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Mechanism of Oxygen-18 Exchange between Water and the Vanadium(V) Oxyanion: $V_{10}O_{28}^{6-}$

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The rate of isotopic oxygen exchange between water and the discrete polyanion $V_{10}O_{28}^{6-}$ has a half-life of ~15 h at 25 °C, 0.01 M, with all oxygens being equivalent. At constant pH the overall rate of exchange is first order in $[V_{10}O_{28}^{6-}]_T$ with a small ionic strength dependence. The rate of exchange is nearly constant in the pH range 4.0–6.3, increases dramatically with increasing hydrogen ion concentration below pH ~4.0, and decreases above pH ~6.3, reaching essentially zero at pH >10.0. This behavior is discussed in terms of the protonated species present in the pH range (2.5–10.0). Comparison of the kinetics of depolymerization and exchange of the ion in slightly basic media suggests a "common intermediate" mechanism involving the one-ended dissociation of a V_4 group leading to dissociation and/or exchange. This mechanism provides for the exchange equivalency of all oxygens and is consistent with the activation parameters: $\Delta V^{\ddagger} = -5.0 \pm 2$ cm³/mol, $\Delta H^{\ddagger} = 21 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = -7 \pm 0.5$ cal/(mol K). A definitive $^{49}VO_4^{3-}$ transfer experiment during exchange and dissociation is in agreement with this mechanism.

Introduction

In aqueous media, the orthovanadate ion undergoes complex hydrolysis–polymerization reactions upon neutralization with acids. Other oxyanions such as niobates, tantalates, chromates, molybdates, and tungstates undergo similar reactions. The species generated by such oligomerization reactions are generally referred to as isopolyanions of which the dichromate ion, $Cr_2O_7^{2-}$, is the best known example. Although studied for over 50 years, only the chromate system is reasonably well understood and only in the early stages of oligomerization. The simplicity of the Cr(VI) hydrolysis reactions is probably related to its strong tendency to retain the tetrahedral coordination arrangement. The other ions named appear to allow variable coordination numbers (4–6) and thus show considerably more structural variability and complexity.

A study of the literature[3] on these ions leads to the conclusion that only a limited number of discrete polyanions exist for a particular system. This is unusual in comparison to other polymerization reactions where generally the whole range of polymeric molecules are formed.[4] $V_{10}O_{28}^{6-}$ is the largest of the known vanadate oligomers and its solid-state x-ray structure has been accurately determined.[5] An ORTEP-Cal-Comp drawing[6] of the ion is given in Figure 1. It exists as the major component over a large pH and concentration range[7] and there is no evidence for V_8, V_9, V_{11}, and V_{12} species in equilibrium with it.[8]

Figure 2 gives the approximate pH–concentration profile[9] for the vanadium(V) system as estimated from various equilibrium constant studies. A large pH–concentration region exists where $V_{10}O_{28}^{6-}$ or its protonated forms appear to be the main component. A preliminary study has been reported[10] showing the rate of oxygen exchange with solvent is slow. Thus, this ion is highly suited for precise studies on the mechanism of the oligomerization process. This paper presents the findings of ^{18}O exchange and base-dissociation studies directed toward understanding the mechanism of oligomerization of the vanadium(V)–H_2O system.

Experimental Section

Materials. $(NH_4)_6V_{10}O_{28}\cdot 6H_2O$ was prepared from V_2O_5 and $Na_6V_{10}O_{28}\cdot 18H_2O$ from $Na_3VO_4\cdot 5H_2O$ as described elsewhere.[11] They were twice recrystallized from warm water before use. Normal and ^{18}O-enriched water was distilled from acid $Cr_2O_7^{2-}$ and basic MnO_4^- before use. All salts used in the exchange and decomposition studies were reagent grade and were recrystallized before use. Decavanadate ion, enriched in ^{18}O, was prepared[10] by a 2-day exchange of a saturated solution with enriched water at 50 °C. The enriched salts were crystallized at 0 °C, collected, and mildly dried in air. Several lots of the enriched salts prepared in this manner had identical physical and exchange properties.

Exchange Kinetics. The exchange of H_2O–oxygen with that of $V_{10}O_{28}^{6-}$ was followed in both directions with the enriched isotope in either the anion or the solvent. The experimental conditions were essentially identical and are described for the normal-water, enriched-$V_{10}O_{28}^{6-}$ system.

Approximately 0.5 g of ^{18}O-enriched $(NH_4)_6V_{10}O_{28}\cdot 6H_2O$ was weighed into a 30-mL Teflon-stoppered flask. The flask and contents were immersed in a constant temperature bath ±0.05 °C and allowed to reach bath temperature. At time zero, 20.0 mL of normal water (or an aqueous solution) at bath temperature was added with stirring. Solution was complete in less than 1 min. At selected time intervals, 1.0-mL portions of the solution were removed, and the exchange was quenched by injecting it into a chilled test tube containing 0.2 mL of a half-saturated, filtered CsCl solution. $Cs_6V_{10}O_{28}$ precipitated immediately and completely. It was collected on a sintered-glass filter and washed twice with 1.0 mL of spectral quality methanol and then with two washes of acetone. Dry nitrogen was passed over the sample during the last washing to prevent water condensation and it was continued until the sample was completely dry. It was transferred to a break-seal tube, placed under vacuum for a 24-h period prior to conversion of its oxygen to CO_2. Approximately 0.15 g of a 1/1 by weight mixture of carefully dried $Hg(CN)_2$ and $HgCl_2$ was added and the tube was sealed and then heated at 425 °C for 1 h. The tube contents were separated by preparative chromatography, and the CO_2 was collected. Its ^{18}O content was a direct measure of the ^{18}O content of $Cs_6V_{10}O_{26}$. The 46/(45 + 44) ratio of the CO_2, R, was measured on a dual collector Nuclide mass spectrometer. It was compared to a normal standard arbitrarily given the value 4.00×10^{-3} and normalized to it (R_n). Low enrichments, less than 4 times normal, were used and shown to be in the linear region of the mass spectrometer.

The isotopic composition of the water, or final solution, was determined in the same manner by transferring ~3 μL of the solution to the break-seal tube containing the $Hg(CN)_2$–$HgCl_2$ mixture.

The pH of solutions were measured with an Orion Model 601 pH meter calibrated at pH 7.00 and 10.00 with certified buffers. The pH of decavanadate solutions, adjusted to less than 6, remained constant (±0.05) without the addition of a buffer. However, because of slow decomposition of the unprotonated $V_{10}O_{28}^{6-}$, the pH of solutions greater than 6 tended to drop. For example, the initial pH of a freshly prepared 0.025 M $(NH_4)_6V_{10}O_{28}\cdot 6H_2O$ solution was 7.2 which dropped to 6.3 in about an hour and then remained essentially constant for the rest of the exchange run (approximately 40 h). Therefore, to study the exchange at a constant pH above 6 it was necessary to either have a buffer present or add, at appropriate intervals, small quantities of 1–2 M NaOH solution. No suitable buffer, compatible with the ^{18}O experiments, was found and thus the latter technique was applied using a pH controller and an electronically driven buret. Using this apparatus at constant temperature, the pH was maintained to better than ±0.05 pH unit.

Acid dissociation constants for the decavanadate ion were measured at 0 °C by measuring the pH change which occurred upon the addition of known amounts of acids to solutions of $Na_6V_{10}O_{28}\cdot 18H_2O$. Since dissociation of the ion is relatively slow compared to the protonation of the ion, association constants could be measured without interference

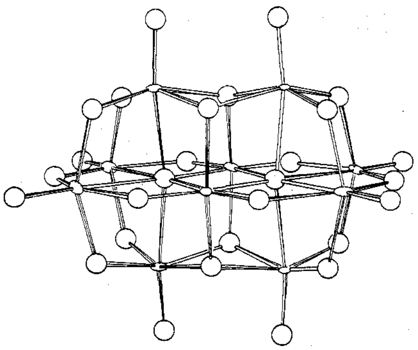


Figure 1.

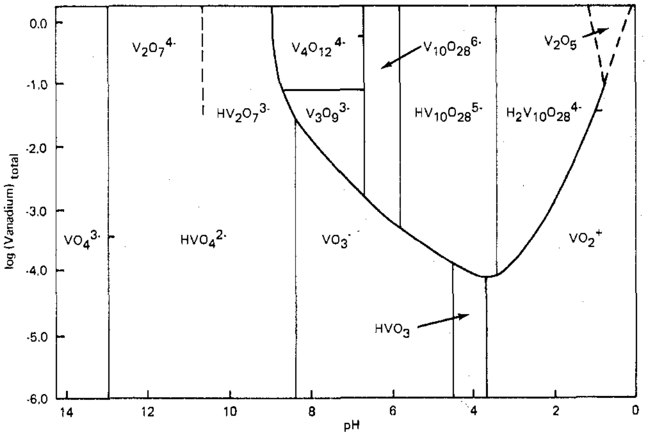


Figure 2. pH–concentration profile of the aqueous vanadium(V) system at 25 °C.

if the time before pH measurement was kept short. Each point of the titration curve was a separate sample whose life since mixing was less than 3 min.

Decomposition Kinetics. The media chosen for these experiments were, as close as possible, the same as that in the exchange studies. Thus, no buffer was used and the pH was maintained at constant temperature at a predetermined value by the controlled addition of 2.0 M NaOH solution. For this purpose a pH meter/controller was used.

A stock solution of $Na_6V_{10}O_{28}{\cdot}18H_2O$ was prepared at pH 4 by adding a trace of acid. A portion was brought to constant reaction temperature and 2.0 M NaOH solution added quickly to the desired pH in a constant temperature water bath. The pH controller was activated and vigorous stirring and a CO_2-free atmosphere maintained. At intervals, 30 μL of the reaction mixture was diluted to 3.00 mL in a spectrophotometer cell and its absorption at 390 nm quickly measured. Graphs of $-\ln [(A_t - A_\infty)/(A_0 - A_\infty)]$ vs. time were linear over several half-times. This procedure gave results in excellent agreement with those of Goddard and Gonas[12] under comparable conditions and allowed us to extend the pH range down to 7.0.

The rate of decomposition was also followed by monitoring the volume of NaOH solution used as a function of time. The initial rate, $-d(OH^-)/dt$, along with the known rate of decomposition (from spectral measurements) allowed the calculation of the number of OH^-'s consumed per $V_{10}O_{28}^{6-}$ decomposed. Conversely, knowing the stoichiometry allowed a calculation of the reaction rate constant.

$V_2O_7^{4-}$ Exchange Kinetics. $Na_4V_2O_7$ was prepared by adding a stoichiometric amount of NaOH to a mixture of V_2O_5 and water. The pH was adjusted to 11 and the product isolated by cooling to 0 °C. A concentrated solution of ^{18}O-enriched $Na_4V_2O_7$ solution was injected into a large volume of normal water at 0 °C. Shortly thereafter a 2 M $BaCl_2$ solution was injected to precipitate $Ba_2V_2O_7{\cdot}2H_2O$. The precipitate was collected by centrifugation, washed with methanol and three times with acetone, and dried in a N_2 stream. All oxygens in the precipitate were converted to CO_2 in the usual manner.

The reverse reaction was also carried out which utilized normal anion and enriched solvent.

Pressure Dependence of k_{exch}. A solution of $V_{10}O_{28}^{6-}$, enriched in ^{18}O, in normal water was prepared at reaction temperature. After a few minutes to allow for pH stabilization, two samples were removed; one for the time-zero standard and the other to be subjected to pressure. The latter was placed in a latex tube with Teflon endplugs. It was inserted in a "bomb" filled with light oil and pressurized while submerged in a constant temperature water bath. A Tempress Hydrogen Research Model HR-1B-2R apparatus was used. After an appropriate time interval, the solution was collected and precipitated as $Cs_6V_{10}O_{28}$ and analyzed for ^{18}O. The time-zero and ∞ samples were similarly treated.

Subjecting a liquid to a sudden large pressure change can create a significant temperature change within the sample[13] and thus may give erroneous rate constants. Since the $t_{1/2}$ for exchange is long, ~15 h, compared to the expected $t_{1/2}$ for approach to temperature equilibrium, this was not expected to be important in this system. However, a check was made. The rate constant for exchange was determined at 1.1 kbar using a t_0 value from a nonpressurized sample and using a t_0 value found for a sample given 2 h under pressure. Within experimental error, the rate constants were the same proving that whatever the temperature rise, it did not cause a significant rise in the rate of exchange.

Treatment of Data. Both ^{18}O exchange kinetic data and decomposition rate data were evaluated utilizing the first-order expression $-\ln (1 - F) = k_{obsd}t$. A weighted least-squares program utilizing the IBM 370/168 calculated the slope and intercept and their errors. The weight was estimated from $w = (R_t - R_\infty)/(\sigma_{R_t})$ where σ_{R_t} was a linear function of R_t with values of 1×10^{-8} at $R_t = 4 \times 10^{-3}$ and 6×10^{-8} at $R_t = 9 \times 10^{-3}$. R_t and R_∞ in the former equation refer to the ^{18}O mole fraction at time t and ∞. The overall rate of oxygen exchange, R, is related to k_{obsd} by

$$R = 28[V_{10}O_{28}^{6-}][H_2O]k_{obsd}/28[V_{10}O_{28}^{6-}] + [H_2O]$$

Assuming a first-order dependency on [anion], $R = k[V_{10}O_{28}^{6-}]$, and if $28[V_{10}O_{28}^{6-}] << [H_2O]$, then $k = 28k_{obsd}$.

$V_{10}O_{28}^{6-}$–VO_4^{3-} Exchange (during Dissociation). Of considerable mechanistic interest was a comparison of the rate of dissociation in base, rate of oxygen exchange between $V_{10}O_{28}^{6-}$ and water, and the rate of vanadium exchange between $V_{10}O_{28}^{6-}$ and $^{49}VO_4^{3-}$ under the same conditions. For this purpose a constant pH of 11 at 22 °C was chosen. To 0.48 g of $Na_6V_{10}O_{28}{\cdot}18H_2O$ in 30 mL of water was added 0.025 g of $Na_3VO_4{\cdot}4H_2O$ containing ^{49}V.

A small sample was set aside for analysis of the radioactivity per $[\text{vanadium}]_T$. This sample is called RM. After division of the rest into two equal portions, one was treated with HCl to a pH of 6.2 and allowed to equilibrate for 5 h, STD, and the other was slowly decomposed for 1.75 h at a constant pH of 11.0 with the slow addition of base, RX. Both STD and RX were treated with CsCl, and the $Cs_6V_{10}O_{28}$ was isolated, washed, and recrystallized in the presence of a trace of normal VO_4^{3-}.

Samples of STD, RM, and RX containing the same amount of V_T were solubilized with base and their radioactivity was measured with a proportional counter and corrected with standards. (RM) represents the activity expected if VO_4^{3-} exchanged completely with $V_{10}O_{28}^{6-}$ during the time allowed, (RX) represents the portion of (RM) that did exchange, and (STD)/(RM) tells what fraction of the VO_4^{3-} was incorporated into $V_{10}O_{28}^{6-}$ at pH 6.2 at equilibrium. This last value gives a lower limit to the fraction of activity which was as $^{49}VO_4^{3-}$ (other nuclides being possible). The purity of the ^{49}V activity was also checked by γ-ray spectroscopy, and no foreign nuclides were observed. Two experiments gave these corrected results: (RM) = 11.42 ±0.31, (STD) = 8.93 ±0.09, (RX) = 0.50 ±0.25 counts/min. From this, one calculates that no more than 4.4 ± 2.7% of the VO_4^{3-} was incorporated into $V_{10}O_{28}^{6-}$ in 1.75 h while it was being dissociated with base at 22 °C. During this same period, it is estimated that 60% of the $V_{10}O_{28}^{6-}$ dissociated into small fragments and about 1% ^{18}O exchange took place.

Results

A previous study[10] established that linear McKay graphs were obtained for the ^{18}O exchange between $V_{10}O_{28}^{6-}$ and H_2O at 25 °C and a pH of 6.5–7.0. Further, all 28 oxygens were equivalent in exchange properties or were so similar that no deviations from the McKay plots could be ascertained up to 93% total exchange when 28 equivalent exchange sites were assumed. These results were confirmed in numerous additional experiments over a pH range of 6–10.

Table I. Kinetics of the $V_{10}O_{28}^{6-}$–H_2O^* Exchange Reaction, 25.0 °C

Run[e]	pH[a]	$10^5k^e_{obsd}$,[b] s^{-1}	[$V_{10}O_{28}^{6-}$], M	No. of O's exchanged
1[d]	7.2–6.7	1.32 ± 0.01	0.044	25.4
2	7.7–6.4	1.36 ± 0.06	0.024	26.3
3[c]	7.5–6.4	1.30 ± 0.02	0.025	26.7
4[c,f]	8.3–6.2	1.19 ± 0.01	0.036	25.9

[a] $(NH_4)_6V_{10}O_{28}$, pH at 25 °C. [b] The ± value equals 2 times standard deviation (90th percentile). Superscript e is exchange. [c] Normal water-enriched $V_{10}O_{28}^{6-}$. [d] All different reagents. [e] Reaction vessels were shielded from light and kept under N_2 to exclude atmospheric CO_2. [f] Na^+ salt.

Table II. Hydrogen Ion Dependence of the $V_{10}O_{28}^{6-}$–H_2O^* Exchange Reaction, 25.0 °C

pH[a]	[$V_{10}O_{28}^{6-}$]$_{total}$,[c] M	10^5k_{obsd},[b] s^{-1}
10.00	0.0163	0.09[e]
9.20	0.0124	0.16[e]
7.00	0.0358	0.81 ± 0.18
6.32	0.0358	1.19 ± 0.01
5.00	0.0254[d]	1.12 ± 0.01
4.25	0.0235	2.00 ± 0.20
3.98	0.0147	2.46 ± 0.16
3.63	0.0164	3.84 ± 0.24
3.20	0.0156	8.30 ± 0.11
2.89	0.0196	14.70 ± 0.80
2.70	0.0159	20.30 ± 0.25
2.45	0.0163	29.30 ± 0.30

[a] Measured at 25 (±1) °C. [b] Errors represent 2 times standard deviation (90th percentile). [c] Source of decavanadate ion was $Na_6V_{10}O_{28}\cdot 18H_2O$. [d] Source of decavanadate ion was $(NH_4)_6V_{10}O_{28}\cdot 6H_2O$. [e] Estimated maximum possible rate constant for exchange (see text).

Table III. Concentration and Salt Dependencies of the ^{18}O-Exchange Reaction

Cation	[$V_{10}O_{28}^{6-}$],[a] M	pH[f]	[Positive ion], M	$10^5k^e_{obsd}$,[d,e] s^{-1}
1. NH_4^+	0.048	6.7	0.291	1.36 ± 0.02
2. NH_4^+	0.044	6.7	0.264	1.32 ± 0.01
3. NH_4^+	0.025	6.4	0.150	1.30 ± 0.02
4. NH_4^+	0.021	6.4	0.126	1.25 ± 0.02
5. NH_4^+	0.025	5.0[b]	0.150	1.12 ± 0.02
6. Na^+	0.036	6.3	0.216	1.19 ± 0.02
7. Na^+	0.024	6.0[b]	0.144	1.05 ± 0.06
8. Na^+	0.016	5.8[b]	0.098	0.92 ± 0.04
9. Na^+	0.006	6.2	0.034	0.92 ± 0.04
10. Na^+	0.010	5.9	0.592[c]	1.32 ± 0.06
11. Na^+	0.024	5.3[b]	0.144	0.99 ± 0.06

[a] Total, $H_2V_{10}O_{28}^{4-} + HV_{10}O_{25}^{5-} + V_{10}O_{28}^{6-}$. [b] HCl added. [c] NaCl added. [d] The ± value equals 2 times standard deviation (90 percentile). [e] Superscript e is exchange. [f] Final.

Table IV. pH Dependence of the Rate Constant for Decomposition of $V_{10}O_{28}^{6-}$

pH	10^5k^d obsd,[b,d] s^{-1}	α_0[g]	10^5k^d, s^{-1}
7.00[a]	1.20 ± 0.08	0.413[c]	2.91
7.50	2.20 ± 0.02	0.691	3.18
8.00	3.22 ± 0.01	0.876	3.68
8.50	4.53 ± 0.02	0.957	4.73
8.85	6.09 ± 0.06	0.976	6.24
9.05	7.00 ± 0.21	0.986	7.10
9.55	9.47 ± 0.18	0.996	9.51
10.05	10.38 ± 0.09	0.999	10.39
11.00	11.40 ± 0.05	1.000	11.40
12.00	13.20 ± 0.05	1.000	13.20
8.50	7.73 ± 0.02[e]		
11.05	9.58 ± 0.06[e]		
8.70	7.9[f]		
9.85	8.1[f]		

[a] ±0.05 maintained by addition of 1.00 M NaOH from pH controller. [b] [$V_{10}O_{28}^{6-}$] = 0.0138 M, 25.0 °C, [Na^+] = 0.084 M. [c] See text. [d] Decomposition. [e] [$V_{10}O_{28}^{6-}$] = 0.0138 M, 25.0 °C, [Na^+] = 0.5 M (NaCl). [f] [$V_{10}O_{28}^{6-}$] = 2.2×10^{-5} M, 25.0 °C, μ = 0.50 (NaCl), Na_2CO_3–$NaHCO_3$ buffer.[12] [g] α_0 = fraction of the decavanadate ion in the unprotonated form.

Table I is a summary of the exchange kinetic experiments in the neutral region. Note that the ± values represent two standard deviations. As can be seen from entries 1, 2, and 3, the rate of exchange is highly reproducible and identical results are obtained with the enrichment either in the solvent or in the anion. This fact helps establish the equivalence of all 28 oxygens since nonuniform, incomplete labeling of the anion would result in differing rate constants for the two methods of study. A moderate rate change is noted when the cation is changed from NH_4^+ to Na^+. Each of these runs was followed as long as significant information could be obtained from it and showed no tendency toward curvature with the later points.

Tables II and III give the results of experiments to ascertain the hydrogen ion and concentration dependencies of the exchange reaction. The observed rate constant is rapid in acidic media, becomes sensibly constant in the neutral region, and diminishes to very small values in basic solutions. It should be noted that the rate constant is given for the V_{10} anion *remaining* since, in both the acid and basic region, decomposition to smaller oligomers occurs simultaneously with exchange, but only the remaining V_{10} anion is isolated and followed. In the more acidic region, initial rate constants are reported since the McKay graphs were not linear.

Above pH 10 and below pH 2.4 the rate of decomposition to smaller units becomes so rapid (compared to the exchange rate) that meaningful exchange data cannot be obtained. In order to ensure that only the oxygen in the V_{10} anion was being measured, IR spectra of the solids were compared with those from the neutral region (analyzed) and found to be the same. The IR spectra are known to be sensitive to the nature of the anion. The concentration and salt dependencies were carried out because ion pairing to oxyanions with large charges is known to be important even in dilute solution and an equilibrium between V_{10} and smaller fragments could be very important in the mechanism of oxygen exchange. From Table III one can see that the ammonium salt is consistently faster than the sodium salt, the rate constant increases with increasing concentration of the exchanging species, and the presence of NaCl in large amounts increases the rate constant. In all exchange experiments there is a tendency for the pH to change with time due to small amounts of decomposition to smaller units. In the neutral region this change was small and since the rate constant for exchange is nearly independent of pH in this range no correction was necessary. However, in either the basic or acidic region acid or base had to be added to keep the pH at a constant value. This was done automatically with a pH driven buret with a very fast response time compared to the reaction rate.

The rate constants for the decomposition of $V_{10}O_{28}^{6-}$ in neutral to basic media are given in Table IV. The values of k^d_{obsd} increase with [OH^-]. Some values are given which fall in the range of conditions used by other authors. The values of α_0 and k^d are discussed and used in the next section.

Tables V and VI contain the temperature effect on the rate constants of isotopic exchange and basic decomposition. Also present are the calculated activation parameters.

In Table VII are given the rate constants of isotopic oxygen exchange as a function of pressure. Using the expression $\Delta V^{\neq} = RT \ln (k_2/k_1)/(P_1 - P_2)$ a least-squares evaluation of $\Delta V^{\neq}$ gave a value of -5.1 ± 1.7 cm^3/mol.

The rate of ^{18}O exchange on V(V) solutions in which $V_2O_7^{4-}$ predominates was conducted at 0 °C, pH 8.5–9.5 and $[V]_T$

Table V. Temperature Dependence of the $V_{10}O_{28}^{6-}$–H_2O ^{18}O-Exchange Reaction[a,e]

Temp,[b] °C	$10^5 k^e_{obsd}$,[c] s^{-1}	$10^5 k'$,[d] s^{-1}
25.0	1.06 ± 0.06	14.84
35.0	3.15 ± 0.04	44.1
45.0	9.87 ± 0.10	138.2

[a] pH 6.2, $[V_{10}O_{28}^{6-}] = 0.017$ M, $[Na^+] = 0.1$ M. [b] ±0.05°. [c] ± values are 2 times standard deviation. [d] $k' = 28(k_{obsd})/2$, where 28 is the number of equivalent oxygens in the ion and 2 is the assumed net number of oxygens exchanged each time the ion "opens" and then relaxes. [e] $\Delta H^{\ddagger} = 20.6 \pm 0.5$ kcal/mol. $\Delta S^{\ddagger} = -7 \pm 0.5$ cal/(mol deg).

Table VI. Temperature Dependence of the $V_{10}O_{28}^{6-}$ Decomposition Reaction[d]

	$10^5 k^d_{obsd}$,[b,c] s^{-1}	
Temp,[a] °C	pH 7.5	pH 12.0
25.0	2.20 ± 0.02	13.1 ± 0.20
35.0	9.10 ± 0.04	52.2 ± 0.30
45.0	29.40 ± 0.06	171.2 ± 0.60

[a] ±0.05 °C. [b] ± values are 1 times standard deviation. [c] Concentration of decavanadate ion = 0.0138 M. [d] At pH 7.5 $\Delta H^{\ddagger} = 23.8 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = 0.0 \pm 3$ cal/(mol K). At pH 12.0 $\Delta H^{\ddagger} = 23.6 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = 3.0 \pm 3$ cal/(mol K).

Table VII. Pressure Dependence of the $V_{10}O_{28}^{6-}$–H_2O ^{18}O-Exchange Reaction

Pressure, kbar	$10^5 k^e_{obsd}$,[a] s^{-1}	Pressure, kbar	$10^5 k^e_{obsd}$,[a] s^{-1}
Atmospheric	1.14 ± 0.02	1.10	1.50
1.00	1.48	1.10	1.49[b]
1.04	1.45	1.81	1.67
1.09	1.47	2.10	1.79

[a] pH 6.25, $T = 25.0$ (±0.05) °C. $[V_{10}O_{28}^{6-}] = 0.016$ M, Na^+ salt. [b] Does not reflect the results of any initial temperature rise (see text).

= (4.5–9) × 10^{-2}. Under these conditions $HV_2O_7^{3-}$ is the major species, but HVO_4^{2-}, $V_3O_9^{3-}$, and traces of $V_4O_{12}^{4-}$ are expected to be present. The half-times for exchange were 5–18 s which is of the same order of magnitude as that found for VO_4^{3-}. The precision of these measurements did not allow a more definitive comparison.

Discussion

The basic features of isotopic water exchange with decavanadate ion (V_{10}) are (a) there is no dependence of the first-order rate constant on the $[V_{10}]_t$, (b) the rate constant increases with ionic strength, (c) protonation of V_{10} in the neutral region increases only slightly the rate constant, (d) specific ion-pair effects are of some importance ($NH_4^+ > Na^+$), (e) above pH 10 the rate constant decreases dramatically, and (f) at low pH's, <3.8, the apparent rate constant increases but the McKay plots become nonlinear. A graph of the pH behavior is shown in Figure 3. Considering only the portion of the curve where linear McKay plots are found (pH 4–10) there is a region of near constancy (pH 4–7). Over this range the number of protons associated with V_{10} varies from 1.8 to 0.6. Thus, protonation has little effect on the exchange rate. For a series of data in the pH region 6–7 where no other interferences are expected, using[14] $pK_{a_1} = 7.15$ one can evaluate the exchange constants for V_{10} and HV_{10} from

$$k^e{}_{obsd} = \frac{k^e [V_{10}] + k_p{}^e [HV_{10}]}{[V_{10}] + [HV_{10}]} \qquad (1)$$

Such a treatment gave $k^e = (5.8 \pm 4.8) \times 10^{-6}$ s^{-1} and $k_p{}^e = (9.8 \pm 0.3) \times 10^{-6}$ s^{-1} at 25 °C.

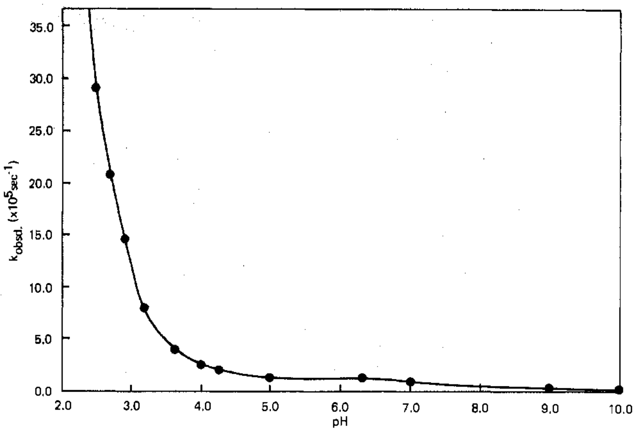


Figure 3. pH dependence of the observed rate constant for $V_{10}O_{28}^{6-}$–H_2O ^{18}O exchange (25 °C, $[V_{10}O_{28}^{6-}]_T = 0.02$ M).

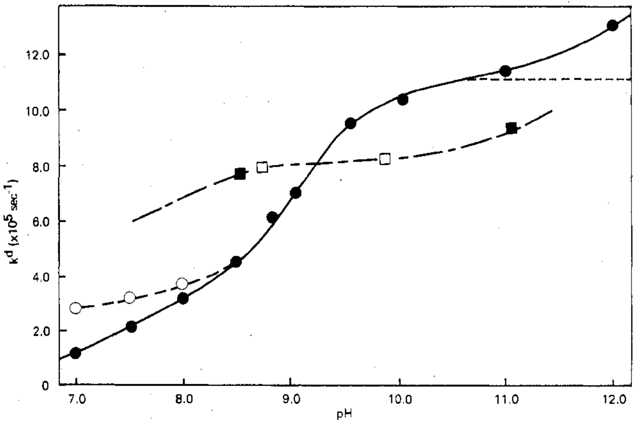


Figure 4. pH dependence of the rate constant for decomposition of $V_{10}O_{28}^{6-}$: —, $k^d_{calcd,eq\ 3}$; – – –, k^d; - - -, $(k_{obsd} - k_{G\&G})$; – - –, k^d_{obsd} (μ = 0.5 (NaCl)); solid symbols, this work; open symbols, ref 12.

Above a pH of 7, decomposition to smaller units simultaneously with exchange becomes apparent and the exchange measured is only on the V_{10} remaining. It is found that oxygen exchange rate constants decrease to essentially zero at high pH's. Dissociation increases with increasing basicity (Figure 4) and due to the similarity of rates and for other reasons given later it is thought that there is a competition for an unstable intermediate by the two reactions. The intermediate (V_{10}^* or HV_{10}^*) may either return to its original state with exchange or dissociate to products (VO_4^{3-}, $V_2O_7^{4-}$, etc.).

The pH dependency of the first-order rate constant of dissociation, k^d_{obsd}, is given in Figure 4. The squares are repeats of the data of Goddard and Gonas[12] at their ionic conditions while the black circles are experimental points at lower ionic strength. Excellent agreement with Goddard and Gonas, and thus with Druskovich and Kepert,[12] is evident. The reaction rate is highly dependent on the ionic concentration and on the nature of the cation. Two corrections have to be made to the experimental curve at the lower and the higher pH ends to obtain the true rate constant of dissociation, k_d of V_{10}. In the pH range 8.5–7, a portion of $(V_{10})_t$ is in the HV_{10} form which is much slower to dissociate. Correction to k_d can easily be made through $k^d_{obsd} = k^d\alpha_0$ where α_0 is the $V_{10}/(HV_{10} + V_{10})$ ratio. Above pH 10.5 a correction needs to be made for the rate term first order in $[OH^-]$ which was found by Goddard and Gonas and confirmed in this work. The curve remaining after these corrections, looking like a titration curve, has its inflection point at about pH 9.2 which is considerably above the pK_{a_1} of HV_{10}. In order to explain this curve, utilizing the common intermediate concept, the following steps, A–C, are suggested (V^* = common intermediate).

$$V_{10} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} V_{10}^* \text{ exchange} \tag{A}$$

$$V_{10}^* \xrightarrow{k_2} \text{products} \tag{B}$$

$$OH^- + V_{10}^* \xrightarrow{k_3} \text{products} \tag{C}$$

Assuming a steady-state concentration of V_{10}^*

$$-d[V_{10}]/dt = k^d[V_{10}] \tag{2}$$

where

$$k^d = \frac{k_1k_2 + k_1k_3[OH^-]}{k_{-1} + k_2 + k_3[OH^-]}$$

This may be put in the linear form

$$1/[(k_1/k^d) - 1] = k_2/k_{-1} + (k_3/k_{-1})[OH^-] \tag{3}$$

which has been applied to the data in Figure 4. The value of k_1 was initially estimated from the high pH values of Figure 4 and subsequently modified to produce the closest linear fit to eq 3. The following values were obtained: $k_1 = (11.2 \pm 0.2) \times 10^{-5}\ s^{-1}$, $k_3/k_{-1} = (1.20 \pm 0.2) \times 10^{-5}$, $k_2/k_{-1} = 0.364 \pm 0.008$. The fit shows that the model is in agreement with the experimental k^d.

Over the full pH range (7–12) corrections for α_0 and for the $k_{OH}[V_{10}][OH^-]$ term have to be applied. When this is done using $pK_{a_1} = 7.15$ to evaluate α_0 and $k_{OH} = 2 \times 10^{-3}\ M^{-1}\ s^{-1}$ at 25 °C and the evaluated parameters for eq 3, the solid black line in Figure 4 is obtained. The fit is excellent and thus is in agreement with the mechanistic picture.

Now we can turn our attention again to an analysis of the exchange data in basic media. The reactive intermediate V_{10}^* is thought to be a partially opened decavanadate ion where a segment (V_4 unit) is bonded to the remaining portion at only one end (half-bonded). (The reasons for this hypothesis are given later.) Using this picture

$$R_{exch} = nk_1[V_{10}]\frac{k_{-1}}{k_{-1} + k_2 + k_3[OH^-]} \tag{4}$$

where n = the average number of oxygens which exchange each time the intermediate is formed and returns to its original state, $k_1[V_{10}]$ is the rate of production of intermediate, and $k_{-1}/(k_{-1} + k_2 + k_3[OH^-])$ is the fraction of the intermediate which does not dissociate to smaller fragments. Qualitatively eq 4 explains Figure 3 very well in that the exchange should approach zero at high $[OH^-]$ and become constant in the neutral region (assuming no HV_{10}, only V_{10}). From this, a value of n can be estimated. From the decomposition data previously described, the ratio $k_2/k_{-1} = 0.364$ rearranges to $k_{-1}/(k_{-1} + k_2) = 0.73$, $k_1 = 11.2 \times 10^{-5}\ s^{-1}$, and the $k_3[OH^-]$ term is essentially zero at pH 7. Equation 4 (recognizing the fact that $R_{exch} = 28k^e[V_{10}]$) gives $n = 28(5.8 \times 10^{-6})\ s^{-1}/0.73(11.2 \times 10^{-5})\ s^{-1} = 1.99$. The estimated error in n is high (about ±1) but the essential feature is that it is a reasonable value and low. Also, each time a portion of the decavanadate ion opens up, it completely dissociates 30% and re-forms 70% of the time ($k_{-1}/(k_{-1} + k_2)$) and that which re-forms has exchanged roughly 2 ± 1 oxygens.

In the proposed common intermediate mechanism for ^{18}O exchange and dissociation, the rate-limiting steps are the same and should have the same activation parameters.

The activation parameters found for "opening" the structure from dissociation data are $\Delta H^‡ = 23.8\ (23.8) \pm 0.05$ kcal/mol and $\Delta S^‡ = 0\ (3) \pm 3$ cal/(mol K) with $[V_{10}]_t = 0.014$ M at pH 7.5 and 12, respectively. The higher values of Goddard and Gonas[12] are due to specific ionic environment factors. Activation parameters for "opening" by exchange on V_{10} cannot be measured free of dissociation. However, at pH 6.2 where HV_{10} is the major species, rate constants for "opening" can be calculated assuming a value for n and the McKay equation. Using $n = 2$ the activation parameters from exchange data are for HV_{10} $\Delta H^‡ = 20.6 \pm 0.5$ kcal/mol and $\Delta S^‡ = -7 \pm 5$ cal/(mol K). The activation parameters appear to be slightly lower from exchange data (HV_{10}) than from dissociation data (V_{10}). Since V_{10} exchanges more slowly than HV_{10}, it is expected that both activation energy terms would be larger for V_{10} than for HV_{10}. This would bring the activation parameters for "opening" of $V_{10}O_{28}^{6-}$, as determined by these two very different methods, in closer agreement and within established error limits. Also, it must be remembered that the activation parameters as determined from exchange data depend on n, a number not known with great precision.

An estimation can be made of the equilibrium constant for the "opening" of the $V_{10}O_{28}^{6-}$ structure as defined by

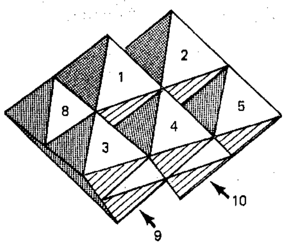
$$V_{10} \overset{k_{eq}}{\rightleftharpoons} V_{10}^*$$

It has been shown that[15] VO_4^{3-} and $V_2O_7^{4-}$ [16] have a $t_{1/2}$ for ^{18}O exchange of about 1 s at 25 °C ($k = 0.53\ s^{-1}$). Assuming the small fragment (V_4) to exchange with a like rate and that two of the nine possible oxygens are exchanged during one "lifetime", then the average lifetime at pH 7 and 25 °C is 0.47 s, $t_{1/2} = 0.33$ s, and k_{-1} is 2.1 s^{-1}. Then $k_1/k_{-1} = K_{eq} = (11.2 \times 10^{-5})/2.1 = 5.3 \times 10^{-5}$. This implies that with the concentration used in this work (~0.01 M) less than 0.01% of the V_{10} is in the partially bonded state at equilibrium and this small fraction could not be seen by any technique which has been applied.

The relationship between oxygen exchange and dissociation of the ion as revealed by pH dependencies of the rates of both reactions is consistent with an open-ended intermediate. In mildly acidic solution, pH 6.3, the partially detached (V_4) unit almost always reattaches its free end so that exchange occurs with essentially no decomposition. On the other hand, in more basic media the intermediate can completely dissociate and these fragments rapidly break down into equilibrium quantities of V_1 and V_2 units. Even very dilute hydroxide assists in cleaving the last V–O–V bridge leading to dissociation.

Two additional experiments tend to support the mechanistic suggestions presented. The first is the determination of the volume of activation of the exchange process. If the activated complex leading to exchange were "far along" toward dissociation into separate ions, then a relatively large negative $\Delta V^‡$ would be expected[13,17] because the number of charge centers would increase with accompanying solvent electrostriction. Thus, the small negative $\Delta V^‡$ observed (−5 cm^3/mol) suggests only a slight opening of the structure overcome with increased solvent water bonding. This is consistent with the small number of oxygens exchanged per event.[18] A completely reversible dissociation into a smaller fragment V_1–V_4 should result in a much larger negative value.

Experiments to determine the $^{49}VO_4^{3-}$–$V_{10}O_{28}^{6-}$ exchange cannot be done because the addition of VO_4^{3-}, at the pH of stability of $V_{10}O_{28}^{6-}$, would result in its almost complete conversion to the decavanadate form. If one conducts the isotopic exchange reaction under conditions where the V_{10} unit is thermodynamically unstable (that is, where decomposition and perhaps O exchange is occurring), then some information can be obtained about the vanadium exchange process. The experiments show clearly that at pH 11 no appreciable exchange takes place between VO_4^{3-} and $V_{10}O_{28}^{6-}$ during the time it takes for over half of the $V_{10}O_{28}^{6-}$ to dissociate into smaller units. During this time some (about 1.0%) oxygen exchange also takes place (not enough to conduct precise kinetic studies at this pH, however). This experiment establishes that the V_{10} unit, while undergoing irreversible



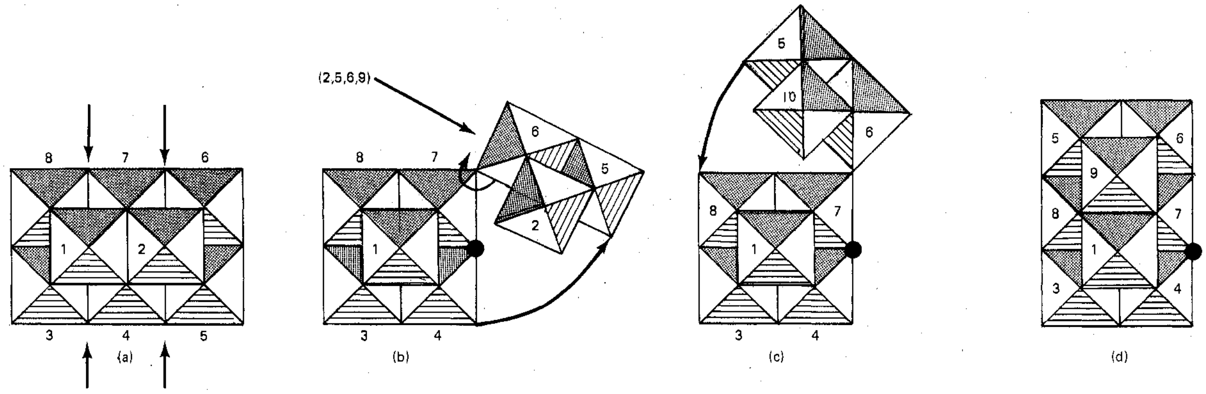
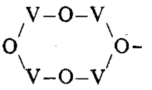


Figure 5. Diagram of the proposed exchange mechanism illustrating the change in the position of an oxygen which occurs as a result of this process. (a) Arrows indicate the four equivalent sites at which cleavage of a V–O–V bridge yields the half-bonded intermediate. (b) Cleavage between V_4 and V_5 produces a half-bonded intermediate. There are four sites to which V_5 may reattach; one is at its original position (V_4); the others (V_1, V_9, V_8) come about through rotation about the V_6–O–V_7 bridge. (c) After rotation about the V_6–O–V_7 bridge, V_5 of the half-bonded intermediate can reattach at V_8 (or V_1, V_9, V_4). (d) The normal decavanadate ion structure is re-formed as V_5 attaches to V_8. The solid oxygen is converted from an "inner" to an "outer" oxygen in the above process.

dissociation at a rate considerable greater than the O-exchange rate, does not reversibly dissociate into monovanadium units. These results are compatible with, but do not prove, an intermediate to oxygen exchange which is partially bonded.

While not conclusive, the evidence in favor of a partially dissociated ion as the oxygen exchange intermediate is strong enough to allow consideration of the size of the partially cleaved unit. Two criteria seem to suggest themselves: (a) the opening and closing process must make all oxygens in the ion equivalent (with respect to exchange); (b) the minimum number of structures should be necessary (preferably only the ion and the intermediate). By examining models it became apparent that the cyclic V_4 unit was unique in that when one end was unbonded it had four equivalent sites to reattach to re-form the parent ion. This act, and also the analogous reaction on the other side of the ion, converts the *central oxygen* atoms into *outer oxygens* and thus on a time average makes all oxygens equivalent. The cyclic V_4 unit



is the smallest which will systematically allow all oxygens to become equivalent without introducing additional ionic structures. Some other fragmentation patterns or combinations of them will also provide this equivalency of the oxygens, but none are as simple or as symmetrical as this model. The number of oxygens added to $V_{10}O_{28}^{6-}$ to give the intermediate with tetrahedral geometry about all four vanadium centers is two.

$$V_{10}O_{28}^{6-} + 2H_2O \rightleftharpoons V_6O_{18}\text{-}O\text{-}V_4O_{11}^{10-} + 4H^+$$

The added solvent oxygens would quickly become equivalent to the decavanadate oxygens and, upon recombination, oxygen exchange would be accomplished. Only a small number of oxygens per event would be exchanged.

Both of the subunits proposed are structurally similar to or identical with characterized species in vanadium(V) and other systems. For example, the V_4 ion has a cyclic structure which has been suggested for aqueous metavanadate ion on the basis of ^{51}V NMR,[19] Raman spectra,[20] and other studies.[21] The other subunit, V_6O_{18}–O, is structurally similar[3] to edge-shared polyanions found with Ta(V) and Mo(VI).

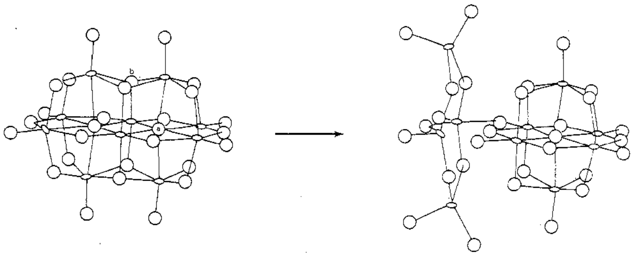


Figure 6. Formation of the proposed "half-bonded" intermediate.

With the ion constrained to remain in one piece in the intermediate, a relatively small volume increase would be involved in going to the activated complex and this would be easily offset by the decrease in volume associated with the loss of water from the solvent to vanadium coordination ($\Delta V \sim -10$ cm^3/mol for 1 mol of water) as it is incorporated into the "open-ended" intermediate. This would account for the small activation volume.

A pictorial description of the "half-bonded" dissociation process is given in Figure 5. The V_{10} unit is composed ideally of close-packed octahedra. By detaching a V_4 unit in a "hinge-like" manner, and reattaching in another equivalent position, V_{10} is re-formed with the internal oxygens now external and partial oxygen exchange with the solvent accomplished. A drawing of the postulated aquated "half-bonded" structure is given in Figure 6. The bonds broken in this dissociation are the longest in the solid structure.

A recent study[22] of the protonation sites of $V_{10}O_{28}^{6-}$ by Klemperer and Shum by ^{17}O NMR shows that the oxygens having the greatest negative charge (weakest bonding to vanadium) are those labeled O_a and O_b (Figure 6) which are the bonds which have to be broken to form the V_4 half-bonded intermediate. Protonation which occurs at O_b first (because O_a is internal) would be expected to weaken the $V–O_b$ bond and make dissociation more probable as is observed.

Finally, in the acidic region, pH >4, the initial rate constant for exchange increases dramatically. However, linear McKay graphs are not obtained indicating either (a) more than one kind of oxygen in the ion or (b) a chemical change with time. Experimentally the apparent rate of exchange decreases with time which makes (b) rather unlikely since it is difficult to suggest how the known depolymerization toward $VO_2^+(aq)$ could lower the rate of exchange of the remaining V_{10} entity. Postulate (a) seems more likely. The change in rate is due to nonequality of oxygens in the structure. The "outer" oxygens are more susceptible to an increase in rate due to protonation, while the "inner" oxygen rate is unperturbed by the acidic environment.

Summary

An interpretation of the ^{18}O exchange and base dissociation kinetics of $V_{10}O_{28}^{6-}$ has been made which postulates that decavanadate ion has an intrinsic rate of unwrapping to a partially bonded intermediate which is common to both the exchange and decomposition reactions. Closure of the partially bonded intermediate leads to oxygen exchange while rupture of the remaining bond leads to decomposition to smaller units. It is suggested that if the ion opens in only one way, the cyclic V_4 unit appears to be the most likely "half-bonded" unit to explain the exchange behavior.

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Registry No. $V_{10}O_{28}^{6-}$, 12397-12-5; ^{18}O, 14797-71-8; $V_2O_7^{4-}$, 22466-30-4; H^+, 12408-02-5.

References and Notes

(1) To whom correspondence should be directed.
(2) Abstracted in part from the M.S. Thesis of K. G., University of Missouri, 1977.
(3) M. T. Pope and B. W. Dale, *Q. Rev., Chem. Soc.*, **22**, 527 (1968); D. L. Kepert in "Comprehensive Inorganic Chemistry", J. C. Bailar, Ed., Pergamon Press, Elmsford, N.Y., 1973; R. J. H. Clark, *ibid.*
(4) For instance with hydroxides of lower valent transition ions or organic polymers.
(5) H. T. Evans, A. G. Swallow, and W. H. Barnes, *J. Am. Chem. Soc.*, **86**, 4209 (1964); A. G. Swallow, F. R. Ahmed, and W. H. Barnes, *Acta Crystallogr.*, **21**, 397 (1966); H. T. Evans, *Inorg. Chem.*, **5**, 967 (1966); H. T. Evans and S. B. Block, *ibid.*, **5**, 1808 (1966).
(6) Courtesy of G. K. Johnson from the data of A.G.S., F.R.A., W.H.B., ref 5.
(7) Schwartzenbach and G. Geier, *Helv. Chim. Acta*, **46**, 906 (1963).
(8) However see F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.*, **10**, 957, 968 (1956).
(9) Modified from K. Schiller and E. Thilo, *Z. Anorg. Allg. Chem.*, **310**, 286 (1961).
(10) R. K. Murmann, *J. Am. Chem. Soc.*, **96**, 7836 (1974).
(11) G. K. Johnson and R. K. Murmann, *Inorg. Synth.*, in press.
(12) J. B. Goddard and A. M. Gonas, *Inorg. Chem.*, **12**, 574 (1973); D. M. Druskovich and D. L. Kepert, *J. Chem. Soc., Dalton Trans.*, 947 (1975).
(13) C. A. Eckert, *Annu. Rev. Phys. Chem.*, **23**, 239 (1972).
(14) This value was obtained by rapid mixing and rapid pH measurement before appreciable dissociation took place. $T = 25\ °C$; $[V_{10}O_{28}^{6-}] = 0.02$ M. pK_{a_2} under the same conditions = 4.70.
(15) R. K. Murmann, *Inorg. Chem.*, **16**, 46 (1977).
(16) This work.
(17) D. R. Stranks and T. W. Swaddle, *J. Am. Chem. Soc.*, **93**, 2783 (1971).
(18) Assuming the oxygens of the partially bound fragment exchange at a rate of the same order of magnitude as VO_4^{3-} or slower.
(19) J. V. Hatton, Y. Saito, and W. G. Schneider, *Can. J. Chem.*, **43**, 47 (1965).
(20) W. P. Griffith and P. J. B. Lesniak, *J. Chem. Soc. A*, 1066 (1969).
(21) F. Brito, N. Ingri, and L. G. Sillen, *Acta Chem. Scand.*, **18**, 1557 (1964); O. Glemser and E. Presiler, *Z. Anorg. Chem.*, **303**, 343 (1960); W. P. Griffith, *J. Chem. Soc. A*, 905 (1967); G. K. Johnson, "Structures and Bonding of Large Polyvanadate Ions Containing V(IV)", Ph.D. Thesis, University of Missouri, 1977, p 7.
(22) W. G. Klemperer and W. Shum, *J. Am. Chem. Soc.*, **99**, 3544 (1977).

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Volumes of Activation for Isomerization and Acid-Catalyzed Aquation Reactions of Diaquobis(oxalato)- and Diaquobis(malonato)chromium(III) Complexes from High-Pressure Studies in Solution

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The effect of high pressure on the rates of isomerization in aqueous perchlorate solutions of *trans*-$[Cr(ox)_2(OH_2)_2]^-$ and *trans*-$[Cr(mal)_2(OH_2)_2]^-$ (ox^{2-} = oxalate; mal^{2-} = malonate) has been evaluated. The isomerization of *trans*-$[Cr(ox)_2(OH_2)_2]^-$ at pH 3.15 exhibits a volume of activation ($\Delta V^\ddagger$) of $-16.6\ cm^3\ mol^{-1}$ with a compressibility coefficient of activation ($\Delta\beta^\ddagger$) of $-1.8\ cm^3\ mol^{-1}\ kbar^{-1}$ which is shown to be consistent with isomerization through one-ended dissociation of an oxalato ligand. For the isomerization of *trans*-$[Cr(mal)_2(OH_2)_2]^-$ at pH 3.0, $\Delta V^\ddagger$ is $+8.9\ cm^3\ mol^{-1}$ with no measurable $\Delta\beta^\ddagger$, consistent with a mechanism via dissociative interchange of an aquo ligand. Enthalpies and entropies of activation evaluated for these systems are consistent with these separate mechanisms. The effect of high pressure on the acid-catalyzed aquation of *cis*-$[Cr(ox)_2(OH_2)_2]^-$ and *cis*-$[Cr(mal)_2(OH_2)_2]^-$ in perchloric acid solutions has also been determined. Volumes of activation are $\Delta V^\ddagger = +1.7\ cm^3\ mol^{-1}$ for *cis*-$[Cr(ox)_2(OH_2)_2]^-$ and $\Delta V^\ddagger = +2.4\ cm^3\ mol^{-1}$ for *cis*-$[Cr(mal)_2(OH_2)_2]^-$ and are consistent with one mechanism operating for both aquation reactions. A mechanism involving direct proton attack at a coordinated carboxylate and subsequent dissociative release of the protonated acid is most consistent with the determined volumes of activation. Enthalpies and entropies of activation were evaluated for each system; the negative $\Delta S^\ddagger$ observed for both reactions is also consistent with a common mechanistic pathway.

Introduction

Extensive investigations of the isomerization kinetics of *trans*-$[Cr(ox)_2(OH_2)_2]^-$ (ox^{2-} = oxalate dianion = $^-OOC–COO^-$) have been reported in the chemical literature.[1-14] The isomerization may be represented as equilibrium reaction 1

$$\text{trans} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \text{cis} \qquad (1)$$

in which $k_f \gg k_b$. The mechanism of the reaction has been interpreted by several authors in terms of a transition state involving a five-coordinate intermediate formed by one-ended dissociation of a bidentate oxalate. The variation of the isomerization rate with solvent,[13] the catalysis of the reaction by added ions,[9] and $H_2{}^{17}O$ ligand-exchange data[7,11] provide strong evidence to support this mechanism. The negative entropy of activation for isomerization has been interpreted

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