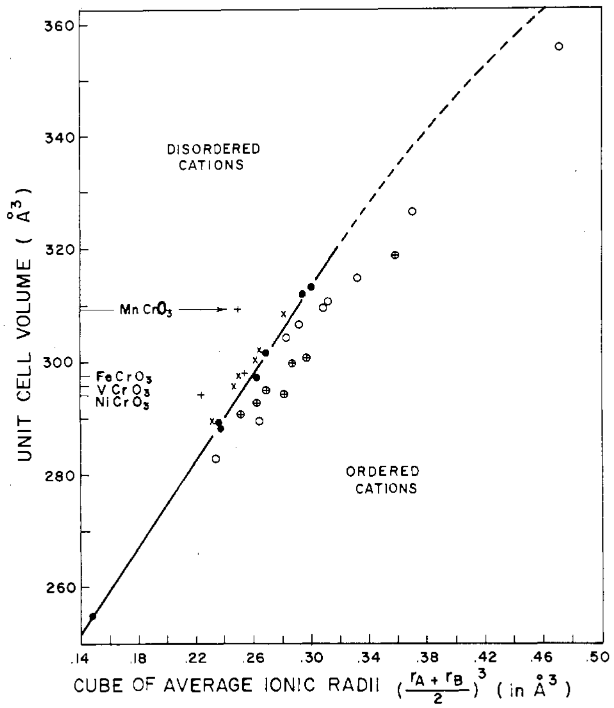

Figure 3. Plot of unit cell volumes vs. the cube of the average ionic radii for various A_2O_3 (corundum) and ABO_3 (mixed corundum and ilmenite) phases. The line and solid circles represent the pure corundum field. The mixed corundum compounds are represented by X (ambient pressure compounds) and by + (high-pressure phases). The ilmenite derivatives are represented by ○ (ambient-pressure phases) and by ⊕ (high-pressure phases).

high-pressure form of PtO_2. The high-temperature $\mu_{eff} = 20^{1/2}$ μ_B is consistent with the ionic configuration $Cr^{III}Mn^{V}O_4$, which would have a spin-only $\mu_{eff} = 23^{1/2}$ μ_B.

The magnetic and crystallographic data for the spinel, $Mn_{1.5}Cr_{1.5}O_4$, are consistent with the ionic configuration $Mn^{II}[Mn^{III}_{0.5}Cr^{III}_{1.5}]O_4$, the observed $\mu_{eff} = 62.1^{1/2}$ μ_B being in good agreement with the corresponding spin-only $\mu_{eff} = 69.5^{1/2}$ μ_B.

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Registry No. $MnCrO_3$, 37267-30-4; $CrMnO_4$, 60645-63-8; $Mn_{1.5}Cr_{1.5}O_4$, 60645-62-7; CrO_2, 12018-01-8; MnO_2, 1313-13-9; Cr_2O_3, 1308-38-9; MnO, 1344-43-0.

References and Notes

(1) The Lincoln Laboratory portion of this work was sponsored by the Department of the Air Force.
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Kinetics of Isotopic Oxygen Exchange between Water and Vanadium(V) in Basic Media

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The exchange between ^{18}O-labeled solvent water and vanadium(V) in basic media ($[OH^-] \geq 0.1$ M) has a half-time of ~20 s at 0 °C and is measurable by conventional sampling methods. Under selected conditions it has been shown that there are 4.0 ± 0.1 equivalent oxygens associated with aqueous vanadium(V) with half-times of exchange as great as 30 s at 0 °C. This supports the orthovanadate (VO_4^{3-}) structure as the predominant species in water at high pH. The rate of exchange follows the equation $R = k[VO_4^{3-}]$ and is essentially independent of $[OH^-]$ and of the nature of other ions in the medium. The rate is an inverse function of ionic strength and has activation parameters of $\Delta H^{\ddagger} = 22.0 \pm 0.8$ kcal/mol and $\Delta S^{\ddagger} = 14.4 \pm 1$ cal deg^{-1} mol^{-1} ($\mu = 1.4$). The reaction mechanism for water exchange is discussed.

Introduction

Progress in understanding the composition of aqueous vanadium(V) solutions, the structure of the oxo-polyanions present, and the kinetics of their interconversion has been hindered by the lack of well-characterized ions of "known" aqueous structure which could be used as "tie-points" in studies of the oligomerization process. An excellent review was presented by Pope and Dale in 1971.[1] In most studies it has been assumed that tetrahedral VO_4^{3-} in strongly alkaline solution and linear VO_2^+(aq) in strongly acidic media are the species present. It has been generally found that the experimental facts are consistent with these assumptions. In alkaline media, for example, investigations of rates of diffusion,[2] emf,[3] ^{51}V NMR,[4] Raman spectra,[5] and light scattering[6] are consistent with tetrahedral VO_4^{3-} in solution as is found in the solid state. Because of the well-established tendency of vanadium(V) to expand its coordination sphere from 4 to 5 or 6 as seen in solid structures,[7] a concern remains that vanadium(V) may exist, for example, as 5- or 6-coordinate $VO_2(OH)_3^{2-}$ or $VO_2(OH)_4^{3-}$ which certain types of studies seem to favor.[8]

This isotopic water-exchange study was undertaken with the hope of finding a slow enough rate of exchange to allow the number of oxygens around vanadium(V) to be counted in dilute water solution. We were encouraged along these lines by the recent observations[9] which showed $V_{10}O_{28}^{6-}$ to exchange its oxygens with solvent at a very slow rate ($t_{1/2} = 15$ h at 25 °C). Also of interest was the form of the rate equation governing exchange which would help in establishing the mechanism by which exchange takes place. In particular the questions of main interest were whether exchange takes place via an activated complex of higher or lower coordination number and/or through an oligomerization process.

While this study limits itself to the very alkaline region, having known standards at both the highly alkaline (VO_4^{3-}) and neutral ($V_{10}O_{28}^{6-}$) regions now allows studies in the middle region where numerous species are simultaneously present.

Experimental Section

Two sources of vanadium were used, $Na_3VO_4 \cdot nH_2O$ and V_2O_5. The former was twice crystallized from a 0.1 M NaOH–H_2O solution while the latter was converted to $(NH_4)_6V_{10}O_{28} \cdot 6H_2O$,[10] boiled with NaOH to release the NH_3 and to convert it to VO_4^{3-}, and recrystallized twice from a 0.1 M NaOH solution. Stock solutions of Na_3VO_4 in ^{18}O water were prepared from solid Na_3VO_4 in ^{18}O enriched water containing NaOH. Since oxygen exchange is rapid, isotopic equilibrium was reached in a few minutes.

Solutions of Li_3VO_4 in LiOH, K_3VO_4 in KOH, and $(Et_4N)_3VO_4$ in Et_4NOH were prepared from highly purified V_2O_5 and an excess of the appropriate base. The salts were not isolated or recrystallized but were analyzed for total vanadium and excess OH^-. All vanadium stock solutions were analyzed for vanadium (oxidation–reduction) and for OH^- (ion exchange) and were protected from changes due to absorption of atmospheric CO_2 or water. No differences were found between the VO_4^{3-} solutions prepared from the different sources. Both $[Co(NH_3)_6](OAc)_3$ and $[Co(en)_3](OAc)_3$ were used as precipitating agents because the chloride salts did not have the desired solubility. The ammine complex gave a faster precipitation and was more easily washed but the en complex was more stable in strongly basic solution and thus was preferable in high OH^-. Conventional methods produced the cobalt ammines as the chloride salt which after careful purification was ground with the stoichiometric amount of AgOAc in a small amount of water. After removal of solid AgCl the solution was concentrated at room temperature and crystallized by the addition of alcohol. After recrystallization the purified $[Co(NH_3)_6](OAc)_3$ was dissolved in the minimum amount of water at 25 °C, checked for neutrality with indicator paper and for excess Ag^+ or Cl^-, and stored at 0 °C until just before use.

Water used in these experiments was distilled from dilute acid $Cr_2O_7^{2-}$ and from basic MnO_4^- to ensure freedom from reducing impurities. All salts were of reagent grade and were recrystallized before use. Enrichments in ^{18}O were up to 4 times normal which has been shown to be in the linear range of the Nuclide ratio mass spectrometer used. Solid samples containing oxygen or water for ^{18}O analysis were converted to CO_2 using a mixture of $Hg(CN)_2$ and $HgCl_2$ at 425 °C for 4 h in sealed glass tubes. Purification of the resulting gases was accomplished by VPC utilizing silicone oil on firebrick at room temperature. The 46/(44 + 45) ratio (R) was determined on the purified CO_2 and compared to that of a normal standard sample arbitrarily given the value 4.00×10^{-3}. All values reported (R_n) have been normalized to this value. The concentrations $[OH^-]$ and $[VO_4^{3-}]_T$ in the exchanging solutions were calculated from the amounts of standard solutions diluted.

The basic experiment consisted of following the reaction

$$V^{18}O_n^{p-} + H_2O \overset{k}{\rightleftharpoons} VO_n^{p-} + H_2{}^{18}O$$

by sampling VO_n^{p-} as a function of time after mixing normal water with a ($V^{18}O_n^{p-}$–$H_2{}^{18}O$) solution. We chose precipitation of the vanadium anion as the sampling method since it conceivably could be done more rapidly and with greater accuracy than sampling solvent water. Considerable effort expended in finding the best precipitating agent led to the use of $[Co(NH_3)_6]^{3+}$. In the exploratory studies the $[Co(NH_3)_6]^{3+}$ salt was precipitated from 0.1–2.0 N NaOH, washed with water, alcohol, and acetone, and dried under vacuum. Anal. Calcd for $[Co(NH_3)_6]_4(V_2O_{11}H_8)_3$: C, 0.0; H, 6.44; N, 22.38; Co, 15.69. Found (water-washed complex): C, 0.28; H, 6.57; N, 22.97; Co, 15.73. This analysis corresponds to the anion $V_2O_7^{4-}$ and 4 H_2O. It was obvious that a change in the physical character of the precipitate occurred upon washing with water. In order to prevent this oligomerization, the initial precipitate from 0.5 M OH^- was washed with a small quantity of MeOH and then acetone; it was then dried in a stream of dry N_2. After vacuum-drying, the solid gave the following analysis, corresponding to the dihydrate of the VO_4^{3-} anion. Anal. Calcd. for $[Co(NH_3)_6]VO_4 \cdot 2H_2O$: C, 0.0; H, 7.11; N, 26.93; Co, 18.8. Found (CH_3OH-washed complex): C, 0.03; H, 7.09; N, 27.17; Co, 18.93. Apparently oligomerization was prevented and the excess NaOH and $[Co(NH_3)_6](OAc)_3$ did not contaminate the product. However, that analysis would conform to either $[Co(NH_3)_6]VO_4 \cdot 2H_2O$ or $[Co(NH_3)_6]VO_2(OH)_4$. In order to decide which structure is correct, experiments were conducted in which a concentrated solution of VO_4^{3-} in base was injected into a large amount of a basic water solution of normal ^{18}O content containing $[Co(NH_3)_6]Cl_3$. Precipitation was essentially instantaneous and complete and when conducted at 0 °C gave the results shown in Table I. Clearly some of the oxygen in the precipitate comes from the solvent but not all of it. For $[Co(NH_3)_6]VO_4 \cdot 2H_2O$ one might expect two oxygens of the final solvent composition and four oxygens of the initial vanadium solution composition. This is what is observed. If $[Co(NH_3)_6]VO_2(OH)_4$ were the correct formulation, one would expect four final solvent oxygens and two more highly enriched. This is clearly not the case. These results show that the vanadium in the precipitate retains four oxygens that it had in solution suggesting that it exists in basic aqueous media as (presumably tetrahedral) VO_4^{3-}. Further, these experiments show the rate of oxygen exchange between VO_4^{3-} and H_2O to be relatively slow at 0 °C and capable of being quantitatively studied by precipitation techniques.

Table I. Formula of Vanadate Ion (0.5 M NaOH, 0 °C)

R_n (vanadium soln)	9.587×10^{-3}
R_n (H_2O solvent)	3.995×10^{-3}
R_n calcd for $[Co(NH_3)_6]VO_4 \cdot 2H_2O$	7.723×10^{-3}
R_n calcd for $[Co(NH_3)_6]VO_2(OH)_4$	5.859×10^{-3}
R_n found	$(7.702 \pm 0.011) \times 10^{-3}$ [a]

[a] Deviation is the average of six determinations.

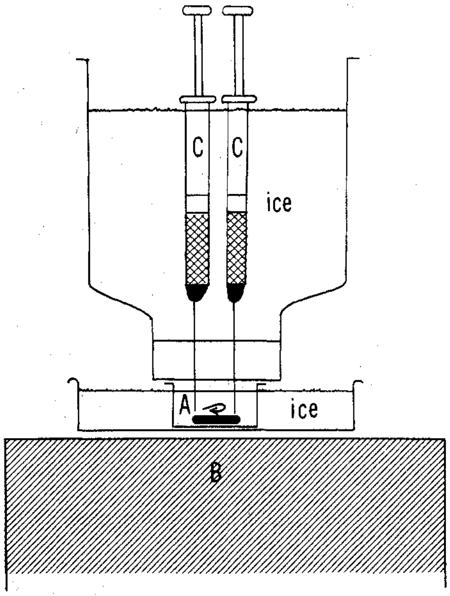


Figure 1. Rapid-injection apparatus: A, reaction vessel; B, Magnetic stirrer; C, reagents.

Utilizing the simple injection system shown in Figure 1 the isotopic exchange rate measurements consisted of injecting at t_0 150 µl of a Na_3VO_4 solution in NaOH equilibrated (>1 h) with $H_2{}^{18}O$ into 10.00 ml of normal H_2O containing NaOH. Rapid stirring and close temperature control (0 °C) were necessary. At carefully measured times, t, 500 µl of a cooled precipitating agent solution was injected. After roughly 10 s the mixture was transferred to a cooled centrifuge tube and the settled precipitate washed two times with small amounts of MeOH (anhydrous, 0 °C). It was shown in separate experiments that the precipitate did not change its isotopic composition ±2% by contact with this solvent at 0 °C for 8 min. Two washes with dry, cold acetone were followed by drying partially in a stream of N_2(dry) until the "cake" was free of the centrifuge tube and nearly dry. It

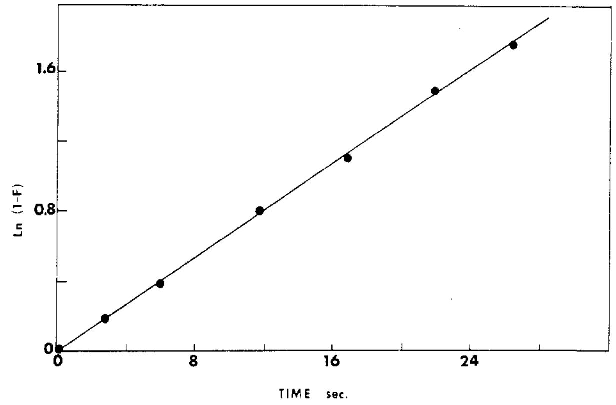


Figure 2. VO_4^{3-}–H_2O exchange: 0 °C, 0.5 M NaOH, 0.5 NaCl, 0.0241 M Na_3VO_4.

Table II. VO_4^{3-}–H_2O Oxygen Exchange (0 °C)

$[VO_4^{3-}]$, M	$[OH^-]$, M	$[Na]_T$, M	μ	10^2k_{obsd}, s^{-1}	$t_{1/2}$, s
0.0417	0.096	0.221	0.343	8.51 ± 0.29[c]	8.1
0.0417	0.186	0.312	0.436	5.32 ± 0.04	13.0
0.0417	0.459[a]	0.579	0.704	2.73 ± 0.10	25.4
0.0513	0.912	1.066	1.220	2.05 ± 0.03	33.8
0.0513	0.231	0.381	0.537	5.10 ± 0.05	13.6
0.0513	0.048[b]	0.248	0.40	6.63 ± 0.05	10.5
0.0513	0.139	0.293	0.45	6.03 ± 0.04	11.5

[a] VO_4^{3-} stock contained no excess OH^-. [b] 0.0484 M NaCl present. [c] ± values represent 1 σ.

was transferred to a break-seal tube and placed under low pressure, 10^{-5} mmHg, at least overnight or until converted into CO_2. The time of injection of $[Co(NH_3)_6]^{3+}$ could be estimated to 0.1 s and precipitation was over in an estimated 0.1 s. (In the very basic regions, crystallization was slightly slower and represents a small systematic error.) In solutions of low basicity, a concentrated NaOH solution was added to convert to 0.5 M OH^- before $[Co(NH_3)_6]^{3+}$ was added. This was done to ensure the correct precipitate composition. No unusual effects were found with this treatment. The time for reagent injection and the time for mixing were judged to be somewhat less than 0.1 s and the measurement of the elapsed time of reaction appeared to be the quantity limiting accuracy in most experiments. Only in the most basic media (1 M NaOH) was the effective reaction time significantly greater than the measured due to slow precipitation. Crude corrections (of 0.2 s or less) were made for this effect. Since the $t_{1/2}$ was greater in the more concentrated salt solutions (including NaOH), this correction introduced only a small uncertainty into the observed rate constant. Graphs of $-\ln(1 - F)$ vs. time, where F equals the fraction exchanged, were linear and k_{obsd} was obtained from the slope of such curves. Error values (±) are one standard deviation (σ) of the slope. Using the usual symbolism and assuming a first- and zero-order dependence on $[VO_4^{3-}]$ and $[H_2O]$, we have

$$k[VO_4^{3-}] = R_{overall} = k_{obsd}\{4[VO_4^{3-}][H_2O]/(4[VO_4^{3-}] + [H_2O])\}\ M\ s^{-1}$$

Assuming $[H_2O] >> 4[VO_4^{3-}]$, which is true to 1–2%, yields k, the rate constant of exchange, $= 4k_{obsd}$. The first-order dependency in $[VO_4^{3-}]$ was demonstrated but the water dependence is not known.

Results

An example of a kinetic determination for one of the slower reactions is given in Figure 2. It is representative of the precision of the timing, sampling, and measurement methods employed. Each rate determination was shown to be linear to at least 2 half-lives but the number of experimental points per determination was smaller, ~4, with a range of 3–8 excluding 0 and ∞ values. It is clear from this graph that the precipitation technique, the ^{18}O analysis, and the timing were accurate to at least 5% and that exchange induced by the precipitation, washing, and drying procedures was negligible.

Table III. Temperature Dependence of k_{obsd}[a]

Temp, °C	10^2k_{obsd}, s^{-1}	Temp, °C	10^2k_{obsd}, s^{-1}
0.0	2.43 ± 0.03	10.0	10.52 ± 0.13
5.0	4.91 ± 0.06		

[a] 0.50 M NaCl, 0.50 NaOH, $[VO_4^{3-}] = 0.0513$ M. $\Delta H^{\ddagger} = 22.0 \pm 0.8$ kcal/mol; $\Delta S^{\ddagger} = 14.4 \pm 1$ eu.

Table IV. $[VO_4^{3-}]$ Dependence of k_{obsd}[a]

$[VO_4^{3-}]$, M	10^2k_{obsd}, s^{-1}	$[VO_4^{3-}]$, M	10^2k_{obsd}, s^{-1}
0.0736	4.42 ± 0.05	0.0269	4.91 ± 0.09
0.0513	4.90 ± 0.07	0.0138	4.93 ± 0.04
0.0393	4.94 ± 0.06		

[a] $[OH^-] = 0.20$ M, $[Na]_T = 0.63$ M using NaCl; 0 °C.

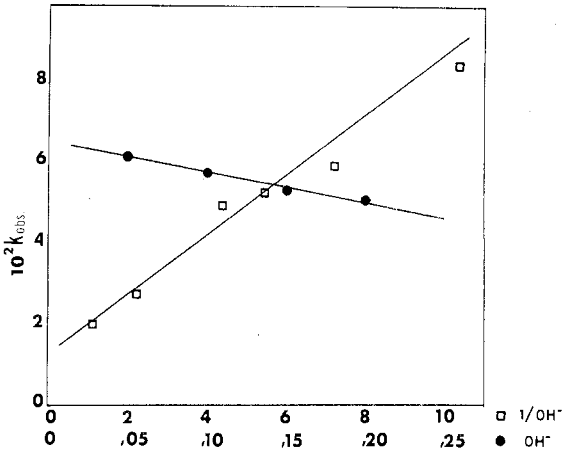


Figure 3. VO_4^{3-}–H_2O exchange rate constants (0 °C): □, μ not constant; ●, $[Na^+]$ constant with NaCl at 0.357 M. (Units: k_{obsd}, s^{-1}; $[OH^-]$, M.)

The standard deviation of the slope, and thus of k_{obsd}, was in the 1–2% range for an individual determination (Table II), while replicate runs with new standard solutions were reproducible to within 3–4%. An independent measurement by another investigator[11] using his own reagents and apparatus but the same mass spectrometer agreed within 5% for nearly identical concentration conditions.

The temperature dependence is shown in Table III. The range is limited since accuracy decreases with $t_{1/2}$. At 5 and 10 °C the reaction mixture was quickly cooled to 0 °C at the same time the precipitant was injected to hasten precipitation. Solutions high in salts were used to lengthen $t_{1/2}$ and deemphasize systematic errors. The reaction follows the equation $k_{obsd} = (2.7 \pm 0.1) \times 10^{16} e^{-22\,500 \pm 800)/RT}$ (s^{-1}) in 0.5 M NaCl, 0.5 M NaOH, and 0.02 M Na_3VO_4.

Studies on the $[VO_4^{3-}]$ dependence are summarized in Table IV. The ionic strength was essentially constant. The aqueous media for exchange had $[Na^+]_T$ at a constant value since it was shown that the rate is a function of [positive ion]$_T$. The constancy of k_{obsd} over a range of $[VO_4^{3-}]$ from 0.014 to 0.074 M is excellent with only the highest concentration deviating significantly. If $R_{overall} = k[VO_4^{3-}]$ (first-order dependence on VO_4^{3-}), then k_{obsd} should be independent of $[VO_4^{3-}]$ as was found.

Of special interest from a mechanistic standpoint is the $[OH^-]$ dependence. A graph of k_{obsd} vs. $1/[OH^-]$ (squares) is given in Figure 3. While $[VO_4^{3-}]_T$ is constant, $[Na^+]_T$ and μ increase with [NaOH]. It would appear that an inverse relationship exists between k_{obsd} and $[OH^-]$. However the rate constant is also highly dependent on the presence of other salts, i.e., NaCl; in fact, NaCl is essentially as effective as NaOH

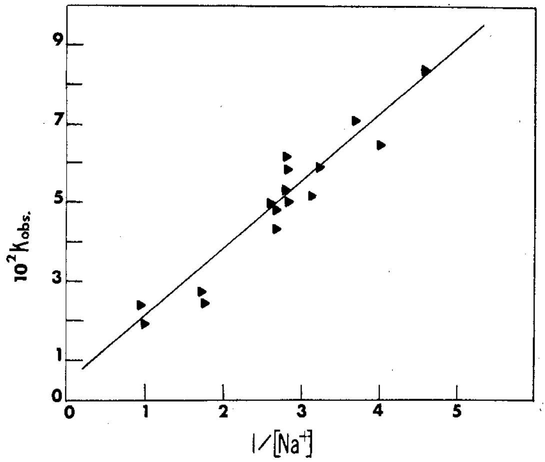


Figure 4. VO_4^{3-}–H_2O exchange rate constants at 0 °C, with $[OH^-]$ varying from 0.1 to 1 M; supporting electrolyte NaCl. (Units: k_{obsd}, s^{-1}; $1/[Na^+]$, M^{-1}.)

Table V. Positive Ion Effects (0 °C)

Salt	$[OH^-]$, M	$[VO_4^{3-}]$, M	10^2k_{obsd}, s^{-1}	μ	$t_{1/2}$, s
Li^+	0.223	0.0291	4.89 ± 0.05	0.809	14.2
Et_4N^+	0.175	0.0114	5.21 ± 0.12	0.648	13.3
Na^+	0.231	0.0241	4.78 ± 0.06	0.915	14.5
K^+	0.200	0.0171	5.08 ± 0.13	0.982	13.6

Table VI. VO_4^{3-}–H_2O Exchange Rates (0 °C)[a]

Salt	$[M^+]_T$, M	$[VO_4^{3-}]$,[b] M	10^2k_{obsd}, s^{-1}	$t_{1/2}$, s
NaCl	1.06	0.0517	2.43 ± 0.08	28.5
KCl	1.06	0.0501	3.54 ± 0.07	19.6
KNO_3	1.04	0.0505	4.13 ± 0.15	16.8
KBr	1.06	0.0501	3.57 ± 0.05	19.4

[a] $[OH^-] = 0.50$ M (same ion as salt). [b] VO_4^{3-} as Na^+ salt.

in diminishing the rate constant. In the same figure k_{obsd} is given as a function of $[OH^-]$ with $[Na^+]_T = 0.357$ (μ is essentially constant also). Over a range of fourfold in $[OH^-]$ the rate constant changes by only 23% with a constant positive ion environment. Figure 4 contains k_{obsd} as a function of $1/[Na^+]_T$. In these runs $[OH^-]$ varied from 0.1 to 1.1 M nonsystematically. The data are consistent with a linear relationship which is useful for prediction purposes ($k_{obsd} = (1.69 \pm 0.15) \times 10^{-2}/[Na^+]_T + (0.49 \pm 0.51) \times 10^{-2}$ s^{-1}). It is felt that the data are not of sufficient precision to warrant fitting with an additional parameter to describe the weak $[OH^-]$ effect.

Table V shows the effect of changing the positive ion. Experimentally it was not possible to prepare solutions of exactly the same concentrations. However, the order $Et_4N^+ > K^+ > Li^+ > Na^+$ is probably correct and it is clear that Na^+ is more effective in diminishing the rate of exchange than the others. This can also be noted in Table VI with respect to Na^+ and K^+. The main conclusion of Table VI, however, is that the negative ion of the supporting electrolyte has practically no specific effect on the rate constant of exchange.

Discussion

Coordination Number of Vanadium(V) in Basic Media. The structure and composition of the first coordination sphere of vanadium(V) when in relatively dilute aqueous media are of fundamental interest. In basic solution it is generally suggested that orthovanadate ion (VO_4^{3-}) is the predominant species but little direct evidence is available to support this contention. It is also generally thought from both qualitative and quantitative studies that the V^V anion tends to have a variable coordination number (especially in the solid state), protonates at relatively low acidity, and oligomerizes at mild vanadium(V) concentrations. The first hydrolysis constant seems to be fairly well agreed upon[12-14] being about pK = 1.0 for

$$VO_4^{3-} + H_2O \rightleftharpoons HVO_4^{2-} + OH^-$$

and the dimerization constant is apparently about[14] pK = −1.7 for

$$2HVO_4^{2-} \rightleftharpoons V_2O_7^{4-} + H_2O$$

Both of these equations could equally well be written with a larger first coordination sphere for either the reactants or products. In 0.5 M NaOH and about 0.02 M total V^V, hydrolysis may be tentatively neglected and we may view in a simplistic manner the various possibilities as a choice between the extremes VO_4^{3-} and $VO_2(OH)_4^{3-}$. While the composition of the $Co(NH_3)_6^{3+}$-precipitated V^V may have no relationship to the composition of the main aqueous vanadium anion, the elemental analysis fits either of these possibilities as $VO_4^{3-}\cdot 2H_2O$ or $VO_2(OH)_4^{3-}$. The ^{18}O-tracer experiments show the precipitated vanadate oxygen to retain some of the enrichment originally in the V^V anion, if a minimal time for exchange is allowed, while reaching the solvent ^{18}O composition after much longer periods. Quantitative experiments of this type were used to distinguish between the possible structures for the aqueous V^V anion. The major pertinent facts revealed by these studies are as follows. (a) Oxygen exchange between the oxy anion and water is slow. By precipitation, at least 95% of the exchange can be prevented at 0 °C. (b) The percent ^{18}O retention by the precipitated anion is reproducible. (c) The ^{18}O enrichment in the precipitate results from a ratio of two vanadium to one solvent oxygen.

Since there are, by analysis, six oxygens in $[Co(NH_3)_6]VO_6H_4$, four have the ^{18}O content of the original vanadium oxygen and two have the final solvent composition. Upon heating of the solid hydrate under vacuum, the initial water driven off proved to be of the same composition as the final solvent. In later portions some exchange apparently occurred. Since $VO_2(OH)_4^{3-}$ would be expected to have four labile and at most two nonlabile oxygens, it does not conform to the experimental results. It is clear that 4.0 ± 0.1 oxygens around V^V are slow to exchange which is consistent with the VO_4^{3-} structure, the other two oxygens being hydration water of the solid. The degree of protonation and thus the charge on the anion in solution cannot be estimated by ^{18}O measurements. If one accepts the suggested protonation constants, an appreciable fraction of the anion is protonated in the experimental media used. Nevertheless, the form crystallized is VO_4^{3-} due perhaps to the like charge on the cation. Little information about this protonation can be obtained from ^{18}O kinetic measurements since, as will be established later, the kinetics of oxygen exchange are surprisingly insensitive to acidity.

VO_4^{3-}–H_2O Oxygen Exchange Kinetics. The equilibration of ^{18}O between VO_4^{3-} and water when expressed as $-\ln(1 - F)$ is linear with time for at least 4 half-lives. This is in agreement with the expected equivalency of the four oxygens in the tetrahedral VO_4^{3-}. It does not allow the presence of significant amounts of oligomers in slow equilibrium with the monomer. Although quite rapid, the exchange rate is reproducible to better than 5% when using new reagents or a different experimenter. The observed rate constant is independent of the total vanadium concentration over a range where a substantial fractional change in the concentration of oligomers but not of the monomer occur (based on suggested K_{eq}'s). This strongly suggests that the rate-controlling expression for exchange is $R = k[VO_4^{3-}]$ (neglecting the unknown order in water) and one may ask if the process leading to the activated state is basically associative or dissociative.

Information relating to this question is limited and lies in the acid–base effects and the salt dependency. It should be noted that because of limited solubility in organic solvents it is not possible to determine the order with respect to water and the rapidity of the exchange prevents a determination of $\Delta V^{\ddagger}$ by pressure dependency studies. A qualitative summary of the pH and salt effects is that the basicity changes possible make only a minor change in the exchange rate while the effect of added salt is by comparison large and negative. This behavior is radically different from that of other oxy anions which have been studied where the acid or base dependency is of major importance and the salt effect minimal. Three reasonable explanations have been considered. First, the apparent decrease in k_{obsd} with increasing $[OH^-]$ is small enough to be a minor specific negative ion effect of about the same magnitude as found for the differences between Cl^- and Br^- or NO_3^- (Table VI). Alternatively, it may be viewed as a positive hydrogen ion dependency of relatively small magnitude. Second, since $K_{a_1}(HVO_4^{2-})$ is about 10^{-13} and $K_{a_2}(H_2VO_4^-)$ is about 10^{-8}, a large portion of the total vanadium is singly protonated in the basic region studied (0.05–1 M OH^-). Using the constant-μ studies, $[OH^-] = 0.05$–0.20 M, and a two-term rate law comprising the major species present, we have

$$R_{overall} = 4k_{obsd}C_0 = k_0[VO_4^{3-}] + k_H[HOVO_3^{2-}] \text{ M s}^{-1}$$

$$4k_{obsd} = k = k_0 + (k_H - k_0)\frac{[H^+]}{[H^+] + K_{a_1}}$$

where $K_{a_1} = 1 \times 10^{-13}$ and C_0 is the total vanadium concentration (0.050 M). A linear least-squares fit gave $r = 0.992$ (correlation coefficient), $k_0 = 0.167 \pm 0.003$ s^{-1}, and $k_H = 0.296 \pm 0.026$ s^{-1}. Third, a likely possibility for explaining the base dependence is suggested by the fact that most oxy anion exchange laws have a second-order and no first-order hydrogen ion dependence.[15,16] Assuming VO_4^{3-} and $HOVO_3^{2-}$ react with the same constant, k_0, and that $(HO)_2VO_2^-$ has a different rate constant, k_{H_2}, the following equation applies using the same symbolism as above

$$4k_{obsd} = k = k_0 + \frac{k_{H_2}[H^+]^2}{K_{a_2}([H^+] + K_{a_1})}$$

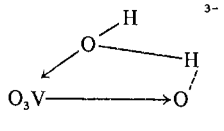
Analysis of the same data by linear least squares gave $r = 0.949$, $k_0 = 0.209 \pm 0.006$ s^{-1}, and $k_{H_2} = (3.4 \pm 8) \times 10^3$ s^{-1}. Obvious curvature to the data was present in the latter graphical evaluation. While other rate laws could be applied, the limited range and accuracy of the data do not warrant more than two fitting parameters. Of the three explanations suggested, the first two fit well and are about equally probable, while the third, having a $[H^+]^2$ term, is not very probable.

The negative salt effect is in the same direction as noted for the water exchange of ReO_4^- [17] and other oxy anions.[18] With VO_4^{3-} the changes are much larger than with the previously studied 1– charged ions and their magnitude is no doubt related to the increased association with the positive ion of the salt. Since the majority of the exchange is carried by the k_0 term, this salt effect must reside primarily in it. Replacing M^+ for H^+ in the VO_4^{3-}–$HOVO_3^{2-}$ equilibria could only have a small negative effect on the rate constant. In explaining the salt effect, the following need to be considered: (a) association with M^+ is considerable; (b) M^+ behaves in an opposite direction to H^+; (c) activity coefficient changes are too small to account for the rate constant changes; (d) Me_4N^+ behaves similarly to alkali metal ions. A complete explanation is not possible but it would appear that decreased availability of water to the anion is responsible for the slower exchange. This comes about through association of the anion oxygens with salt cations and through water association to the added salt. This would suggest that, in the activated complex, appreciable bonding to an incoming water molecule has occurred which implies that bond making has achieved more importance than in other systems.

A comparison of the Arrhenius parameters for VO_4^{3-} compared to those for ReO_4^- [17] shows remarkable differences in view of the fact that the ionic radius is about the same for V^V (0.59 Å) and Re^{VII} (0.56 Å).[19]

	E^*, kcal/mol	log A
VO_4^{3-}	22	16.4
$ReO_4^-(k_0)$	15	3.5

If the mechanism of the exchange follows the suggested[17] solvent-assisted oxygen dissociation



the activation energy would be a function of the requirements for stretching the VO bond and those required for increasing the coordination number by bringing a solvent molecule into the first coordination sphere. With ReO_4^- it has been shown[20] that the solvent H_2O does not enter the rate equation and thus dissociation facilitated by solvent hydrogen bonding describes the mechanism. If a similar mechanism exists for VO_4^{3-}, association with the solvent must be much more important. On charge alone V^V should have a lower E^* than Re^{VII} and size mitigates against vanadium also. Thus the higher E^* can be viewed as required to bring a water molecule into the inner coordination sphere with the concurrent V–O bond stretching. The higher activation energy is more than overcome by the larger A value. One expects this to arise from a more easily deformed tetrahedral ion in VO_4^{3-}, that is, one which has a higher probability of expanding its coordination number due to the lower formal charge on the metal ion. This is in qualitative agreement with the known tendency of V^V to expand its coordination number in solid structures and the reluctancy of Re^{VII} to do so.

These results suggest a prediction that TcO_4^- should be almost as slow as ReO_4^- (on the basis of size and charge) while MoO_4^{2-} and WO_4^{2-} would exchange at about the same velocity as VO_4^{3-}.

A comparison with the well-studied CrO_4^{2-} system[21] is of especial interest. It was clearly established that when the pH was >10, the exchange followed the expression

$$R = k[CrO_4^{2-}] \quad (k_{CrO_4^{2-}} = 2.7 \times 10^{-7}, k_{VO_4^{3-}} = 10^{-2} \text{ s}^{-1})$$

with only a very small positive hydrogen ion dependency, which is analogous to that found for VO_4^{3-}. On the other hand, no salt dependence was found ($NaClO_4$) in the range $\mu = 2.5$–6.0 for CrO_4^{2-}. The large changes in k_{obsd} found for VO_4^{3-} due to inert salts are in the lower concentration region $\mu < 1.2$ and are not apparent at the higher salt concentrations. In the pH range 6.7–10 dimerization reactions become dominant and the overall rate has the form

$$R = k[H^+][Cr^{VI}]^2 + k'[H^+]^2[Cr^{VI}]^2$$

It is likely that similar terms in the less basic regions exist for the vanadate system as well.

One may conclude from K_{hyd} of VO_4^{3-} and the dimerization constant that an appreciable amount of "dimer" is present under the conditions used in these studies, especially in the low-base region. This does not show up in the ^{18}O-exchange rate. Preliminary experiments[22] using solutions containing predominantly $V_2O_7^{4-}$ and Ba^{2+} as the precipitating agent give an exchange rate in the same range as those presented for VO_4^{3-}. While not highly precise, these results establish that the rate of ^{18}O exchange of $V_2O_7^{4-}$ and the rate of reversible "dimerization" are of the same magnitude as the exchange rate of VO_4^{3-}.

Further ^{18}O studies are anticipated to give information concerning the extent of oligomerization and the nature of the ions in the region between VO_4^{3-} and $V_{10}O_{28}^{6-}$.

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Registry No. VO_4^{3-}, 14333-18-7; H_2O, 7732-18-5; $[Co(NH_3)_6]_4(V_2O_7)_3$, 60645-68-3; $[Co(NH_3)_6]VO_4$, 60645-69-4.

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Synthesis of Binary Gold Carbonyls, $Au(CO)_n$ (*n* = 1 or 2). Spectroscopic Evidence for Isocarbonyl(carbonyl)gold, a Linkage Isomer of Bis(carbonyl)gold

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The cocondensation reaction of Au atoms with CO/M mixtures (where M = Ne, Ar, Kr, or Xe) at 6–10 K leads to the formation of authentic binary gold carbonyls, $Au(CO)_n$ (where *n* = 1 or 2). These complexes were characterized using metal and ligand concentration studies, $^{12}C^{16}O/^{13}C^{16}O/M$ isotopic substitution, and warm-up experiments in conjunction with matrix infrared and uv–visible spectroscopy as well as isotope frequency and intensity calculations. The infrared data for bis(carbonyl)gold favor a linear, symmetrical $D_{\infty h}$ structure. Detailed investigations of the complexes in inert gas matrices revealed a variety of interesting site effects and matrix-induced frequency shifts. The latter can be rationalized in terms of Buckingham's theory of nonspecific solvent shifts applied to matrix-isolated species. Particularly noteworthy were the unusual vibrational isotope patterns observed for the product formed when gold atoms were deposited with $^{12}C^{16}O/^{13}C^{16}O$, $^{12}C^{16}O/^{12}C^{18}O$, and $^{12}C^{16}O/^{13}C^{18}O$ mixtures. Ten distinct, mixed isotopic molecules containing *nonequivalent* carbonyl ligands were identified. An a priori interpretation of the isotopic shifts was in terms of an isocarbonyl(carbonyl)gold complex, (OC)Au(OC), a linkage isomer of bis(carbonyl)gold. The existence of the linkage isomer is thought to be a consequence of the head-to-tail orientational requirements of the CO molecules in the fccub lattice of crystalline carbon monoxide, rather than an inherent preference for the isocarbonyl isomer. Similar results were obtained in the isomorphous α-N_2 lattice under both high- and low-concentration conditions and lend credence to the idea of a lattice-stabilized isocarbonyl–carbonyl complex. Additional information was obtained from the corresponding uv-visible spectra in Ar/CO and CO matrices, respectively. In this context, the results of extended Hückel molecular orbital calculations proved to be quite helpful for understanding the differences between a symmetrical C-bonded dicarbonyl, an asymmetrical C-bonded dicarbonyl, and an isocarbonyl–carbonyl complex.

Introduction

Since the very early failures to synthesize group 1B carbonyls,[1] the chemistry of zerovalent gold has remained elusive. However, with the recent discovery that group 1B metal atoms are highly reactive toward carbon monoxide at cryogenic temperatures, it has proven possible to synthesize and characterize binary carbonyls of the form $M(CO)_n$ and $M_2(CO)_6$ (M = Cu, Ag; *n* = 1–3) using matrix-isolation techniques.[2]

We have now extended our earlier studies with Cu and Ag atoms to include Au atoms in an effort to complete our knowledge of the carbon monoxide complexes of the coinage metals. Rather than providing a simple extension of the Cu/CO and Ag/CO systems, the Au/CO reaction products exhibited some chemically intriguing differences.

In brief, only *two* mononuclear carbonyls of gold, $Au(CO)_n$ (*n* = 1 or 2), could be synthesized in CO/M matrices (M = Ar, Kr, Xe) whereas *three* carbonyls, $M(CO)_m$ (*m* = 1–3), could be obtained for copper and silver.

Of considerable chemical interest was the discovery that a complex with the spectroscopic characteristics of isocarbonyl(carbonyl)gold, Au(CO)(OC), a linkage isomer of $Au(CO)_2$, could be stabilized in pure CO and N_2 lattices, whereas no compelling evidence was obtained for linkage isomers of the corresponding copper or silver carbonyls.

The following is a detailed account of our investigations.

Experimental Section

Monatomic Au was generated either by directly heating a thin tungsten rod (0.025 in.) around the center of which was wound gold wire (0.005 in.) or by directly heating a tantalum Knudsen cell (wall thickness 0.015 in., orifice diameter 0.010–0.020 in.), the Au being contained in a boron nitride liner (wall thickness 0.010 in.). The gold metal (99.99%) was supplied by Imperial Smelting Co., Toronto. Research grade $^{12}C^{16}O$ (99.99%) was supplied by Matheson of Canada, $^{12}C^{16}O/^{13}C^{16}O$ and $^{12}C^{16}O/^{12}C^{18}O$ isotopic mixtures were supplied by Stohler, Montreal, and $^{12}C^{16}O/^{13}C^{18}O$ mixtures were supplied by Prochem, Summit, N.J. The furnace used for the evaporation of the metal has been previously described.[3] The rate of metal atom deposition was continuously monitored using a quartz crystal microbalance.[4] To obtain quantitative data for Au/CO and Au/CO/M (M = Ne, Ar, Kr, Xe, or N_2) cocondensations, it was necessary to calibrate carefully the rate of deposition of both metal