

ording to the gravimetric results. The optimum fit to the absorbance data, which is based upon a minimum average deviation of eq 13 for all experimental points, and which is shown in Figure 2, is found for $K = (1.46 \pm 0.13) \times 10^{-9} \text{ mol}^{-1} \text{ L}$, $K' = (0.75 \pm 0.11) \times 10^{-9} \text{ mol}^{-1} \text{ L}$, $\epsilon_{\text{Se}_2\text{Cl}_2} = 3300 \text{ cm}^{-1} \text{ mol}^{-1} \text{ L}$, and $\epsilon_{\text{SeCl}_2} = 500 \text{ cm}^{-1} \text{ mol}^{-1} \text{ L}$. The agreement with the gravimetric equilibrium constants is excellent. However, for reasons given above, the spectrophotometric equilibrium constants are preferred. Moreover, the fit of these constants to the gravimetric results is within the error of the gravimetric analysis as shown in Figure 3. Unfortunately the c_0 data are of insufficient precision to determine the solubility of elemental selenium in hydrochloric acid.

Conclusion

Although the presence of Se_2Cl_2 in concentrated HCl solutions is not unexpected at these concentrations, the presence

of SeCl_2 has not yet been reported. The precise nature of the Se(I) and Se(II) species in these solutions is not known, but in view of the weak chloride acceptor power of SeOCl_2 in aqueous solution,⁴ it is unlikely that the lower oxidation state species would form Se_2Cl_3^- , SeCl_3^- , or similar anions. The existence of species such as ClSeSe(OH) or ClSe(OH) is a possibility however.

Resolution of the electronic spectrum of the Se(II) species is made difficult by the strong absorbance of SeOCl_2 and Se_2Cl_2 in the spectra, but work is continuing in this direction for both aqueous and nonaqueous media.

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Registry No. SeO_2 , 7446-08-4; SeCl_2 , 14457-70-6; Se_2Cl_2 , 10025-68-0; HCl, 7647-01-0; Se, 7782-49-2.

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Kinetics and Mechanism of the Oxidation of Hexaaquovanadium(II) Ions by Aliphatic Radicals¹

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$\text{V(H}_2\text{O)}_6^{2+}$ is oxidized to V^{3+} by $\cdot\text{C(CH}_3)_2\text{OH}$ and by $\cdot\text{CH(CH}_3)_2\text{OC}_2\text{H}_5$, with formation of $(\text{CH}_3)_2\text{CHOH}$ and $(\text{C}_2\text{H}_5)_2\text{O}$, respectively. The rate constants were determined by kinetic competition methods based on the homolytic decomposition of organopentaaquochromium(III) cations. The rate constants for the respective reactions are 2.1×10^5 and $5.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (at 25 °C, 0.2–1.0 M H^+). The former reaction has $k = 3.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ in 92% D_2O . The mechanisms considered are (1) rate-limiting acidolysis of a seven-coordinate organovanadium species present in steady-state equilibrium with the reactants and (2) abstraction by the aliphatic radical of a hydrogen atom from a water molecule coordinated to vanadium(II). These possibilities are considered in light of data on the oxidation of $(\text{CH}_3)_2\text{CHOH}$ by Co^{3+} and Mn^{3+} .

Introduction

To the best of our knowledge no kinetic or other studies of the reactions of vanadium(II) complexes with aliphatic radicals have been reported. Generation of $\cdot\text{CH}_3$ in the presence of $\text{V(H}_2\text{O)}_6^{2+}$ results in the formation of methane,² suggesting a direct reaction of V^{2+} and the free radical, lest the latter dimerize.

We earlier found that a large number of organochromium cations $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ undergo homolytic decomposition in aqueous acidic solution.³ This opened the door to a new method for evaluating free-radical rate constants, not just because the decomposition of the CrR^{2+} complexes generates the free radical by the reaction $\text{CrR}^{2+} \rightleftharpoons \text{Cr}^{2+} + \cdot\text{R}$ but because (a) the slowness of this reaction keeps the free-radical concentration at a low, steady-state value, preventing its dimerization or disproportionation, and (b) its reversibility by addition of Cr^{2+} occurs at a known rate for a large number of radicals.⁴ This method⁵ relies on the competitive fate of the radical between its return to CrR^{2+} by reaction with Cr^{2+} vs. its reaction with the substrate of interest, $\text{V(H}_2\text{O)}_6^{2+}$ in the present case.

We chose to examine the reactions of $\text{V(H}_2\text{O)}_6^{2+}$ and two aliphatic radicals— $\cdot\text{C(CH}_3)_2\text{OH}$ and $\cdot\text{CH(CH}_3)_2\text{OC}_2\text{H}_5$ —in aqueous perchloric acid solutions, pH 0–3. These widely investigated radicals typically act as thermodynamically powerful and kinetically reactive reducing agents. E° has been estimated⁶ as $\sim -1.2 \text{ V}$ vs. NHE for $(\text{CH}_3)_2\text{CO} + \text{H}^+ + \text{e}^- = \cdot\text{C(CH}_3)_2\text{OH}$. Although much less often exemplified in practice, these free radicals may also function as oxidizing agents, e.g., $\cdot\text{C(CH}_3)_2\text{OH} + \text{H}^+ + \text{e}^- = (\text{CH}_3)_2\text{CHOH}$. Relatively few examples of the latter have been reported, however, especially for transition-metal complexes. Of the few cases examined, the reactions appear to involve metastable organometallic intermediates. Such reactions include Cr^{2+} ,^{4,7} Fe^{2+} ,⁸ Ni^+ ,⁹ Zn^+ ,¹⁰ Cd^+ ,¹¹ Pb^+ ,¹² Ti^{3+} ,¹³ and possibly Cu^+ .¹⁴

- (1) Based on the Ph.D. thesis of J.T.C., Iowa State University, 1982.
- (2) Gold, V.; Wood, D. L. *J. Chem. Soc., Dalton Trans.* **1982**, 2462.
- (3) Kirker, G. W.; Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 1249.
- (4) Cohen, H.; Meyerstein, M. *Inorg. Chem.* **1974**, *13*, 2434.
- (5) Espenson, J. H.; Shimura, M.; Bakač, A. *Inorg. Chem.* **1982**, *21*, 2537.

- (6) Endicott, J. F. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; pp 90–92.
- (7) Schmidt, W. A.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1116.
- (8) Pribush, A. G.; Brusentseva, S. A.; Shubin, V. N.; Dolin, P. I. *High Energy Chem. (Engl. Transl.)* **1975**, *9*, 206.
- (9) Rabani, J.; Mulac, W. A.; Matheson, M. S. *J. Phys. Chem.* **1977**, *81*, 99.
- (10) Kelm, M.; Lilie, J.; Henglein, A.; Janata, E. *J. Phys. Chem.* **1974**, *78*, 882.
- (11) Kelm, M.; Lilie, J.; Henglein, A. *J. Chem. Soc., Faraday Trans. 1* **1975**, *5*, 1132.
- (12) Breitenkamp, M.; Henglein, A.; Lilie, J. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 973.
- (13) Behar, D.; Samuni, A.; Fessenden, R. W. *J. Phys. Chem.* **1973**, *77*, 2055.

The reactions of $V(H_2O)_6^{2+}$ with these two aliphatic radicals were studied to identify the reactions, to show that they are bimolecular reactions between V^{2+} and $R\cdot$, to evaluate their rate constants, to search directly for possible reaction intermediate (such as organovanadium complexes), and to apply indirect methods such as the deuterium isotope effect and kinetic analogies to the determination of the reaction mechanism.

Experimental Section

Reagents. The organochromium complexes were prepared^{3,7} from the reaction of chromium(II) ions and hydrogen peroxide in perchloric acid solutions containing 2-propanol (~1 M) or diethyl ether (~0.5 M).^{5,7,15} The short lifetime of $CrC(CH_3)_2OH^{2+}$ prevented its isolation and purification, and it was used immediately after preparation in solutions containing a known excess of Cr^{2+} . Solutions containing the complex $CrCH(CH_3)OC_2H_5^{2+}$ were purified by anaerobic ion-exchange chromatography on Sephadex C-25, eluting this species with slightly acidified 0.25 M sodium perchlorate. Solutions of $CrCH(CH_3)OC_2H_5^{2+}$ were stored up to 2 weeks at $-10^\circ C$ under nitrogen.

The solution of vanadium(II) perchlorate was prepared by reduction of perchloric acid solutions of vanadyl perchlorate by amalgamated zinc. The vanadyl perchlorate was prepared in solution by ion-exchange elution of vanadyl sulfate with sodium perchlorate after all sulfate ions were rinsed from the resin column. Concentrations of VO^{2+} were determined spectrophotometrically, $\epsilon_{760} = 17.2 M^{-1} cm^{-1}$, and the concentration of H^+ was determined by titrating the ion-exchange eluent with standard sodium hydroxide.

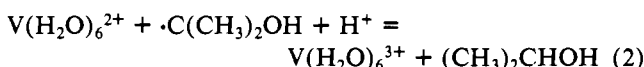
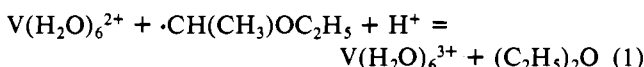
Products. Organic products were separated from the aqueous or semiaqueous reaction solutions and identified by GLC, HPLC, or GC-MS with use of authentic compounds for comparison. Diethyl ether, separated by extraction into chloroform, was identified and determined by GLC on a 5% FFAP column with use of a Perkin-Elmer 3920 B instrument with FID. 2-Propanol was separated by sorption onto XAD-4, elution with chloroform, GLC separation on a nonpolar capillary column, and mass spectrometric determination of $(C-H_3)_2CDOD$ carried out in the presence of larger amounts of protonated compound. The formation of $V(H_2O)_6^{3+}$ from the reaction of V^{2+} with $\cdot C(CH_3)_2OH$ was confirmed by studying the subsequent reaction of the product solution with Cr^{2+} .

Kinetics. The decomposition of the organochromium cations was monitored at an absorption maximum (λ 311 and 407 nm for $CrC(CH_3)_2OH^{2+}$, λ 396 nm for $CrCH(CH_3)OC_2H_5^{2+}$) with a Cary Model 219 recording spectrophotometer equipped with a thermostated cell holder. In a typical experiment involving $CrCH(CH_3)OC_2H_5^{2+}$, the desired concentrations of chromium(II) and vanadium(II) ions, perchloric acid, and lithium perchlorate (to maintain constant ionic strength) were introduced into a serum-capped cuvette purged with Cr^{2+} -scrubbed nitrogen. After temperature equilibration, reaction was initiated by injection of $CrCH(CH_3)OC_2H_5^{2+}$. A modified procedure was used for $CrC(CH_3)_2OH^{2+}$, whose faster decay makes purification impossible. Into a deaerated solution containing 2-propanol, perchloric acid, lithium perchlorate, and chromium(II) perchlorate an insufficient quantity of hydrogen peroxide was first injected (leaving behind known concentrations of Cr^{2+} and $CrC(CH_3)_2OH^{2+}$), followed immediately by V^{2+} , all solutions being separately thermostated.

The kinetic data followed a pseudo-first-order rate equation and were analyzed by standard least-squares methods to yield rate constants designated herein as k_{obsd} .

Results

Products and Stoichiometry. In both reactions vanadium(II) ions are oxidized by the free radical, according to

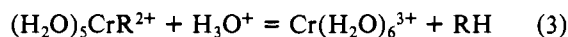


The first reaction is easier to deal with because (a) the longer-lived organochromium cation can be purified chromatographically and thus freed of all organic material and (b) this organochromium cation decomposes almost exclusively by the homolytic pathway in the presence of V^{2+} , the non-radical, heterolytic pathway ("acidolysis") being so slow as to contribute <1% under the conditions used in the product determinations.³ The reaction between $CrCH(CH_3)OC_2H_5^{2+}$ and a large excess of V^{2+} was carried out in a solution initially containing no Cr^{2+} . The chloroform extracts were shown to contain diethyl ether as the only organic product detectable by GLC; in particular, acetaldehyde was absent. The yield of diethyl ether was 90% of that expected from eq 1 based on calibration with the authentic material similarly extracted.

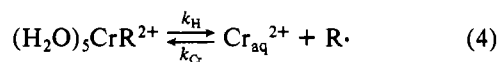
In the case of $CrC(CH_3)_2OH^{2+}$, where 2-propanol is present in the reaction, resort to isotopic labeling was essential. A concentrated solution of this complex in H_2O having a relatively low [2-propanol] was injected, immediately after its preparation, into a solution of $V(D_2O)_6^{2+}$ in 99% D_2O having $[D_3O^+] = 0.1 M$. The organic product(s) were taken up on XAD-4, eluted therefrom with chloroform, and examined on a nonpolar capillary GC column. Blanks consisted of (a) authentic 2-propanol and (b) identical solutions except that acidolysis of the organochromium cation was allowed to proceed to completion according to eq 3 before addition to $V(D_2O)_6^{2+}$ in D_2O . Acetone was absent from the reaction products, and only 2-propanol was detected. It was significantly enriched in deuterium in comparison to both blanks. This qualitative result supports eq 2.

The production of $V(H_2O)_6^{3+}$ in eq 2 was verified by injecting additional Cr^{2+} at the end of the run. There ensued a measurable spectral change, which we attribute to the reaction $V^{3+} + Cr^{2+} = V^{2+} + Cr^{3+}$ because (a) the amplitude of the absorbance change at λ 408 nm agrees with that calculated by the assumption that V^{3+} was quantitatively produced in eq 2 and (b) the rate constant determined from the experiment with the assumption of initial concentrations of V^{3+} and Cr^{2+} , based on the reactions shown, is $0.75 M^{-1} s^{-1}$, which agrees with the literature value,¹⁶ $0.71 M^{-1} s^{-1}$ at these conditions ($25^\circ C$, $0.77 M H^+$).

Kinetics. Three competing chemical reactions are important in the analysis of the reaction kinetics. The first is the previously studied^{3,5,7} acidolysis reaction



The rate constants for acidolysis (k_A) of both of the complexes studied are known or were evaluated under the conditions of the study.¹⁷ The second (eq 4) consists of the homolytic



dissociation of the chromium-carbon bond. The rate constant for its reverse—capture of the aliphatic radical by Cr^{2+} —has been evaluated directly with the pulse radiolysis technique.⁴ Both rate constants are known from earlier work.¹⁸ The reactions with vanadium(II), eq 1 and 2, have rate constants we symbolize as k_V . Self-reaction between two radicals is not important under any of the conditions employed, since the

(16) Espenson, J. H. *Inorg. Chem.* **1965**, *4*, 1025.

(17) The value for $CrCH(CH_3)OC_2H_5^{2+}$ is $k_A/s^{-1} = (5 \times 10^{-7}) + (3.1 \times 10^{-3})[H^+]$.⁷ For $CrC(CH_3)_2OH^{2+}$ the values of $10^3 k_A/s^{-1}$ at $25.0^\circ C$ are as follows: $3.85 + 3.50[H^+]$ ($\mu = 0.10 M$), $3.31 + 4.91[H^+]$ ($\mu = 1.00$),⁷ and $3.29 + 6.90[H^+]$ ($\mu = 1.50 M$). The composite values at $0.200 M H^+$ and $\mu = 0.50 M$ are 4.64×10^{-3} and $1.43 \times 10^{-3} s^{-1}$ in H_2O and D_2O (92%), respectively.

(18) The rate constants for $CrCH(CH_3)OC_2H_5^{2+}$ are $k_H = 2.04 \times 10^{-3} s^{-1}$ ($25.0^\circ C$)³ and $k_{Cr} = 3.4 \times 10^7 M^{-1} s^{-1}$ ($22 \pm 3^\circ C$).⁴ For $CrC(CH_3)_2OH^{2+}$, $k_H = 0.127 s^{-1}$ ($25.0^\circ C$)³ or $0.129 s^{-1}$ in D_2O ,⁵ and $k_{Cr} = 5.1 \times 10^7 M^{-1} s^{-1}$ ($22 \pm 3^\circ C$).⁴

(14) Buxton, G. V.; Green, J. C. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 697.

(15) Bakač A.; Espenson, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 2721.

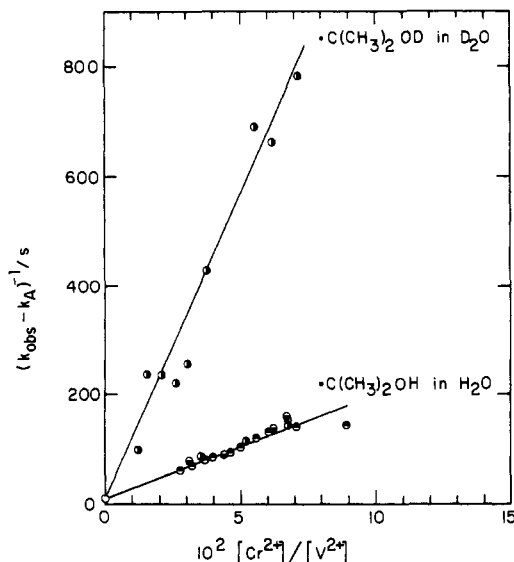


Figure 1. Linear relationship between the reciprocal of the rate constant enhancement, $1/(k_{\text{obs}} - k_A)$, and the ratio of the concentrations of the competing metal ions in H_2O (lower line) and in 92% D_2O (upper line) as expected from eq 6. Different values of $[\text{H}^+]$ and ionic strength are indicated by the following symbols: (●) 0.2 M H^+ and 1.0 M ionic strength; (◐) 0.5 and 1.5; (◑) 1.0 and 1.5; (◒) 0.5 and 1.0.

added quantities of the reactive Cr^{2+} and V^{2+} ions keep the radical concentrations quite low.

In view of that, the steady-state approximation for the concentration of the free radical will be applicable. The rate of disappearance of the organochromium complex is thus given by

$$-\frac{d[\text{CrR}^{2+}]}{dt} = \left(k_A + \frac{k_H k_V [\text{V}^{2+}]}{k_{\text{Cr}} [\text{Cr}^{2+}] + k_V [\text{V}^{2+}]} \right) [\text{CrR}^{2+}] \quad (5)$$

Provided experiments are done with initial concentrations of vanadium(II) and chromium(II) ions that are much higher than that of the organochromium complex, the reaction will follow pseudo-first-order kinetics with the quantity in parentheses being k_{obs} . Rearrangement of the expression for k_{obs} affords a relation (eq 6) that permits a graphical analysis of the data as shown in Figure 1. The value of k_V is the only unknown in this equation, and its value

$$\frac{1}{k_{\text{obs}} - k_A} = \frac{1}{k_H} + \frac{k_{\text{Cr}}}{k_H k_V} \frac{[\text{Cr}^{2+}]}{[\text{V}^{2+}]} \quad (6)$$

can be calculated from the slope of the straight line drawn through the data.

In practice the numerical analysis was done with use of a nonlinear least-squares program to fit the data to eq 5, with the values of k_A , k_H , and k_{Cr} fixed at their independently known values. The resulting values of k_V , which proved to be independent of $[\text{H}^+]$ from 0.2 to 1.0 M, are summarized in Table II. The ratio k_V/k_{Cr} and presumably k_V and k_{Cr} individually also were invariant with ionic strength, $0.5 < \mu < 1.5$ M. (In that analysis allowance was made for small changes¹⁷ of k_A with ionic strength, although k_H is known to be constant.)

A second set of determinations was carried out to evaluate the rate constant for the reaction of $\cdot\text{C}(\text{CH}_3)\text{OD}$ with $\text{V}(\text{D}_2\text{O})_6^{2+}$ in $\text{D}_2\text{O}/\text{D}_3\text{O}^+$ solutions having a 92% enrichment of D_2O . The effect of deuterium substitution on the other rate constants, k_A and k_H , needed for the analysis of the kinetic data according to eq 5 can be evaluated independently; k_A is appreciably altered,^{3,7,17} but k_H changes by $<1\%$. As is immediately clear from Figure 1, there is a very major kinetic

Table I. Kinetic Data for the Oxidation of $\text{V}(\text{H}_2\text{O})_6^{2+}$ by 2-Hydroxy-2-propyl Radicals^a

$[\text{H}^+]$, μM	$[\text{Cr}^{2+}]_0/[\text{V}^{2+}]^b$	$10^2 k_{\text{obs}}/\text{s}^{-1} \text{ c}$	
		exptl	calcd ^d
1.0, 1.5	0.0280	2.64	2.65
0.2, 1.5	0.0311	1.86	1.95
1.0, 1.5	0.0320	2.44	2.47
0.2, 0.5	0.0355	1.61	1.78
1.0, 1.5	0.0368	2.25	2.30
1.0, 1.5	0.0400	2.18	2.21
0.2, 1.5	0.0446	1.58	1.54
1.0, 1.5	0.0463	2.11	2.06
1.0, 1.5	0.0500	2.09	1.99
0.2, 0.5	0.0518	1.35	1.40
1.0, 1.5	0.0559	1.84	1.89
1.0, 1.5	0.0561	1.82	1.89
1.0, 1.5	0.0603	1.78	1.83
0.2, 1.5	0.0624	1.20	1.25
0.2, 0.5	0.0682	1.16	1.19
0.2, 1.0	0.0682	1.08	1.15
0.2, 1.5	0.0682	1.09	1.19
1.0, 1.5	0.0709	1.73	1.72
1.0, 1.5	0.0890	1.71	1.58

^a At 25.0 °C in aqueous solution containing 1.0 M 2-propanol.

^b Individual ranges: $2.5 < 10^3 [\text{Cr}^{2+}] < 4.2$; $3.6 < 10^2 [\text{V}^{2+}] < 11.2$.

^c The pseudo-first-order rate constant. ^d According to eq 5 with all the rate constants fixed at their known values (see text and ref 17 and 18) except k_V , which refined to the value $(2.10 \pm 0.05) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

Table II. Summary of the Rate Constants for the Oxidation of Vanadium(II) Ions by Aliphatic Radicals

radical	$10^3 k_V/k_{\text{Cr}}^a$	$k_V/\text{M}^{-1} \text{ s}^{-1} \text{ b}$
$\cdot\text{C}(\text{CH}_3)_2\text{OH}$ (in H_2O)	4.12 ± 0.09	2.1×10^5
$\cdot\text{C}(\text{CH}_3)_2\text{OD}$ (in D_2O) ^c	0.707 ± 0.095	$3.6 \times 10^4 \text{ d}$
$\cdot\text{CH}(\text{CH}_3)\text{OC}_2\text{H}_5$ (in H_2O)	1.74 ± 0.12	5.9×10^4

^a At 25.0 °C; the uncertainty shown for the ratio represents one standard deviation in the least-squares analysis of the kinetic data according to eq 5. ^b Using $k_{\text{Cr}} = 5.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ($\cdot\text{C}(\text{CH}_3)_2\text{OH}$) and $3.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (for $\cdot\text{CH}(\text{CH}_3)\text{OC}_2\text{H}_5$), as determined at 22 ± 2 °C with an accuracy of $\sim 15\%$. ^c In 92% D_2O . ^d Assuming k_{Cr} has no solvent isotope effect.

effect accompanying deuterium enrichment. The kinetic data still adhere to the linear relation of eq 6 but with a markedly steeper slope (the intercept is, of course, common to both since it represents only the isotopically independent k_H). The steeper slope thus implies $(k_{\text{Cr}}/k_V)_{\text{D}_2\text{O}} > (k_{\text{Cr}}/k_V)_{\text{H}_2\text{O}}$; the ratio of these values is 5.8 by comparing 92% D_2O with H_2O .

Interpretation and Discussion

Kinetic Isotope Effects. There is a substantially larger value of $(k_{\text{Cr}}/k_V)_{\text{D}_2\text{O}}$ as compared to that of $(k_{\text{Cr}}/k_V)_{\text{H}_2\text{O}}$. We suggest that the effect lies almost entirely in the change of k_V . Although the deuterium isotope effect on k_{Cr} has not been explicitly determined, arguments can be advanced that it is small. The same technique has recently been used to evaluate the kinetics of the reaction of $\cdot\text{C}(\text{CH}_3)_2\text{OH}$ with $\text{Co}(\text{NH}_3)_6^{3+}$ in the two solvents.⁵ In this case, unlike the V^{2+} reaction, the protons of coordinated NH_3 's do not exchange rapidly with solvent protons; thus one can separate the two isotopic effects. The results give $(k_{\text{Cr}}/k_{\text{Co}})_{\text{D}_2\text{O}}/(k_{\text{Cr}}/k_{\text{Co}})_{\text{H}_2\text{O}} = 0.9$ for $\text{Co}(\text{NH}_3)_6^{3+}$ and 1.2 for $\text{Co}(\text{ND}_3)_6^{3+}$. The likely conclusion is that the values of k_{Cr} and of k_{Co} themselves, as well as the ratio, are each largely independent of the isotopic change in the solvent. Although it could always be argued that the rate constants k_{Co} and k_{Cr} change by the same amounts, the simpler conclusion is strengthened by two chemical arguments. First, the chemical reaction represented by k_{Cr} consists of chromium-carbon bond formation accompanied or preceded by chromium-oxygen scission; no solvent isotope effect should accompany this process. Second, the microscopic reverse of

the k_{C_r} reaction is homolysis, characterized by the isotopically independent rate constant k_H . Since it is not likely that the equilibrium constant for homolytic scission, given by k_H/k_{C_r} , will vary appreciably with the proportion of D_2O , k_{C_r} can also be taken as nearly constant.

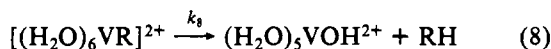
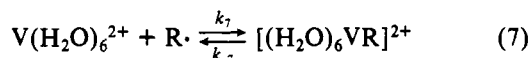
On that basis, therefore, we estimate $(k_V)_{H_2O}/(k_V)_{D_2O}$ is ~ 6 . The whole-number accuracy suffices because the measurements were done only at 92% D_2O and because the argued constancy of k_{C_r} is only an approximation.

These arguments do not settle a similar but separate matter—how to apportion the isotope effect on k_V between solvent effects (included in which is the change from $\cdot C(CH_3)_2OH$ to $\cdot C(CH_3)_2OD$) and genuine chemical effects of the two entities $V(H_2O)_6^{2+}$ and $V(D_2O)_6^{2+}$. We suggest that the former factor is much smaller. Note that the previously mentioned findings⁵ for hexaamminecobalt(III) ions—a situation where the two phenomena are distinct—gave $(k_{Co})_{D_2O} \approx (k_{Co})_{H_2O}$. In the one case the radical reduces the Co(III) complex; in the other it oxidizes V(II). The role of the solvent may also be very different. Nonetheless the ratio of the k_V 's is so large that it seems necessary to attribute the majority of the isotope effect to authentic differences in reactivity between $V(H_2O)_6^{2+}$ and $V(D_2O)_6^{2+}$.

Reaction Mechanism. The results served to substantiate that the reaction occurring consists of the oxidation of $V(H_2O)_6^{2+}$ by the radicals as shown in eq 1 and 2. An acceptable mechanism must not only yield these products but must account for (1) the kinetic expression, $-d[V^{2+}]/dt = k_V[V^{2+}][R\cdot]$, which is implicit in the derivation of eq 5 and has been confirmed by the precise fit of the kinetic data, (2) the isotope effect, which, as discussed above, gives $(k_V)_{H_2O}/(k_V)_{D_2O} \approx 6$, and (3) the magnitude of the k_V values considering other chemistry of the reactants.

Most if not all of the previous examples of the oxidation of metal ions by these radicals are believed to proceed by formation of a metal-carbon bond. If such is the case here, then the following features are characteristic in this case: (1) the organovanadium intermediate (VR^{2+} , formally a V(III) complex) is not $V(H_2O)_5R^{2+}$ since the requisite displacement of coordinated water in the primary coordination sphere of $V(H_2O)_6^{2+}$ is too slow ($k < \sim 30 M^{-1} s^{-1}$) in comparison with k_V , unless the radical somehow avails itself of a pathway not open to two-electron ligands; (2) a seven-coordinate organovanadium intermediate, if invoked in the mechanism, would need to have a lifetime short compared to the timing of these kinetic experiments, or < 5 s, since no intermediate could be detected; (3) formation of an organovanadium intermediate could not reasonably be postulated as the rate-limiting step since it should show an insignificant deuterium isotope effect contrary to the large effect for k_V .

One mechanism fitting these requirements consists of seven-coordination, followed by acidolysis of the postulated adduct:



If the steady-state approximation is made for the concentration of the intermediates,¹⁹ the expression for k_V is $k_7k_8/(k_{-7} + k_8)$. It is necessary, since neither k_7 nor k_{-7} would show an appreciable isotope effect, for k_8 to be a small or negligible part of the summation in the denominator of the general expression.

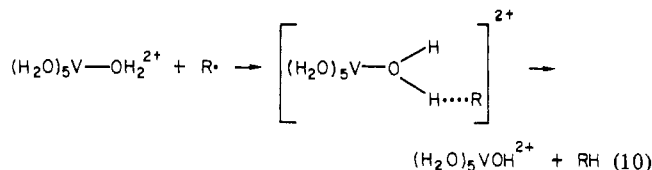
(19) Or, a preequilibrium approximation, leading to rate = $k_8k_7[V^{2+}]/(1 + K_7[V^{2+}])$, which reduces to the requisite second-order form only if an inappreciable concentration of the intermediate is present, such that $K_7[V^{2+}] \ll 1$. In that case $k_V = k_8K_7$, a result equivalent to the steady-state treatment given in the text.

Indeed the most likely form has

$$k_V \approx k_7k_8/k_{-7} \quad (9)$$

A very substantial isotope effect is to be expected for k_8 , as modeled by analogous results observed directly for several CrR^{2+} complexes.^{5,20,21} For example, $(H_2O)_5CrC(CH_3)_2OH^{2+}$ and $(H_2O)_5CrCH_2OH^{2+}$ have $(k_A)_{H_2O}/(k_A)_{D_2O} = 6.3^5$ and 8.4^{21} respectively. These values are in accord with the ratio found for k_V .

A second mechanism can be proposed to account for the observations. In this alternative, no organovanadium intermediate is invoked; rather, the mechanism consists of direct hydrogen atom abstraction from a water molecule coordinated to a vanadium(II) ion:



following which the hydroxovanadium(III) ion very rapidly equilibrates with H_3O^+ to yield $V(H_2O)_6^{3+}$ ($pK_a \approx 3-4$). The attractive feature of this mechanism is that it provides explanations for the form of the rate equation and for the existence of an appreciable deuterium isotope effect without resort to an unverified organometallic intermediate.

The thermodynamic feasibility of this process—despite the fact that it consists of hydrogen atom abstraction from an O-H bond by a carbon-centered radical—is indicated by the weakened O-H bond strength of water molecules coordinated to metal ions²³ and by the reducing strength of V^{2+} .

Both mechanisms appear to be in accord with the data available at this time. Examples, as yet unknown, of the free-radical oxidation of $V^{II}L_6$ complexes with $L \neq H_2O$ would be instructive, as would the search for the transient interaction of aliphatic radicals with vanadium(II) ions.

Implications for the Oxidation of 2-Propanol. The oxidation of $(CH_3)_2CHOH$ to acetone by powerful one-electron oxidizing agents proceeds in two steps by way of the $\cdot C(CH_3)_2OH$ radical as an intermediate. The first step is rate limiting, and it can be considered in the context of the present work since it is the exact reverse of the transformation effected by $V(H_2O)_6^{2+}$. The considerations offered here are limited to reactions of $Co(H_2O)_6^{3+}$ ²⁴ and $Mn(H_2O)_6^{3+}$ ²⁵ since in the other cases studied complicated (Ce^{IV})²⁶ or uncertain (Cr^{IV})²⁷ hydrolytic equilibria may intervene. The two hydrated cations oxidize 2-propanol by rate laws of strikingly different form

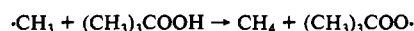
$$-d[M^{3+}]/dt = k_M[M^{3+}][(CH_3)_2CHOH][H^+]^n \quad (11)$$

where the major if not exclusive pathways have $n = -1$ for Co^{3+} and $n = 0$ for Mn^{3+} .

(20) Ryan, D. A.; Espenson, J. H. *Inorg. Chem.* **1981**, *20*, 4401.

(21) Gold, V.; Wood, D. L. *J. Chem. Soc., Dalton Trans.* **1981**, 2452.

(22) Note, however, that suitably strong C-H bonds do form at the expense of weak O-H bonds, as in



as reported by: Seubold, F. H.; Rust, F. F.; Vaughan, W. E. *J. Am. Chem. Soc.* **1951**, *73*, 18.

(23) Berdnikov, V. M. *Russ. J. Phys. Chem. (Engl. Transl.)* **1973**, *47*, 1547. This author considers whether a hydrogen atom abstraction mechanism can account for the oxidation of certain hydrated metal ions by hydroxyl radical, $HO\cdot + M(H_2O)_6^{2+} \rightarrow (H_2O)_5MOH^{2+} + H_2O$, a point discussed further by: Buxton, G. V.; Sellers, R. M. *Coord. Chem. Rev.* **1977**, *22*, 202.

(24) Hoare, D. G.; Waters, W. A. *J. Chem. Soc.* **1962**, 965.

(25) Wells, C. F.; Davie, G. *Trans. Faraday Soc.* **1967**, *63*, 2736.

(26) Wells, C. F.; Hussain, M. *Trans. Faraday Soc.* **1970**, *66*, 679.

(27) Rahnan, M.; Roček, J. *J. Am. Chem. Soc.* **1971**, *93*, 5455.

The inverse $[H^+]$ dependence for Co^{3+} undoubtedly signals $(H_2O)_5CoOH^{2+}$ to be the kinetically active form. This *might*, as suggested earlier, be because the labilizing effect of coordinated OH^- accelerates the rate of alcohol penetration of the coordination sphere of the low-spin d^6 $Co(III)$ complex. On the other hand, it might instead imply a more definite chemical role of the OH group in the mechanism, possibly through a hydrogen atom transfer mechanism. Such a possibility is then, by the microscopic reversibility, the effective reverse of one of the mechanisms suggested for $V(H_2O)_6^{2+}$ (eq 10). It further

suggests that there may be differences between the mechanisms for Co^{3+} and Mn^{3+} that should not be overlooked.

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Registry No. $V(H_2O)_6^{2+}$, 15696-18-1; $-C(CH_3)_2OH$, 7277-18-1; $-CH(CH_3)OEt$, 2229-06-3; deuterium, 7782-39-0.

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Isomeric Forms of the Complexes of Tetraammineruthenium(III) and -(II) with Glycinamide and Derivatives

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When *cis*-diaquopentaammineruthenium(III) at a pH such that one of the coordinated water molecules is deprotonated reacts with any of the three amides featured in this work, glycylglycine, glycinamide, and *N*'-ethylglycinamide, in the resulting tetraammine the chelate ring closes on the nitrogen of the amide group (the (N,N') form). The uncatalyzed transformation of these chelates to the (N,O) forms is extremely slow, but the latter can be produced by reducing ruthenium to the 2+ state in acidic solution and reoxidizing. The two forms are distinguished by the differences in pK_a —these are ~ -1 and 5.0 ± 0.2 , respectively, for the (N,N') and (N,O) forms of the glycinamide chelates—and by the differences in the ligand to metal charge-transfer absorptions, which at a pH of 1 lie at much lower energies for the (N,N') chelates. By taking advantage of the lability of the $Ru(II)$ chelates and the labilization of the $Ru(III)$ species by $Ru(II)$, and by applying electrochemical and other equilibrium measurements, it has been possible to measure the equilibrium quotients governing the distribution of the species between the (N,N') and (N,O) forms. For glycinamide as the ligand, the equilibrium ratio $Ru^{II}(N,N')/Ru^{II}(N,O)$ at 25 °C when both species are protonated is 1.6×10^{-4} , but as the pH is raised, the (N,N') chelate becomes stable relative to the (N,O) because it is the more acidic ($pK_{a(N,N')} = 4.3 \pm 0.2$). For the same ligand, the equilibrium ratio $[Ru^{III}(N,O)]/[Ru^{III}(N,N')][H^+]$ is 16. As the pH is raised, the (N,N') chelate becomes more stable: $Ru^{III}(N,O)/Ru^{III}(N,N')$ when both species are deprotonated is 1.6×10^{-5} . Kinetic studies on substitution in $Ru^{II}(N,O)$ in acidic solution indicate that the chelate ring is in fact closed. The (N,N') form in acidic solution is short-lived: $t_{1/2}$ for transformation to the (N,O) form is ~ 0.2 s.

Studies with the substitution-inert center $Co(III)$ have contributed much to improve our understanding of the way in which amino acids and related more complex biological molecules interact with metal ions.¹ The advantages of working with substitution-inert rather than labile centers are as follows: (a) the site and mode of binding of the ligand to the metal ion can be determined with greater certainty (if necessary a determination of the crystal structure can be made, and in most instances the structure is preserved in passing from the solution to the solid phase); (b) where there is a multistep interaction, the intermediate states can be characterized with much greater ease and confidence.

Little systematic work has been done with other substitution-inert centers which favor coordination number 6. A beginning has been made with $Ru(III)$, and even the small amount of work that has been done suffices to show that the behavior of the $Ru(III)$ complexes can be strikingly different from those of $Co(III)$. Whereas (ethylglycinato)pentaamminecobalt(III) in acidic solution at room temperature changes little over a period of 1 month, the corresponding ruthenium(III) complex undergoes a facile linkage isomerization from the *N*- to the *O*-bound form, followed by the parallel processes of hydrolysis and aquation.² A similar linkage isomerization was first reported for *N*-bound pentaammine(glycine)ruthenium(III).^{3a}

Differences such as those noted alone justify the extension of studies of the kind done with $Co(III)$ to $Ru(III)$. The ruthenium systems offer an additional opportunity that is not available for $Co(III)$. The complexes of $Ru(II)$ are readily obtained from those of $Ru(III)$ by reduction, and the $Ru(II)$ complexes are also substitution inert. The preferred interaction of $Ru(II)$ with the ligand can be quite different from that of $Ru(III)$ —this difference has in fact been exploited in a system studied earlier^{3b}—and thus the interaction of ligand and metal center can be controlled by simple electron transfer. We have taken advantage of this particular feature of the ruthenium ammine system in the studies we have performed on the interaction of the tetraammines with glycinamide, *N*'-ethylglycinamide, and glycylglycine and which are described herein. For each oxidation state the ligands are bound as chelates by the amino nitrogen, the ring being closed either by the amide nitrogen (the (N,N') form) or the carbonyl oxygen ((N,O) form). The special properties of the ruthenium system have made it possible to evaluate the standard free energy difference between the two isomeric forms for each oxidation state. To our knowledge, this energy difference has not been determined for any other metal ion.

Experimental Section

Chemicals and Reagents. Chloropentaammineruthenium(III) chloride was prepared by the method of Vogt et al.⁴ and was purified by recrystallization from 0.1 M HCl. *cis*-Diaquotetraammine-

(1) Buckingham, D. A. In "Biological Aspects of Inorganic Chemistry"; Addison, A. W., Cullen, W. R., Dolphin, D., James, B. R., Eds.; Wiley: New York, 1977; p 141.
(2) Yeh, A.; Taube, H. *J. Am. Chem. Soc.* **1980**, *102*, 4725.

(3) (a) Diamond, S. E.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 5921. (b) Diamond, S. E.; Taube, H. *J. Chem. Soc., Chem. Commun.* **1974**, 622.
(4) Vogt, L. H.; Katz, J. L.; Wiberly, S. E. *Inorg. Chem.* **1965**, *4*, 1157.