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Kinetics and Mechanism of the Vanadium(IV) Oxidation of the (Hydroxymethyl)chromium(III) Ion

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We have previously reported[1,2] that (α-hydroxyalkyl)chromium(III) complexes can be easily oxidized, even with mild oxidizing agents such as Cu^{2+} and Fe^{3+}. (Some but not all of these complexes also react in the same manner with Hg^{2+}, although others react by electrophilic attack.[2]) The oxidation reactions occur with the overall stoichiometry of eq 1, and the dominant term in the rate law shows an inverse-first-order dependence on $[H^+]$ (eq 2). This along with the apparent

$$CrCR'R''OH^{2+} + 2Cu^{2+} \text{ (or } Fe^{3+}) \rightarrow Cr^{3+} + 2Cu^{+} \text{ (or } Fe^{2+}) + CR'R''O + H^{+} \quad (1)$$

$$-d[CrCR'R''OH^{2+}]/dt = (k + k'[H^{+}]^{-1})[CrCR'R''OH^{2+}][Cu^{2+} \text{ (or } Fe^{3+})] \quad (2)$$

importance of the kinetic lability of the oxidants (halopentaammine complexes of cobalt(III) failed to react) and some other considerations[2] led us to propose a mechanism in which the oxidant attack takes place at the alcoholic OH group of the organochromium complex. Subsequent slow electron transfer then leads to the final products. This result appears particularly well substantiated for Cu^{2+}; among other findings, Cu^{2+} fails to react with the analogous alkoxyalkyl complexes $CrCR'R''OR^{2+}$. We have now decided to investigate the oxidation of the (hydroxymethyl)chromium(III) ion by VO^{2+} in order to obtain more information about the mechanism(s) of oxidation of this type of chromium complexes.

Experimental Section

The stock solution of vanadium(IV) perchlorate was prepared by ion exchange (Dowex 50W-X8) of the sulfate and standardized spectrophotometrically (λ_{max} 760 nm, ϵ 17.2 M^{-1} cm^{-1}). The solutions of chromium(III) perchlorate, chromium(II) perchlorate, and $CrCH_2OH^{2+}$ were prepared as previously described.[1-3] The deuterated complex $CrCD_2OH^{2+}$ was prepared analogously with use of CD_3OD.

Product analysis was done in the presence of $(NH_3)_5CoBr^{2+}$. This reagent does not react with $CrCH_2OH^{2+}$ but was added to scavenge the Cr^{2+} produced in the reaction of $CrCH_2OH^{2+}$ and VO^{2+}. The rate constant for the oxidation of $(NH_3)_5CoBr^{2+}$ by Cr^{2+} is high enough (6.0×10^6 M^{-1} s^{-1}) in comparison to that for the reaction of Cr^{2+} and VO^{2+} (1.4×10^6 M^{-1} s^{-1}) to permit almost quantitative formation of $CrBr^{2+}$ even in the presence of an equimolar amount of VO^{2+}.[4] The products were separated by ion exchange and analyzed as previously described.[1,2] Formaldehyde was determined with use of chromotropic acid.[5]

Kinetic data were obtained spectrophotometrically by using a Cary 219 recording spectrophotometer equipped with a thermostated cell holder. The progress of the reactions was measured by monitoring the disappearance of $CrCH_2OH^{2+}$ at 300 or 390 nm. The experiments were done under Cr^{2+}-scrubbed nitrogen at 25 °C and 1.00 M ionic strength, maintained with lithium perchlorate and perchloric acid, in 1.0 M aqueous methanol (~4% v/v).

Results

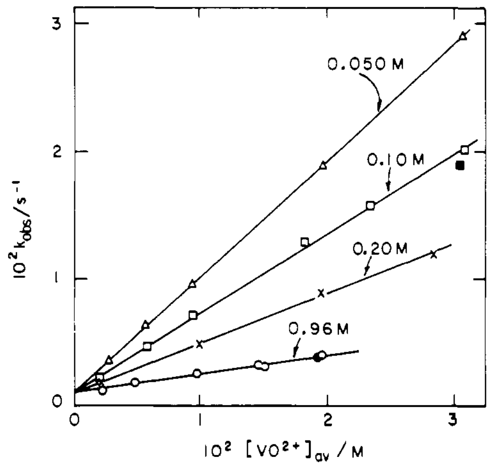

Figure 1. Variation of the pseudo-first-order rate constant with the average concentration of VO^{2+} at different acidities for the oxidation of $CrCH_2OH^{2+}$ (open symbols) and $CrCD_2OH^{2+}$ (filled symbols) by VO^{2+}.

Table I. Kinetic Data for the Oxidation of $CrCH_2OH^{2+}$ by VO^{2+} at 25 °C[a]

$[H^+]$, M	k_{VO}, M^{-1} s^{-1}	$[H^+]$, M	k_{VO}, M^{-1} s^{-1}
0.960	0.149 ± 0.003 (6)	0.125	0.542 (1)
0.800	0.161 (1)	0.100	0.642 ± 0.007 (6)
0.500	0.223 (1)	0.067	0.801 (1)
0.300	0.311 (1)	0.050	0.916 ± 0.005 (5)
0.200	0.392 ± 0.010 (4)		

[a] Conditions: 1 M aqueous methanol, 1.0 M ionic strength, $[CrCH_2OH^{2+}]_0 = (2.0\text{–}8.0) \times 10^{-4}$ M, $[VO^{2+}]_0 = (0.20\text{–}3.1) \times 10^{-2}$ M. The uncertainty, where given, is the standard deviation among the number of runs which is shown in parentheses.

Product Analysis. A mixture of 1.0 mmol of $(NH_3)_5CoBr^{2+}$ and 1.0 mmol of VO^{2+} was added to a solution of 0.20 mmol of $CrCH_2OH^{2+}$ in 1.0 M methanol at 0.10 M $HClO_4$ and 1.0 M ionic strength. After correction for the amount of $CrCH_2OH^{2+}$ which undergoes acidolysis,[3,6] 0.19 mmol of $CrCH_2OH^{2+}$ was left to react in the redox reaction. When the reaction was completed, an aliquot of the mixture was analyzed for Co^{2+} by the thiocyanate method[7] (λ_{max} 623 nm, ϵ 1.842×10^3 M^{-1} cm^{-1} in 1:1 acetone–water); 0.17 mmol of Co^{2+} were found. The rest of the solution was ion exchanged, and individual fractions were analyzed for CH_2O (0.19 mmol) and $CrBr^{2+}$ (0.16 mmol). Formation of $CrBr^{2+}$ was essentially quantitative,[8] proving that Cr^{2+} is the initial product of the reaction which we can now write as in eq 3. Subsequent rapid reaction of Cr^{2+} with $(NH_3)_5CoBr^{2+}$ (eq 4) leads to the observed stoichiometry (eq 5). In the absence of $(NH_3)_5CoBr^{2+}$,

$$VO^{2+} + CrCH_2OH^{2+} + H^{+} = V^{3+} + Cr^{2+} + CH_2O + H_2O \quad (3)$$

$$Cr^{2+} + (NH_3)_5CoBr^{2+} + 5H^{+} = CrBr^{2+} + Co^{2+} + 5NH_4^{+} \quad (4)$$

$$CrCH_2OH^{2+} + VO^{2+} + (NH_3)_5CoBr^{2+} + 6H^{+} = CrBr^{2+} + Co^{2+} + V^{3+} + CH_2O + 5NH_4^{+} \quad (5)$$

the Cr^{2+} produced in reaction 3 reacts with a second mole of VO^{2+} resulting in the stoichiometry of eq 6.

$$CrCH_2OH^{2+} + 2VO^{2+} + 3H^{+} = Cr^{3+} + 2V^{3+} + CH_2O + 2H_2O \quad (6)$$

Kinetics. In all kinetic experiments VO^{2+} was used in large excess over $CrCH_2OH^{2+}$. First-order plots were linear for at least 3 half-lives. The rate constants so evaluated show a linear dependence on the concentration of VO^{2+} at constant acidity

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(8) Under the conditions of the experiment 80% of Cr^{2+} reacts with $(NH_3)_5CoBr^{2+}$, the rest being oxidized by VO^{2+}.[4]

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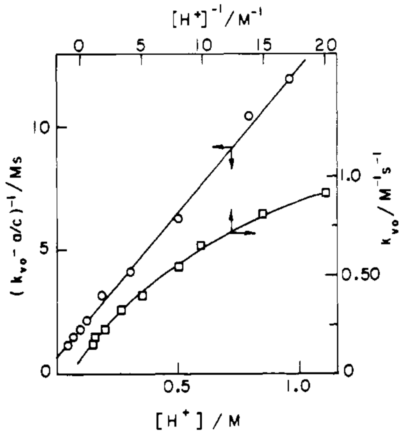

Figure 2. Illustration of the linear variation of $1/(k_{VO} - a/c)$ with $[H^+]$ according to eq 8 and the nonlinearity of a plot of k_{VO} vs. $[H^+]^{-1}$.

(Figure 1) with a small intercept corresponding to the acidolysis of $CrCH_2OH^{2+}$.[3,6] The rate law can thus be written as

$$k_{obsd} = k_d + k_{VO}[VO^{2+}] \qquad (7)$$

The summary of the kinetic data at different acidities is given in Table I. The values of the rate constants for the oxidation of the deuterated complex, $CrCD_2OH^{2+}$, are identical within the experimental error to the ones measured for $CrCH_2OH^{2+}$. The values of k_{VO} are consistent with a dependence on $[H^+]$ between 0 and −1 order. However the data are not well correlated by a two-parameter expression such as that given by eq 2. The rate expression of eq 8 provides a good fit for

$$k_{VO} = (a[H^+] + b)/(c[H^+] + 1) \qquad (8)$$

the data. A nonlinear least-squares analysis yields $a = 1.35 \pm 0.23$ M^{-2} s^{-1}, $b = 1.80 \pm 0.11$ M^{-1} s^{-1}, and $c = 20.7 \pm 2.1$ M^{-1}. The average deviation of the experimental points from the fitted curve is 1.5%. Equation 8 can be rearranged into eq 9. As further confirmation of this equation, Figure 2

$$k_{VO} - a/c = (b - a/c)/(c[H^+] + 1) \qquad (9)$$

depicts the plots of k_{VO} vs. $[H^+]^{-1}$ (as implied by eq 2) and $(k_{VO} - a/c)^{-1}$ vs. $[H^+]$ (from eq 9). The former is distinctly curved, but the latter can be seen to define a good straight line.

Detailed studies of the reactions of $CrCH(CH_3)OH^{2+}$ and $CrC(CH_3)_2OH^{2+}$ with VO^{2+} were not done. The former appears to react at a rate roughly comparable to $CrCH_2OH^{2+}$. On the other hand no reaction with VO^{2+} was detected for $CrC(CH_3)_2OH^{2+}$, in part because it would need to be seen above the substantial background rate of unimolecular homolysis, the rate constant k_{hom} being 0.127 s^{-1} for the reaction $CrC(CH_3)_2OH^{2+} \rightarrow Cr^{2+} + \cdot C(CH_3)_2OH$. Even here, a 50% rate increase would have been found at $[VO^{2+}] = 0.1$ M and $[H^+] = 0.1$ M were the rate constant the same as that for $CrCH_2OH^{2+}$, but k_{obsd} was only 0.133 s^{-1}, which is within experimental error identical with k_{hom}. It thus appears VO^{2+} reacts directly with $CrC(CH_3)_2OH^{2+}$, if it does so at all, much more slowly than with $CrCH_2OH^{2+}$.

Discussion

The complicated acid dependence (eq 8) almost certainly rules out an outer-sphere mechanism for reaction 3. Protonation or deprotonation of reactants or transition states present no obvious gain if all the bonds remain intact during the reaction. Also, the lack of any deuterium isotope effect strongly argues against possible hydrogen atom abstraction reactions.

We are now left with several possibilities concerning a detailed mechanism of an inner-sphere reaction. Vanadium(IV) can bind to the chromium center (cis or trans to the organic group) through an oxygen provided by either reactant, or it can attack at the alcoholic OH group. An argument against the former is the form of the acid dependence. If VO^{2+} attacked directly at the chromium center, one would expect a very minor (positive) or no acid dependence. This has been observed before in the vanadium(IV) oxidations of divalent transition-metal ions which were shown (Cr^{2+},[9] V^{2+} [10]) or proposed (Eu^{2+},[11] Fe^{2+} [12,13]) to proceed at least in part by an inner-sphere mechanism. Admittedly $CrCH_2OH^{2+}$ is formally a chromium(III) complex, but many of its characteristics relevant to this discussion are reminiscent of Cr^{2+}. The position trans to the organic group is very labile,[14] and the acidity of the water molecules coordinated to Cr^{2+} and $CrCH_2OH^{2+}$ is expected to be of the same order of magnitude due to the 2+ overall charge on both ions.

If on the other hand, VO^{2+} oxidizes $CrCH_2OH^{2+}$ in a process similar to the copper(II) oxidation of this and other (α-hydroxyalkyl)chromium(III) complexes,[2] one would expect a dominant term in the rate law to show an inverse dependence on $[H^+]$. Since mechanisms which give a rate law consistent with eq 9 are variants of the mechanism for Cu^{2+}, we start with an analogous process (eq 10 and 11), where Int^{3+} is used

$$CrCH_2OH^{2+} + VO^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Int^{3+} + H^+ \qquad (10)$$

$$Int^{3+} \xrightarrow[2H^+]{k_2} Cr^{2+} + V^{3+} + HCHO \qquad (11)$$

to denote a steady-state binuclear intermediate written in a manner which does not necessarily imply a structure such as $CrCH_2OVO^{3+}$, analogous to $CrCH_2OCu^{3+}$. There are two evident modifications which lead to the correct form. Proposal A consists of reactions 10 and 11 in addition to a parallel acid-independent pathway (k_0). The expression for k_{VO} then becomes eq 12. Proposal B consists of reaction 10 and in

$$k_{VO} = k_0 + \frac{k_1 k_2}{k_{-1}[H^+] + k_2} = \frac{k_0 k_{-1}[H^+]/k_2 + (k_1 + k_0)}{k_{-1}[H^+]/k_2 + 1} \qquad (12)$$

addition assumes that reaction 11 occurs by two pathways: $k_2 = k_3 + k_4[H^+]$. The expression for k_{VO} is then given by eq 13. In the first of these mechanisms, proposal A, reaction

$$k_{VO} = \frac{k_1 k_4[H^+]/k_3 + k_1}{(k_{-1} + k_4)[H^+]/k_3 + 1} \qquad (13)$$

occurs by way of two intermediates which differ by one proton, in effect Int^{3+} and $(IntH)^{4+}$, which then undergo acid-independent redox processes. In contrast, proposal B involves only one intermediate, but it may react in two independent electron-transfer steps, one independent of $[H^+]$ and the other directly proportional to $[H^+]$.

It should be noted that both mechanisms lead to rate expressions consistent with the experimental results. One might involve other possibilities, but we have deliberately ignored any mechanism in which the intermediate does not follow the steady-state expression (i.e., in which Int^{3+} may attain bulk concentration). The reason is that the reaction rate remains precisely first order in $[VO^{2+}]$ even at the highest $[VO^{2+}]$ (0.031 M) and lowest $[H^+]$ (0.050 M) studied, which means that no appreciable concentration of $CrCH_2OH^{2+}$ is converted to Int^{3+}, even under forcing conditions. Other than this, it is

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difficult to advance a case for one of the possible mechanisms, A or B, over the other. Indeed the oxidation of $CrCH_2OH^{2+}$ and other (α-hydroxyalkyl)chromium complexes with Cu^{2+} and Fe^{3+} shows a pronounced k_0 term although in these instances $k_{-1}[H^+] \gg k_2$. On this basis mechanism A certainly seems reasonable. On the other hand the $k_4[H^+]$ term of mechanism B is also plausible in view of the different degree of hydrolysis of the initial (VO^{2+}) and final (V^{3+}) oxidation states of the vanadium.

The rate laws of eq 12 and 13 imply that the electron-transfer step (k_2 or $k_3 + k_4[H^+]$) and dissociation of the binuclear complex into reactants ($k_{-1}[H^+]$) take place at comparable rates; i.e., electron transfer is not the sole rate-determining step. This is different from our findings on the oxidation of $CrCH_2OH^{2+}$ by Cu^{2+} and Fe^{3+}. The reason for this is not quite clear. One might expect that VO^{2+} would utilize the very labile axial position[15–17] to bind to $CrCH_2OH^{2+}$ in the transition state, in which case a dissociation of the intermediate is expected to be a very favorable process too. However it was pointed out before that substitutions on VO^{2+} most likely occur at one of the four equatorial positions.[12] If this is the case, the stability of the intermediate toward dissociation could be greatly enhanced, making the electron-transfer rate comparable to the dissociation.

Our arguments about the detailed mechanism of the inner-sphere oxidation of $CrCH_2OH^{2+}$ by VO^{2+} are based mainly on the acidity dependence of the reaction rates. This approach, although very useful, has limitation, especially for the reactions of metal ions in higher oxidation states where the hydrolysis of the reactants and/or products may obscure the mechanistic picture. However even with that limitation the results of this work support the idea that $CrCH_2OH^{2+}$ (and other (α-hydroxyalkyl)chromium complexes) preferably react with oxidants in inner-sphere reactions, most likely by forming bridged activated complexes through the alcoholic OH group.

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Registry No. $(H_2O)_5CrCH_2OH^{2+}$, 32108-95-5; VO^{2+}, 20644-97-7.

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Multidentate Ligand Kinetics: Exchange of Aminocarboxylate Ions with (Tetraethylenepentamine)nickel(II)

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The nickel polyamine formation and dissociation reactions have been thoroughly studied in the past.[1,2] The dissociation of nickel polyamine complexes has been shown to involve the following two steps repeated sequentially:[2] nickel–nitrogen bond breakage followed by nickel–solvent bond formation. This sequence continues until the polyamine completely dissociates from the nickel ion. Excluding strongly acidic conditions the rate-determining step is the last nickel–nitrogen bond rupture.

Table I. Resolved Rate Constants and Activation Parameters for the Substitution Reaction of Nickel(II) Polyamine by Aminocarboxylates

(I) $NiTet^{2+}$–TMDTA Reaction System

$k_L = 18.2\ M^{-1}\ s^{-1}$
$k_{HL} = 8.9\ M^{-1}\ s^{-1}$
$k_{H_2L} = 142\ M^{-1}\ s^{-1}$
$E_a = 5.47$ kcal
$\Delta H^{\ddagger} = 4.88$ kcal
$\Delta S^{\ddagger} = -34.11$ eu
$pZ = 2.06 \times 10^5\ cm^{-1}$

(II) $NiTet^{2+}$–HEEDTA Reaction System

$k_L = 8.10\ M^{-1}\ s^{-1}$
$k_{HL} = 12.6\ M^{-1}\ s^{-1}$
$k_{H_2L} = 6.3 \times 10^3\ M^{-1}\ s^{-1}$
$E_a = 11.90$ kcal
$\Delta H^{\ddagger} = 11.31$ kcal
$\Delta S^{\ddagger} = -15.66$ eu
$pZ = 2.22 \times 10^9\ cm^{-1}$

The reaction reported in this note (shown without protonation) is

$$NiTet^{2+} + L^{n-} \rightarrow NiL^{2-n} + Tet \qquad (1)$$

where Tet is tetraethylenepentamine and L is TMDTA (trimethylenediaminetetraacetic acid) or HEEDTA (hydroxyethylethylenediaminetriacetic acid).

A mechanism for the exchange reaction is proposed which involves the formation of a series of mixed-ligand complex intermediates where in each succeeding step the nickel ion increases its coordination to the incoming aminocarboxylate and decreases the number of coordinate bonds to the leaving polyamine. The final conclusion is the same as that arrived upon by previous workers.[3,4]

Experimental Section

The purification of Tetren and the preparation and standardization of NiTet solutions were carried out by methods previously reported.[2] TMDTA was prepared and recrystallized by a method described in the literature.[5a] HEEDTA was obtained from K & K Labs. The ionic strength was maintained at 0.1 M with $NaClO_4$. All absorption measurements were made with a Toshniwal Model RL-02 (Beckman DU type) spectrophotometer which was equipped with a thermostated cell compartment. The reaction was followed by a cyanide quenching method described in literature.[4]

Results and Discussion

Both the reactions have been carried out at a pH of 11.0 ± 0.1. The rate constants have been determined by the initial rate method. The orders with respect to NiTet and aminocarboxylate are found to be one in each reactant. The rate expression can be written as

$$Re = -\frac{d[NiTet]_T}{dt} = k_{L_T}{}^{NiTet}[NiTet]_T[L]_T \qquad (2)$$

The rate constants for the two reactions are 19.88 ± 1.41 and $8.87 \pm 1.10\ M^{-1}\ s^{-1}$ for TMDTA and HEEDTA reactions, respectively. Activation parameters have been calculated and are given in Table I. It was also found that reaction rates are strongly dependent on pH in the pH range 5–11. The observed dependence can be attributed to the formation of various protonated and unprotonated forms of reactants present at the working pH values.[6] On the basis of acid protonation

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