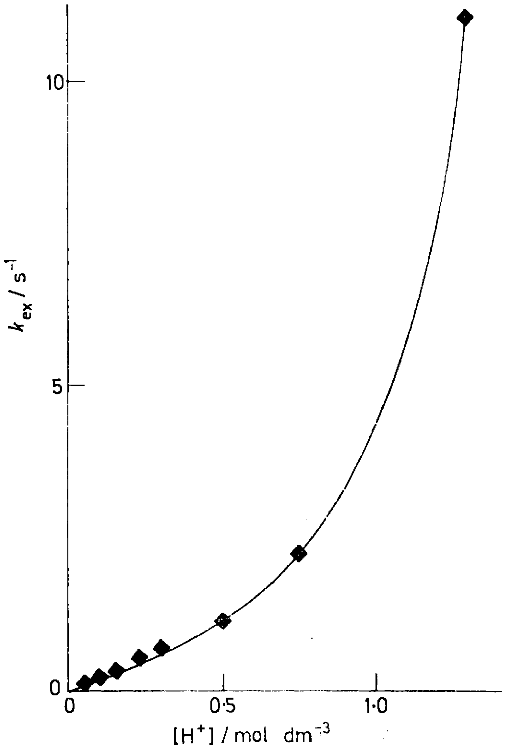


FIGURE 6 The dependence of the rate constant for the decomposition of the 3 : 7 reduced decavanadate on acid concentration in the presence of tetramethylammonium nitrate, maintaining the ionic strength at 1·3 mol dm^{-3}

When the data yielding poor rate plots was converted to plots of absorbance against time, they gave the appearance of involving two consecutive first-order reactions. It seems likely that in these cases the reaction involves disproportionation to less reduced and more reduced decavanadates, followed by first-order decomposition of the products.[3]

Large onium ions in general have sparingly soluble decavanadates. Apart from the well defined compounds in Table 5 (Experimental section), precipitates were obtained with tetraphenylarsonium, triphenylmethylarsonium, tetrabutylphosphonium, triphenylmethylphosphonium, and triphenylsulphonium. Two classes of precipitate were obtained, those corresponding to the formula $T_4H_2V_{10}O_{28}$, and those of formula $T_2H_4V_{10}O_{28}$. The former precipitated on mixture of the onium salt with the decavanadate solution; compounds of the latter formula required the addition of acid to induce rapid precipitation.

Conclusion.—The finding of greater ion pairing of decavanadate with the tetra-alkylammonium ions than the smaller alkali-metal cations indicates that the ion association is not of the simple electrostatic Bjerrum type. The anomalously high ion-pair association constants of tetra-alkylammonium ions with *large* anions has been studied by others,[4] and has been related to the low entropy of large hydrophobic ions, resulting in a 'solvent structure enforced ion pairing.'[5]

Thus the data in Table 2 show that the effect of ion pairing becomes more pronounced the *larger* the cation.

EXPERIMENTAL

The Durrum–Gibson stopped-flow apparatus was modified as described earlier.[1,3] The solutions were prepared as before.[1] Successive kinetic runs gave superimposable traces on the oscilloscope (±1%).

Sodium nitrate, potassium nitrate, rubidium nitrate, and ammonium nitrate were AnalaR samples. Caesium nitrate, lithium nitrate, tetramethylammonium nitrate, tetraethylammonium nitrate, phenyltrimethylammonium nitrate, trimethylsulphonium nitrate, trimethylselenonium nitrate, triethylsulphonium nitrate, and butyltrimethylammonium nitrate were prepared by standard methods.[3] *N*-Methylpyridinium nitrate could not be obtained solid, and the solution was prepared from the iodide and the stoicheiometric amount of silver nitrate. Analyses are in Table 4.

TABLE 4

Analysis of onium salts

Compound		C (%)	H (%)	N (%)	
Tetramethylammonium nitrate	Found	35·4	8·9	20·7	
	Calc.	35·3	8·9	20·6	
Tetraethylammonium nitrate	Found	49·8	10·4	14·4	
	Calc.	50·0	10·5	14·6	
N-Methylpyridinium iodide	Found	32·6	3·6	6·0	I = 56·8
	Calc.	32·6	3·6	6·3	57·4
Trimethylselenonium nitrate	Found	19·5	5·0	7·4	Se = 42·3
	Calc.	19·4	4·9	7·5	42·4
Trimethylsulphonium nitrate	Found	26·0	6·5	10·0	S = 23·2
	Calc.	25·9	6·5	10·0	23·0
Triethylsulphonium nitrate	Found	39·6	8·2	7·6	S = 17·9
	Calc.	39·8	8·3	7·7	17·7
Phenyltrimethylammonium nitrate	Found	54·0	7·1	14·2	
	Calc.	54·5	7·1	14·1	

Decavanadates of Onium Cations.—Sodium decavanadate (stock solution) was mixed with an excess of a solution of the onium chloride or nitrate. The mixture

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

[5] R. M. Diamond, *J. Phys. Chem.*, 1963, **67**, 2513.

was then immediately acidified with nitric acid. Diphenyliodonium nitrate, hexamethylenetetramine methonitrate, and commercial dimethyldibenzylammonium chloride precipitated the corresponding decavanadates immediately. Tetrabutylammonium nitrate and tetrapropylammonium nitrate precipitated the corresponding decavanadates only on addition of nitric acid. The precipitates were washed with water, collected by filtration or centrifugation, and dried (P_2O_5) at 100 °C *in vacuo*. Analyses are in Table 5.

TABLE 5

Analysis of the onium decavanadates

	C	H	N	V
Tetrabutylammonium	27·7	5·6	2·3	35·9
Calc. for $\{(C_4H_9)N\}_4H_4V_{10}O_{28}$	26·7	5·0	1·9	35·3
Tetrapropylammonium	22·4	4·2	2·14	39·0
Calc. for $\{(C_3H_7)_4N\}_2H_4V_{10}O_{28}$	21·6	4·53	2·10	38·2
Diphenyliodonium	27·1	2·38		24·2
Calc. for $\{(C_6H_5)_2I\}_4H_2V_{10}O_{28}$	27·7	2·03		24·4
Hexamethylenetetramine Me$^+$	13·4	3·2	9·1	37·5
Calc. for $(CH_3\cdot C_6H_{12}N_4)_2H_4V_{10}O_{28}$	13·2	2·7	8·8	40·0
Dibenzyldimethylammonium	38·9	4·5	3·2	26·1
Calc. for $\{(C_6H_5CH_2)_2Me_2N\}_1H_2V_{10}O_{28}$	41·2	4·4	3·0	27·3

Reduced Decavanadates.—Attempts were made to repeat the preparations given by Ostrowetsky.[6] Satisfactory results were obtained only in the case of the compound $Na_4H_9V^{V}_3V^{IV}_7O_{28},15H_2O$ (Found: V^{IV}/V^{V}, 0·67. Calc., 0·70). Other compounds were obtained only as ill-defined products containing much crystalline sodium sulphate.

Carbon, hydrogen, and nitrogen analyses were by the Australian Microanalytical Service. Vanadium(IV) in the reduced decavanadates was determined by titration with standard permanganate after dissolving the compound in dilute sulphuric acid. Total vanadium was determined similarly, after reduction of the vanadium(V) to vanadium(IV) with sulphur dioxide.[7]

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[6] S. Ostrowetsky, *Bull. Soc. chim. France*, 1964, 1018.

[7] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' 2nd edn., Longmans, London, p. 319.