ceed through kinetic paths with inverse hydrogen ion dependencies. White and Newton[26] have tabulated the available information on hydrogen ion independent oxidations of f-electron reductants. They note that the activation entropies of these reactions are surprisingly similar (*ca.* −30 to −35 eu) despite differences in charge type and in the nature of the oxidant. The much more negative activation entropy (*ca.* −47 eu) observed herein for the oxidation of Np(III) by $(NH_3)_6Ru^{3+}$ and $(NH_3)_5RuOH_2^{3+}$ is consistent with an unorthodox transition state[24] being involved in these reactions. It is interesting to note that it is the more favorable entropy term which provides almost the entire difference in rate between the U(III)-$Co(NH_3)_4(H_2O)_2^{3+}$ reaction ($k = 1.64 \times 10^3$ F^{-1} sec^{-1} at 25°, $\Delta H^* = 3.67 \pm 0.04$ kcal/mol, $\Delta S^* = -31.5 \pm 0.3$ eu)[26] and the Np(III)-Ru(III) reactions. While the greater rate of the U(III)-Co(III) reaction is not unexpected in light of the fact that U(III) is a better reductant than Np(III) by 0.79 V and Co(III) is a better oxidant than Ru(III),[4b] it is not clear from *a priori* considerations that the predominant factor should be the difference in entropies of activation.

It has been observed that rate ratios of closely related reactions can often be correlated using the Marcus cross relation,[27] even though the mechanisms involved may not be outer sphere.[26,28] Thus, assuming that the Marcus relation holds in the Np(III)-Ru(III) reactions, the data in Table II may be used to calculate that the $(NH_3)_6Ru^{2+,3+}$ exchange rate is 2.5 times as fast as the $(NH_3)_5RuOH_2^{2+,3+}$ exchange rate at both 25 and 15°. From Meyer and Taube's[4a] hexaammine exchange rate of 8.2×10^2 F^{-1} sec^{-1} (25°, $I = 0.013$), the aquopentaammine exchange rate can be estimated as 3.3×10^2 F^{-1} sec^{-1}.

For the reverse reactions of eq 7 and 8, values calculated for k_r (F^{-1} sec^{-1}) at 25°, ΔH^* (kcal/mol), and ΔS^* (eu) are 4.37 ± 0.21, 12.9 ± 0.4, −12.1 ± 1.2 and 9.8 ± 0.5, 15.4 ± 1.2, 3 ± 4, respectively. The very small activation entropy associated with the $Np^{4+} + (NH_3)_6Ru^{2+}$ reaction is noteworthy. These results may be compared with the kinetic parameters obtained for the hydrogen ion independent path in the reaction between V(II) and Np(IV):[29] $k = 2.53$ F^{-1} sec^{-1}, $\Delta H^* = 9.72 \pm 0.05$ kcal/mol, $\Delta S^* = -24.0 \pm 0.2$ eu. The authors noted that for this reaction the hydrogen ion, chloride ion, and temperature-dependence data are inconsistent with an inner-sphere mechanism. Thus, the specific rate constants for the reductions of Np(IV) by the t_{2g}-electron donors V(II), $(NH_3)_6Ru^{2+}$ and $(NH_3)_5RuOH_2^{2+}$ are remarkably similar despite the fact that ΔS^* and ΔH^* vary markedly from system to system. A similar phenomenon has been reported by Price and Taube[4b] for the reduction of a series of carboxylatopentaamminecobalt(III) complexes by hexaammineruthenium(II) in perchlorate media. This lack of any readily discernible correlation precludes further discussion of the results.

The salient point to be emphasized, however, is the importance of the ΔS^* term in determining the rate of reactions between highly charged ionic species of the type considered in this work. Further developments necessary to aid in the understanding of such observations have been pointed out by Linck.[30]

Registry No. $Ru(NH_3)_6^{2+}$, 19052-44-9; $Ru(NH_3)_6^{3+}$, 18943-33-4; $Ru(NH_3)_5H_2O^{2+}$, 21393-88-4; $Ru(NH_3)_5H_2O^{3+}$, 25590-52-7; Np, 7439-99-8.

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Kinetics of the Dissociation of Decavanadate Ion in Basic Solutions

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The kinetics of dissociation of decavanadate ion, $V_{10}O_{28}^{6-}$, in basic solution was studied spectrophotometrically from 15 to 50°. At pH 8–10, the rate is independent of pH. In hydroxide ion solution of constant $[M^+]$ (M = Li, Na, or K), a $[OH^-]$-dependent dissociation path exists as well. The rate of dissociation equals $\{k_1' + k_2[OH^-]\}[V_{10}O_{28}^{6-}]_{tot}$, where $[V_{10}O_{28}^{6-}]_{tot}$ is the total (free and ion-paired) decavanadate ion concentration. k_2 depends on the alkali metal, increasing in the order Li < Na < K; $k_2 = 0$ for $(CH_3)_4N^+$. The linear dependence of k_2 on $[Na^+]$ at $\mu = 2.5$ is explained by the presence of a reactive ion pair.

Introduction

Although serious studies on the aqueous solution chemistry of alkali metal vanadates(V) commenced with Dullberg[1] in 1903, it has only been within the last 10 or 15 years that the degree of aggregation of the aqueous vanadates has been reasonably well understood and agreed upon. In particular, the degree of condensation of the decavanadate ion, $V_{10}O_{28}^{6-}$, was difficult to ascertain, partly because of the presence of the weak acids $HV_{10}O_{28}^{5-}$ and $H_2V_{10}O_{28}^{4-}$ and because of the slow attainment of equilibrium of the decavanadate ion with the more basic vanadates. Very carefully performed potentiometric studies[2] and X-ray diffraction analyses of

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Table I. Observed First-Order Rate Constants for Decomposition of Decavanadate Ion (2.20×10^{-4} *M* V) in Buffered Solutions, $\mu = 2.5$ (NaCl)

Temp, °C	Buffer, molarity of Na_2CO_3–molarity of $NaHCO_3$	pH	$10^5 k_{obsd}$, sec^{-1}
15.0	0.01–0.04	9.3	0.83
15.0	0.04–0.01	10.0	0.80
25.0	0.02–0.08	8.6–8.8	4.8, 5.7,[a] 5.3,[b] 4.5,[c] 6.7,[d] 7.9[e]
25.0	0.08–0.02	9.8–9.9	5.3, 5.9,[a] 5.8,[b] 5.1,[c] 6.6,[d] 8.1[e]
25.0	0.16–0.04[f]	7.8–8.4	4.9, 4.7[g]
25.0	0.04–0.16[f]	9.0–9.4	5.4, 5.9[g]
30.0	0.08–0.02	9.8	10.3
35.0	0.06–0.04	9.6	23.6
35.0	0.01–0.04[f]	9.5	22.9[g]
40.0	0.04–0.06	9.2	52
45.0	0.06–0.04	9.7	112
50.0	0.04–0.06	9.6	182
50.0	0.08–0.02	10.1	192
50.0	0.03–0.02[f]	8.8	190[g]

[a] 8.80×10^{-3} *M* V. [b] $\mu = 2.5$ ($NaClO_4$). [c] $\mu = 2.5$ (KCl). [d] $\mu = 1.0$ (NaCl). [e] $\mu = 0.50$ (NaCl). [f] Molarity of NH_4Cl–molarity of NH_4OH. [g] $\mu = 2.5$ (LiCl).

crystalline compounds[3,4] have confirmed the tenfold degree of aggregation for the decavanadate anion.

The slow decomposition of the decavanadate ion in basic solutions is interesting kinetically and a study of this reaction finds practical application in vanadium process metallurgy. Only very crude kinetic data have appeared in the literature regarding this reaction,[1,5] which prompted us to study it more thoroughly.

Experimental Section

Alkali metal chlorides were reagent grade, the LiCl being very low in other alkali metals. Tetramethylammonium chloride and aqueous 10% tetramethylammonium hydroxide were from Eastman Kodak Co. Solutions of the chloride were filtered before use. A vanadium stock solution was prepared by dissolving V_2O_5 (99.7%) in the stoichiometric amount of aqueous NaOH to give Na_3VO_4. To an aliquot of this solution was added a 5 *M* solution of a chloride salt for ionic strength control and concentrated HCl to give a pH of ~3.5 (pH 4.0-5.0 for [V] $\geqslant 8.8 \times 10^{-3}$ *M*). Conversion to the decavanadate anions $H_2V_{10}O_{28}^{4-}$ and $HV_{10}O_{28}^{5-}$ occurs rapidly.[6-8] To initiate the dissociation reaction, base was added, and the solution was diluted to volume and immersed in a constant-temperature bath (±0.1°). Reactions were followed by observing spectral changes (Figure 1) at 270 or 360 nm on a Cary 14 spectrophotometer with thermostated cell holders (±0.1°). Longer wavelengths were used for the few runs with [V] $> 2.2 \times 10^{-4}$ *M*. Plots of ln $|A_t - A_\infty|$ *vs.* time, where A_t and A_∞ are absorbances at time *t* and at completion of reaction, yielded straight lines of slope k_{obsd}. Activation parameters were calculated by a GE-400 computer from the least-squares Arrhenius plot.

Results

Tables I and II present the kinetic results of the decomposition of decavanadate ion in carbonate-bicarbonate and ammonia-ammonium ion buffers. The reactions are all cleanly first order. The observed rate constants do not change significantly on substitution of $NaClO_4$, KCl, or LiCl for the NaCl used to maintain ionic strength (μ) 2.5. The rate constants are independent of the type of buffer used and are virtually independent of pH over the pH range ~8-10 (although rate increases of ~10-25% apparently do occur with this 100-fold hydroxide ion increase). Increasing the vanadium concentration by a factor of 40 increases the rate only slightly. Decreasing the ionic strength apparently increases the rate (Table I), but decreasing [Na^+] while maintaining μ at 2.5 with tetramethylammonium chloride increases the rate even more (Table II). This suggests that the actual effect of a decrease in μ is a *decrease* in rate.

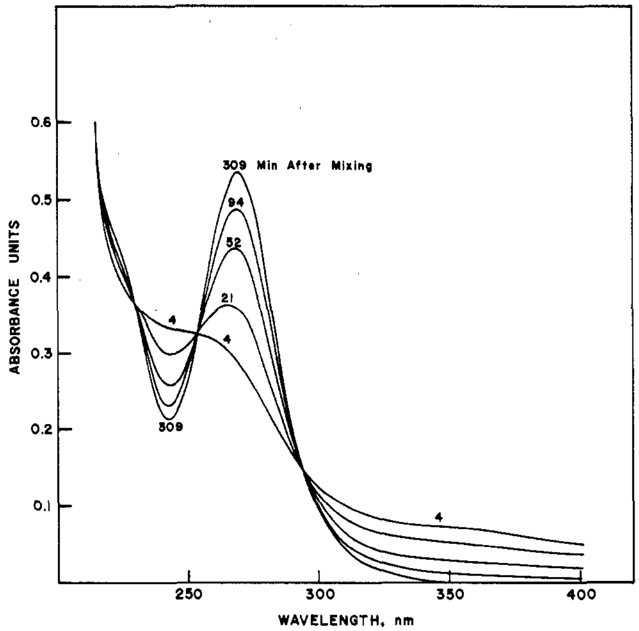

Figure 1. Uv spectra for decomposition of decavanadate ion (8.8×10^{-4} *M* V) in 0.20 *M* NaOH, μ 2.5 (NaCl), 25.0°, 0.100-cm cell.

A computer-calculated least-squares Arrhenius plot for decomposition of decavanadate ion in carbonate-bicarbonate ion buffers at $\mu = 2.5$ (NaCl) yielded $\Delta H^{\ddagger} = 28.3 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = +17 \pm 2$ eu (limits of error are standard deviations). Table III gives the least-squares values of the first-order rate constants k_1.

Selected data for decomposition of decavanadate ion in hydroxide ion solutions are given in Table IV. The observed rate constants are all first-order. Again, as for the buffered systems, the rate constants are virtually independent of initial vanadium concentration and of substitution of $NaClO_4$ for NaCl. However, the rates are also first-order in hydroxide ion concentration; plots of k_{obsd} *vs.* [OH^-] are linear with positive slopes (k_2) and positive ordinate intercepts (k_1'). Table III compares the values of k_1' with those of k_1. The rates are also dependent on the alkali metal cation, increasing in the order Li < Na < K (Figure 2).

Arrhenius plots of the second-order rate constants k_2 (the

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(3) H. T. Evans, Jr., A. G. Swallow, and W. H. Barnes, *J. Amer. Chem. Soc.*, 86, 4209 (1964).

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Table II. Observed First-Order Rate Constants for Decomposition of Decavanadate Ion (2.20×10^{-4} *M* V) in Carbonate Buffers, 25.0°, $\mu = 2.5$ (NaCl-$(CH_3)_4NCl$)

0.020 *M* Na_2CO_3-0.080 *M* $NaHCO_3$ buffer			0.080 *M* Na_2CO_3-0.020 *M* $NaHCO_3$ buffer		
$[Na^+]$, *M*	pH	$10^5 k_{obsd}$, sec^{-1}	$[Na^+]$, *M*	pH	$10^5 k_{obsd}$, sec^{-1}
2.00	8.7	7.3	2.00	9.0	8.1
1.50	8.7	10.5	1.50	9.8	10.3
1.00	10.0	14.2	1.00	10.7	14.2
0.50	10.4	23.6	0.50	11.1	24.1
0.12	10.3	22.1	0.18	11.1	25.7

Table III. Comparison of Rate Constants for the First-Order (pH-Independent) Path of Decomposition of Decavanadate Ion, $\mu = 2.5$ (NaCl)

Temp, °C	$10^5 k_1$,[a] sec^{-1}	$10^5 k_1'$,[b] sec^{-1}	Temp, °C	$10^5 k_1$,[a] sec^{-1}	$10^5 k_1'$,[b] sec^{-1}
15.0	0.87	4	40.0	49	80
25.0	4.7	7	45.0	103	110
30.0	10.6	20	50.0	209	200
35.0	23.2	40			

[a] Values from least-squares Arrhenius plot for reaction in carbonate-bicarbonate ion buffers. [b] Ordinate intercepts of plots of k_{obsd} *vs.* $[OH^-]$ for reaction in hydroxide ion solutions.

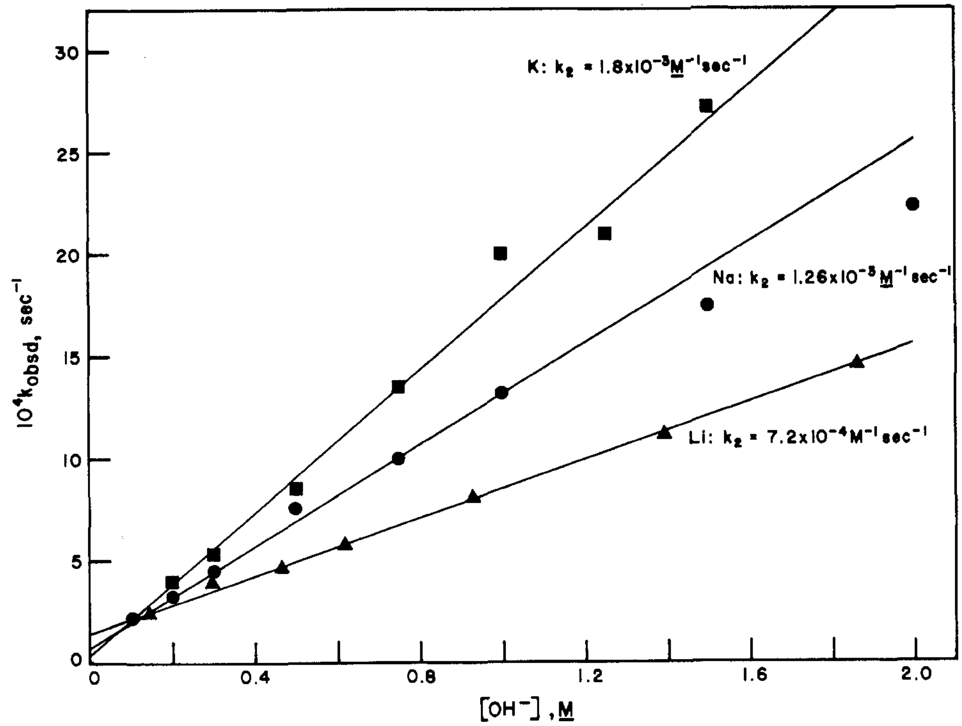

Figure 2. Plot of k_{obsd} *vs.* $[OH^-]$ for decomposition of decavanadate ion (2.20×10^{-4} *M* V) in MOH solutions (M = Li, Na, or K), μ 2.5 (MCl), 25.0°.

slopes of plots of k_{obsd} *vs.* $[OH^-]$) for the alkali metal systems at 2.5 *M* M^+ led to the activation parameters of Table V. The computer-calculated least-squares k_2 values are given in Table VI.

Observed first-order rate constants for decavanadate ion dissociation in mixed sodium hydroxide-tetramethylammonium hydroxide systems are given in Table VII. In the absence of sodium ion, the rate of reaction is independent of $[OH^-]$. Plots of k_{obsd} *vs.* $[OH^-]$ at constant $[Na^+]$ for these mixed systems are given in Figure 3. The second-order rate constants obtained from these plots (or from Table VI for 2.5 *M* Na^+) are plotted against $[Na^+]$ in Figure 4. The reasonably linear plot indicates a first-order rate dependence also on sodium ion, with the overall third-order rate constant $k_3 = 4.3 \times 10^{-4}$ M^{-2} sec^{-1} at 25°, $\mu = 2.5$.

Discussion

Conversion of the protonated decavanadate species $HV_{10}O_{28}^{5-}$ and $H_2V_{10}O_{28}^{4-}$ to $V_{10}O_{28}^{6-}$ on raising the pH above ~7.5 can be considered complete[7] and instantaneous.[5,9] At the low concentrations used in this study (2.20×10^{-4} *M* V), in the buffered solutions (pH ~8-10) the products of the slow decomposition of $V_{10}O_{28}^{6-}$ are mixtures of metavanadate ions $(VO_3^-)_x$ ($x = 1, 3$, or 4)[7,10] and monohydrogen orthovanadate ions HVO_4^{2-}.[7] Reaction rates were taken from absorbances at 360 nm where the products are transparent, but isosbestic points in the spectral traces showed the ratio of metavanadate to monohydrogen orthovanadate to be invariant throughout the reaction. The rate of reaction in no way depends on the type or ratio of products in this pH range. Thus the dissociation of decavanadate ion at pH ~8-10 may simply be described by eq 1, where $[V_{10}O_{28}^{6-}]_{tot}$ represents the total deca-

$$-d[V_{10}O_{28}^{6-}]_{tot}/dt = k_1[V_{10}O_{28}^{6-}]_{tot} \qquad (1)$$

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[9] M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, *Progr. React. Kinet.*, 2, 287 (1964).

[10] F. Brito, N. Ingri, and L. G. Sillen, *Acta Chem. Scand.*, 18, 1557 (1964).

Table IV. Observed First-Order Rate Constants for Decomposition of Decavanadate Ion (2.20×10^{-4} M V) in Hydroxide Ion Solutions, $\mu = 2.5$ (LiCl, NaCl, or KCl)

	$10^5 k_{\text{obsd}}$, sec^{-1} for systems		
[OH$^-$], M	Li	Na	K
		15.0°	
0.100		7.5	10.2
0.143	7.2		
0.449	15.2		
0.500		21.5	33.4
0.750		31.3	46.3
0.897	26.1		
1.00			65.7
1.25		49.4	
1.35	39.1		
		25.0°	
0.050		14.2	8.7
0.100	22.9	21.4, 18.3,[a] 15.7,[b] 12.8[c]	20.5
0.300	39.4	44.6, 41.9[a]	52.7
0.500		75.9, 69.5,[a] 40.5,[b] 29.3,[c] 69.1[d]	85.2
0.620	57.0		
0.750		100, 60.2,[b] 96[d]	135
0.930	80		
1.00		132, 76[b]	202
2.33	181		
		30°	
0.100		38.1	44.3
0.143	45.0		
0.269	64		
0.500		119	152
0.672	108		
1.00		190	298
1.063	156		
1.50		284	455
		35°	
0.100	80	63	79
0.200	96	95	135
0.500		186	286
0.620	169		
1.00		323	519
1.86	356		
		40.0°	
0.100		128	144
0.500		329	387
1.00		541	752
1.25		683	865
		45.0°	
0.143	261		
0.150		240	284
0.200		286	342
0.269	300		
0.300		355	448
0.443	376		
0.500		535	659
0.709	489		
		50.0°	
0.100		314	376
0.143	396		
0.200		436	551
0.269	463		
0.300		532	722
0.443	600		
0.500		756	1090
0.886		850	

[a] $\mu = 2.5$ ($NaClO_4$). [b] $\mu = 1.0$ (NaCl). [c] $\mu = 0.50$ (NaCl). [d] 8.80×10^{-3} M·V.

Table V. Activation Parameters Based on the Second-Order Rate Constants k_2 for Decomposition of Decavanadate Ion in Alkali Metal Hydroxide Solutions, $\mu = 2.5$ (MCl)

System	$\Delta H^\ddagger$,[a] kcal/mol	$\Delta S^\ddagger$,[a] eu
Li	16.0 ± 0.3	−19 ± 1
Na	17.6 ± 0.5	−13 ± 2
K	17.1 ± 0.5	−14 ± 2

[a] Error limits are standard deviations.

Table VI. Second-Order Rate Constants (k_2) from Least-Squares Arrhenius Plots of Decomposition of Decavanadate Ion in Alkali Metal Hydroxide Solutions, $\mu = 2.5$ (MCl)

	$10^3 k_2$, M^{-1} sec^{-1}, for systems		
Temp, °C	Li	Na	K
15.0	0.26	0.38	0.60
25.0	0.69	1.10	1.69
30.0	1.10	1.82	2.77
35.0	1.72	2.97	4.5
40.0	2.65	4.8	7.1
45.0	4.0	7.6	11.1
50.0	6.1	11.8	17.1

Table VII. Observed First-Order Rate Constants for Decomposition of Decavanadate Ion (2.20×10^{-4} M V) in Hydroxide Ion Solutions, 25.0°, $\mu = 2.5$ ($NaCl-(CH_3)_4NCl$)

[OH$^-$],[a] M	$10^5 k_{\text{obsd}}$, sec^{-1}	[OH$^-$],[a] M	$10^5 k_{\text{obsd}}$, sec^{-1}
2.00 M Na^+		1.00 M Na^+	
0.200	34	0.200	30
0.500	61	0.500	42
0.800	86	0.800	55
1.00	97	1.00	66
1.50 M Na^+		0.0 M Na^+	
0.200	31	0.059	53
0.500	49	0.198	58
0.800	71	0.395	52
1.00	82		

[a] Added as NaOH, or as $(CH_3)_4NOH$ for [Na^+] = 0.0.

vanadate concentration (free and ion paired, as discussed below); k_1 values are given in Table III.

The products of the decomposition of decavanadate ion at high [OH$^-$] are HVO_4^{2-} and VO_4^{3-}.[7,11] The ratio of these products remains virtually constant during the reaction because [OH$^-$] is constant. Isosbestic points in the spectral traces also show this (Figure 1). Rate constants are the same for data taken at 270 nm (spectral maxima for HVO_4^{2-} and VO_4^{3-}) or at 360 nm (where HVO_4^{2-} and VO_4^{3-} are transparent). Thus, whatever are the actual *instantaneous* products of decavanadate ion dissociation in basic solution, they must rapidly form the anions stable at equilibrium.

At high [OH$^-$] a first-order dependence of rate on [OH$^-$] is seen (Figure 2), although the pH-independent rate of reaction still exists, as the positive ordinate intercepts of Figure 2 illustrate. These intercepts (k_1'), while difficult to ascertain accurately, are nevertheless significantly higher than the k_1 values at pH 8-10 (Table III), except at 45 and 50° where they are experimentally the same. Thus a slight change in the mechanism of this "pH-independent" reaction occurs on increasing [OH$^-$] from 10^{-4} to 10^{-1} M. In hydroxide media at constant μ and constant alkali metal ion concentration, the rate law is given by eq 2. The very

$$-d[V_{10}O_{28}{}^{6-}]_{\text{tot}}/dt = \{k_1' + k_2[OH^-]\}[V_{10}O_{28}{}^{6-}]_{\text{tot}} \qquad (2)$$

similar activation parameters for the k_2 path for the lithium, sodium, and potassium systems (Table V) suggest the same mechanism is operative in all three cases.

The k_1' values seem to be somewhat dependent on the alkali metal cation (Figure 2), unlike the k_1 values. However, as sodium ion is replaced by tetramethylammonium

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(11) L. Newman, W. J. La Fleur, F. J. Brousaides, and A. M. Ross, *J. Amer. Chem. Soc.*, 80, 4491 (1958).

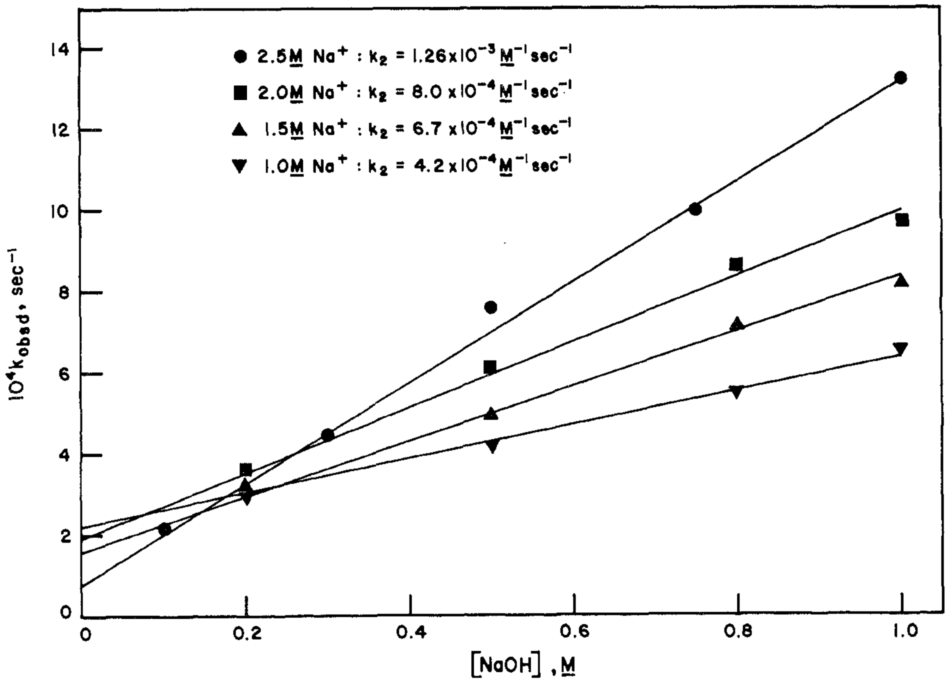

Figure 3. Plot of k_{obsd} *vs.* $[OH^-]$ for decomposition of decavanadate ion (2.20×10^{-4} *M* V) in NaOH solutions, μ 2.5 (NaCl-$(CH_3)_4NCl$), 25.0°.

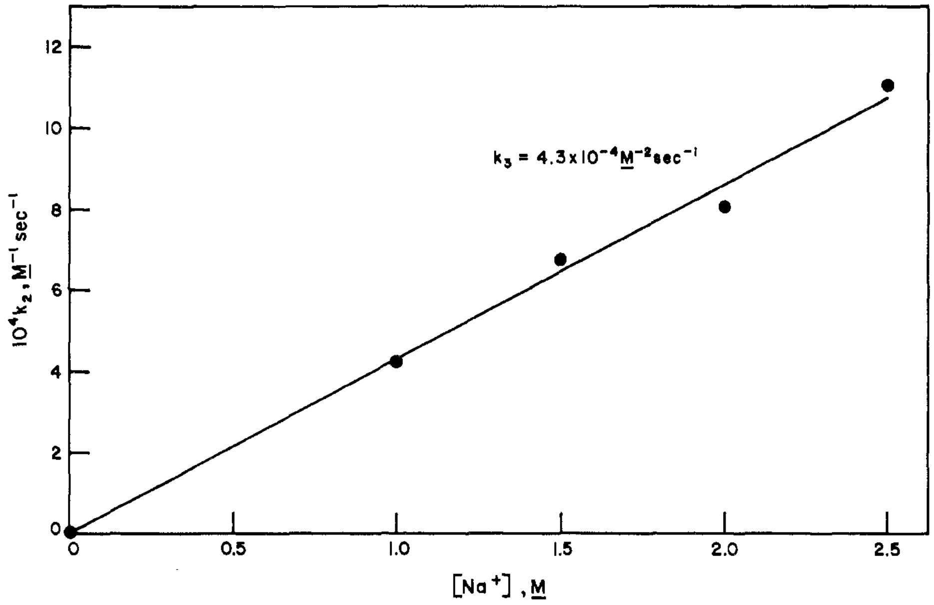

Figure 4. Plot of k_2 *vs.* $[Na^+]$ for decomposition of decavanadate ion (2.20×10^{-4} *M* V) in hydroxide ion solutions, μ 2.5 (NaCl-$(CH_3)_4NCl$), 25.0°.

ion while maintaining μ at 2.5 (Table II), k_1 increases by a factor of 4. A similar but less distinct trend for k_1' can also be extracted from the data of Figure 3 and Table VII; again the k_1' values for the hydroxide system are significantly greater than the carbonate buffer k_1 values. Thus the alkali metal ion plays a role in the dissociation of decavanadate ion in carbonate buffers, although Li^+, Na^+, and K^+ are indistinguishable kinetically in this system.

As Figure 2 points out, k_2 is clearly dependent on the alkali metal cation and is experimentally zero for the tetramethylammonium ion. For the mixed Na^+-$(CH_3)_4N^+$ system at $\mu = 2.5$, a first-order dependence of rate on $[Na^+]$ was established (Figure 4). Thus, k_2 may be redefined by eq 3. At 25° and $\mu = 2.5$, for the sodium system $k_3 = 4.3 \times 10^{-4}$ M^{-2} sec^{-1}. However, k_1' decreases as $[Na^+]$ increases, and the values of k_1' from the intercepts of plots such as those of Figure 3 are not sufficiently accurate to redefine eq 2 completely in terms of $[Na^+]$.

$$k_2 = k_3[Na^+] \qquad (3)$$

The dependence of k_1' and k_2 on alkali metal cation is not surprising based on earlier work. Potentiometric titrations of vanadates with alkali metal hydroxides indicated some ion association.[12] Jahr, Fuchs, and Preuss[13] showed that different alkali, alkaline earth, and other metal cations altered the base conductometric titration curve of the decavanadate ion, although their postulation of the existence of

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"enclosure" complexes has been refuted by X-ray evidence.[3,4] By potentiometric titration and rapid neutralization (continuous flow) tests with freshly prepared decavanadate ion solutions, Schwarzenbach and Geier[14] showed that the alkali metal cations formed the ion-pair complexes $MHV_{10}O_{28}^{4-}$, $MV_{10}O_{28}^{5-}$, and $M_2V_{10}O_{28}^{4-}$. $(CH_3)_4N^+$, a very large ion, was assumed not to form ion pairs.[14] Formation constants for $MV_{10}O_{28}^{5-}$ were 40 (M = Li, Na) and 250 (M = K), and the stepwise formation constants for $M_2V_{10}O_{28}^{4-}$ were 4 (M = Li, Na) and 10 (M = K). As with the protonated decavanadates, higher degrees of ion association were not found. Based on these formation constants, which did not vary greatly with ionic strength,[14] at 20° and $[M^+] \doteq 2.5\ M$ and $[V_{10}O_{28}^{6-}]_{tot} = 2.20 \times 10^{-5}\ M$, 91% of the decavanadate is in the form $M_2V_{10}O_{28}^{4-}$ and 9% in the form $MV_{10}O_{28}^{5-}$ for M = Li or Na; for M = K, the values are 96 and 4%, respectively. Free $V_{10}O_{28}^{6-}$ is <0.1% in both cases.

It seems likely that the sodium ion dependence comes from the formation of such ion-pair complexes. However, very little dependence of rate on $[Na^+]$ should be expected in our system if formation of the ion-pair complexes is >90% complete. Actually, there is no theoretical reason precluding ion-pair complexes containing more sodium ions than $Na_2V_{10}O_{28}^{4-}$. Solutions of 0.1 *M* sodium paratungstate contain ions of average composition $Na_{3.5}HW_6O_{21}^{1.5-}$, according to Bjerrum's theory.[15,16] The ion-pair formation theory of Fuoss[17] and Eigen[18] also predicts considerable ion association beyond $Na_2V_{10}O_{28}^{4-}$.

The first-order dependence of rate on $[Na^+]$ can be explained if we assume that the decavanadate ion is largely in the form of a specific ion pair $Na_xV_{10}O_{28}^{(6-x)-}$. The work of Schwarzenbach and Geier[14] suggests $x = 2$. Further ion association may then occur to a limited extent according to eq 4. The new pair then reacts with hydroxide ion according to eq 5. The rate law (excluding the pH-independent, or k_1', path) is given by eq 6. For only limited formation of $Na_{x+1}V_{10}O_{28}^{(5-x)-}$, $1 \gg K_{IP}[Na^+]$ and a first-order dependence of rate on $[Na^+]$ results. For that case, the product $k_2'K_{IP}[Na^+]$ equals the k_2 of eq 2 and Table VI.

$$Na^+ + Na_xV_{10}O_{28}^{(6-x)-} \overset{K_{IP}}{\rightleftarrows} Na_{x+1}V_{10}O_{28}^{(5-x)-} \qquad (4)$$

$$Na_{x+1}V_{10}O_{28}^{(5-x)-} + OH^- \xrightarrow{k_2'} \text{products} \qquad (5)$$

$$-d[V_{10}O_{28}^{6-}]_{tot}/dt = k_2'K_{IP}[Na^+][OH^-][V_{10}O_{28}^{6-}]_{tot}/(1 + K_{IP}[Na^+]) \qquad (6)$$

The basic decomposition of decavanadate ion is very slow compared to its formation by the reverse reaction and compared to its acid decomposition.[14] The more basic vanadates also interconvert rapidly on changes of pH or vanadium concentration.[14,19] The slowness of the basic decavanadate dissociation may be due to the compactness of its structure in which disruption of the V–O–V bond network may be difficult. Also, decavanadate ion is structurally dissimilar to the reaction products, which may hinder the formation of the activated complex. Crystalline decavanadates contain distorted VO_6 octahedra.[3,4] This structure is probably retained in solution, whereas all vanadates more basic than decavanadate apparently contain tetrahedrally coordinated vanadium in solution.[8,20]

Similar kinetic behavior is seen for condensation and dissociation of the structurally similar paramolybdate ion (eq 7).[21] Formation of the paramolybdate ion is rapid despite the complexity of reaction, while the reverse reaction is relatively slow. Evidence was presented which indicated that the addition of protons to tetrahedral MoO_4^{2-} ions expands the coordination number of Mo to 6; heptamerization then occurs rapidly, with condensation of water aided by hydrogen-bond formation.[21] However, in the formation of the paratungstate-A anion $W_6O_{19}(OH)_3^{5-}$, Tytko and Glemser[22] claimed that expansion of the coordination sphere of W in HWO_4^- to an octahedron comes only on addition to another tetrahedron or to an octahedron already formed by a previous addition. The rate of paratungstate-A formation is rapid because formation of a hexameric tungsten species is merely a series of addition reactions; to form the paratungstate, two water molecules are then condensed out rapidly because of the favorable location of the hydrogen atoms. A similar mechanism was considered applicable to paramolybdate formation.[22]

$$7MoO_4^{2-} + 8H^+ = Mo_7O_{24}^{6-} + 4H_2O \qquad (7)$$

Similar arguments may obtain in the condensation of basic vanadates to $V_{10}O_{28}^{6-}$; and, as with the decavanadate ion, the relatively slow dissociation of the paramolybdate ion may be caused by the difficulty of reducing the coordination number of Mo from 6 to 4, which involves the scission of Mo–O bonds in a compact structure.

Registry No. $V_{10}O_{28}^{6-}$, 12-397-125; LiOH, 1310-65-2; NaOH, 1310-73-2; KOH, 1310-58-3.

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