

Vanadium(V) Induced Electron Transfer in Pentaamminecobalt(III) Complexes in Presence of Oxalic acid

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Vanadium(V), which acts as both one- and two-equivalent oxidant towards pentaamminecobalt(III) complexes of α -hydroxy acids, induces an electron transfer in these complexes by one-equivalent route, leading to reduction at cobalt(III) centre with nearly synchronous carbon-carbon bond fission to the extent of 50%. The product of two-equivalent oxidation is cobalt(III)-phenylglyoxylato complex, formed to the extent of 50%. Addition of oxalic acid, probably, favours the two-equivalent path via a ternary complex, resulting in an increased yield of cobalt(III)-phenylglyoxylato complex and decreased yield of cobalt(II) and benzaldehyde.

Vanadium(V) oxidation of alcohols, α -hydroxy acids and keto acids is reported¹ to occur in one-electron transfer step. However, V(V) behaves as both one- and two-electron oxidant towards hydrazine², yielding NH_3 and N_2 . An earlier work from our laboratory³ on V(V) induced electron transfer in pentaamminecobalt(III) complexes of α -hydroxy acids, suggests transfer of a total three electrons to two V(V). In view of this and Rocek's work on Cr(VI) oxidation⁴ we envisage that possibly a similar route may also be available to V(V) induced electron transfer in pentaamminecobalt(III) complexes of α -hydroxy acids in the presence of oxalic acid (OxH_2).

Materials and Methods

Oxalic acid and HClO_4 used were of reagent grade (BDH). Vanadium perchlorate solution was prepared by dissolving V_2O_5 in 1 mol dm^{-3} HClO_4 , kept overnight and standardised both spectrophotometrically⁵ and by direct titration⁶. The cobalt(III) complexes of lactic, mandelic, glycolic and phenylglyoxylic acids were prepared as their perchlorates by the method of Fan and Gould⁷.

Rate measurements

Kinetic experiments were carried out with V(V) in excess, by spectrometrically following the decrease in absorbance at 502 nm due to the disappearance of Co(III) complex and the decrease in absorbance at 370 nm due to the decrease in [V(V)] at $30^\circ \pm 0.2^\circ\text{C}$ and ionic strength = 1.2 mol dm^{-3} . The specific rates calculated from successive half-lives agreed within $\pm 7\%$ and the average values from duplicate runs did not differ from those obtained from a logarithmic plot of change in absorbance against time.

Stoichiometry and product analyses

One of the products of V(V) oxidation of pentaamminecobalt(III) complexes of α -hydroxy acids is Co(II) and it was estimated both in the presence and absence of oxalic acid (OxH_2), by diluting the reaction mixture ten-times with conc. HCl, allowing the evolution of chlorine to cease. The absorbance of chloro-complex of Co(II) was measured at 692 nm ($\epsilon = 560 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)⁸. Suitable blank corrections were applied by measuring absorbances of solutions (without Co^{III} complex) with conc. HCl at 692 nm and it corresponded to nearly 40% of the total absorbance when $[\text{V(V)}]_{\text{initial}} = 3.3 \times 10^{-2} \text{ mol dm}^{-3}$. From the change in absorbance at 370 nm/502 nm, the amount of original $\text{Co(III)}_{\text{reduced}}/\text{V(V)}_{\text{consumed}}$ was calculated both in the presence and absence of OxH_2 . At varying initial concentrations of mandelato-pentaamminecobalt(III) complex in the presence of OxH_2 , the amount of benzaldehyde formed was estimated after extraction with diethyl ether and measuring the absorbance at 250 nm ($\epsilon = 11,400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)⁹. The other product of V(V) reaction with $(\text{H}_3\text{N})_5\text{Co}^{\text{III}}$ -mandelato complex, isolated as described in an early procedure³ was characterised (IR) as the known $(\text{H}_3\text{N})_5\text{Co}^{\text{III}}$ -phenylglyoxylato complex. Table 1 summarises the stoichiometric data. Consequent upon increase in $[\text{OxH}_2]$, there was a progressive decrease in the amount of Co(II), benzaldehyde and Co_2 formed with a progressive increase in Co^{III} -phenylglyoxylato complex in the case of V(V)- Co^{III} -mandelato reaction. Similar observations were made even with lactato and glycollato-cobalt(III) complexes, evidencing the operation of a similar mechanism in all these oxidation reactions.

Table 1—Stoichiometric Data in Vanadium(V) Induced Electron Transfer in Pentaamminecobalt (III) Complexes of α -Hydroxy Acids in Presence of Oxalic Acid^a

| [Co(III)] initial (mmol dm ⁻³) | [V(V)] (mmol dm ⁻³) | [Oxalic acid] (mmol dm ⁻³) | [Co(III)] reduced (mmol dm ⁻³) | [Co(II)] ^b (%) (mmol dm ⁻³) | $\overset{\text{O}}{\parallel}$ [-C-] ^b (%) (mmol dm ⁻³) | [Ketoacid complex] ^b (%) (mmol dm ⁻³) | Δ [V(V)] |
|--|------------------------------------|---|--|---|---|--|-----------------|
| Mandelato Complex | | | | | | | |
| 2.0 | 33 | — | 0.97 | 0.94(47) | 0.93(46) | 0.95(48) | 2.6 |
| 2.0 | 33 | 6.0 | — | 0.68(34) | — | — | — |
| 4.0 | 33 | 6.0 | 1.60 | 0.80(40) | 0.82(41) | — | — |
| 6.0 | 33 | 6.0 | 2.76 | 0.92(46) | 0.93(44) | 0.97(49) | — |
| 2.0 | 16.3 | 2.0 | 0.92 | 0.90(45) | — | — | 3.2 |
| 2.0 | 27 | 2.0 | 0.89 | 0.88(44) | — | — | 2.9 |
| 2.0 | 33 | 2.0 | 0.78 | 0.76(38) | 0.74(37) | 0.78(58) | 2.8 |
| 2.0 | 38 | 2.0 | 0.74 | 0.72(36) | — | — | — |
| 2.0 | 33 | 0.50 | — | 0.90(45) | 0.88(40) | — | 2.6 |
| 2.0 | 33 | 2.0 | 0.78 | 0.76(38) | 0.74(34) | — | 2.8 |
| 2.0 | 33 | 3.0 | — | 0.72(36) | 0.70(30) | — | 2.9 |
| 2.0 | 33 | 12.0 | — | 0.66(33) | 0.63(26) | — | 3.2 |
| Lactato complex | | | | | | | |
| 2.0 | 33 | — | 0.99 | 0.98(49) | — | — | 2.7 |
| 2.0 | 33 | 6.0 | — | 0.707(35) | — | — | — |
| 4.0 | 33 | 6.0 | 1.64 | 0.82(41) | — | — | — |
| 6.0 | 33 | 6.0 | 2.70 | 0.90(45) | — | — | — |
| 2.0 | 16.3 | 2.0 | 0.94 | 0.92(46) | — | — | 3.0 |
| 2.0 | 27 | 2.0 | 0.90 | 0.89(44.5) | — | — | 2.9 |
| 2.0 | 33 | 2.0 | 0.86 | 0.84(42) | — | — | 3.2 |
| 2.0 | 38 | 2.0 | — | 0.70(35) | — | — | — |
| 2.0 | 33 | 0.50 | — | 0.98(49) | — | — | — |
| 2.0 | 33 | 2.0 | 0.86 | 0.84(42) | — | — | — |
| 2.0 | 33 | 3.0 | — | 0.74(37) | — | — | — |
| 2.0 | 33 | 12.0 | — | 0.64(32) | — | — | — |
| Glycollato complex | | | | | | | |
| 2.0 | 33 | — | 0.98 | 0.98(49) | — | — | 2.5 |
| 2.0 | 16.3 | 2.0 | 0.76 | 0.74(37) | — | — | 2.9 |
| 2.0 | 27 | 2.0 | 0.65 | 0.64(32) | — | — | 2.7 |
| 2.0 | 33 | 2.0 | 0.58 | 0.56(28) | — | — | 2.8 |

^aStoichiometric studies were made in 1.2 mol dm⁻³ HClO₄ at 30°C.

^bAmounts of cobalt(II), benzaldehyde and Co^{III}-phenylglyoxylato complex were calculated with respect to [Co(III)]_{initial}.

Results and Discussion

Table 2 summarises the kinetic data for the V(V) induced electron transfer in pentaamminecobalt(III) complex of mandelic acid both in the presence and absence of oxalic acid. The reaction exhibits total second order kinetics—one each in [Co(III)] and [V(V)]. At higher [OxH₂] the order in [OxH₂] is nearly one, in its reaction with V(V). But the rate of V(V) oxidation of mandelato complex in the presence of OxH₂ seems to have a complex dependence on [OxH₂]. Addition of OxH₂ enhances the rate of V(V) co-oxidation factor (Table 2). With increase in [OxH₂], the co-oxidation factor increases, evidencing the participation of OxH₂ in the redox reaction. These results are similar to those obtained by Rocěk and Hasan⁴ as well as Kalidoss and Srinivasan¹¹.

Increase in absorbance due to the addition of OxH₂ to either V(V) or V(V) and Co(III) complex, is only marginal. Also due to greater reactivity of the mixture of V(V) and Co(III) complex in the presence of OxH₂, the determination of neither λ_{max} nor ϵ of the ternary complex was meaningful.

As V(V) can behave as one- or two-equivalent oxidant towards pentaamminecobalt(III) complexes of α -hydroxy acids with equal ease³, the one-equivalent path will involve reduction at the Co(III) center with nearly synchronous carbon-carbon bond fission and the two-equivalent path will involve oxidation of ligand only, leaving the Co(III) unchanged. With increase in [OxH₂] the amounts of Co(II) and benzaldehyde formed by one-equivalent path decrease whereas that of cobalt(III)-phenylglyoxylato complex formed by two-

Table 2 – Kinetic Data in Vanadium(V) Induced Electron Transfer in Pentaamminecobalt(III) Complex of Mandelic Acid in Presence of Oxalic Acid^{a,f}.

| $10^3[\text{Co(III)}]$ (mmol dm ⁻³) | $10^2[\text{V(V)}]$ (mmol dm ⁻³) | $10^3[\text{oxalic acid}]$ (mmol dm ⁻³) | $10^6 k_1^b$ (s ⁻¹) | $10^3 k_1^c$ (s ⁻¹) | $10^3 \Sigma k_1^d$ (s ⁻¹) | $10^3 k_1^e$ (s ⁻¹) | $k_1^e / \Sigma k_1 + k_1^f$ |
|--|---|--|------------------------------------|------------------------------------|---|------------------------------------|------------------------------|
| 2.0 | 3.3 | — | — | 2.0 | 2.0 | — | — |
| 2.0 | 3.3 | 0.50 | 1.43 | 2.0 | 2.0 | 2.7 | 1.35 |
| 2.0 | 3.3 | 2.0 | 2.6 | 2.0 | 2.0 | 3.1 | 1.55 |
| 2.0 | 3.3 | 3.0 | 4.5 | 2.0 | 2.0 | 3.3 | 1.65 |
| 2.0 | 3.3 | 6.0 | 9.9 | 2.0 | 2.0 | 3.5 | 1.75 |
| 2.0 | 3.3 | 12.0 | 15.2 | 2.0 | 2.0 | 4.7 | 2.4 |
| 2.0 | 1.63 | 2.0 | — | — | — | 1.64 | — |
| 2.0 | 2.7 | 2.0 | — | — | — | 2.4 | — |
| 2.0 | 3.8 | 2.0 | — | — | — | 3.3 | — |
| 4.0 | 3.3 | 6.0 | — | — | — | 3.5 | — |
| 6.0 | 3.3 | 6.0 | — | — | — | 3.7 | — |

^aReactions were carried out in 1.2 mol dm⁻³ HClO₄ at 30°C at constant ionic strength.

^b k_1 refers to the specific rate for the V(V) oxidation of oxalic acid under same conditions

^c k_1^f is the specific rate for the V(V) oxidation of cobalt-mandelato complex.

^d $\Sigma k_1 = k_1^b + k_1^c$.

^e k_1^g is the specific rate for the V(V) oxidation of a mixture of oxalic acid and cobalt(III) mandelato complex.

^f k_1^f is referred to as the specific rate for co-oxidation.

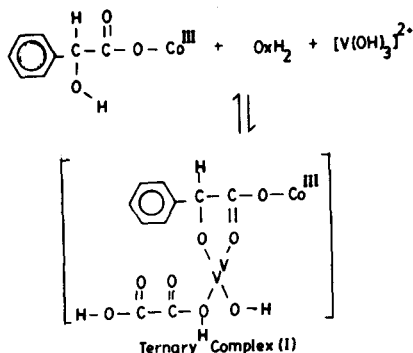
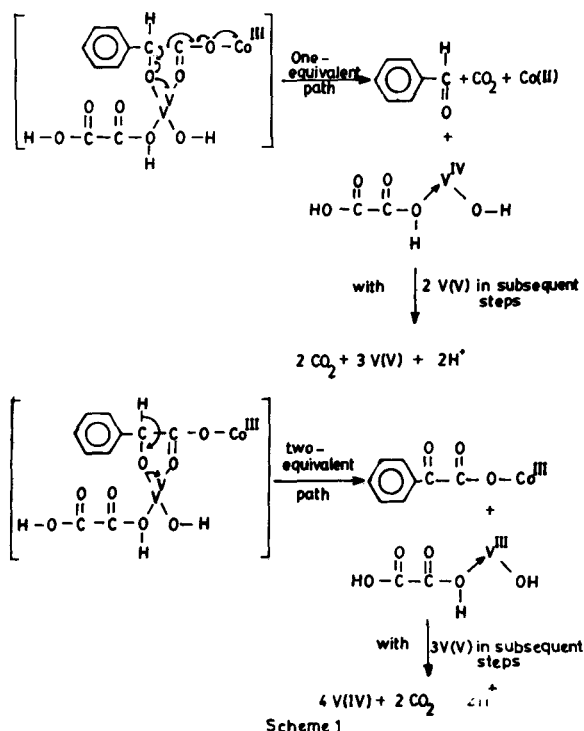
^fSimilar rate behaviour has been observed in V(V) oxidation of cobalt(III) complexes of lactic acid and glycollic acids in the presence of oxalic acid.

^g $k_1^g / \Sigma k_1$ is the co-oxidation factor for V(V) oxidation of mixture OxH₂ and cobalt(III) complex.

equivalent path increases (Table 2). Possibly the presence of OxH₂ stabilises Co(III) in the ternary complex, favouring V(V) to react by two-equivalent path. The consumption of V(V) is also higher in the presence of OxH₂ as it is used more by the ligand in the absence of decreased assistance from Co(III).

The increase in consumption of V(V) to the extent of 25% is close to the decrease in reduction of original Co(III)- α -hydroxy acid complex or the amount of Co(II) formed.

Based on the results two possible reaction paths are suggested for V(V) reaction with cobalt(III) complex in the presence of OxH₂ (see Scheme 1). Of the two paths, one involving two-electron transfer seems to be favoured by the presence of OxH₂ in the ternary complex(I), yield-



ing more of cobalt(III)-phenylglyoxylato complex. As oxalic acid will be mostly undissociated in 1.2 mol dm⁻³ HClO₄, the ternary complex(I) probably has the acid-form of oxalic acid (H₂C₂O₄) where it behaves as a monodentate ligand. This is

similar to the scheme proposed in V(V) oxidation of OxH_2 at higher acid concentration by Jones and Waters¹².

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