Estimated Distribution between One- and Two-equivalent Reaction Paths in Vanadium(V)-induced Electron Transfer

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The reactions of V^V with $[Co(NH_3)_5L]^{2+}$ complexes of α-hydroxy-acids, mandelic (α-hydroxybenzene-acetic), lactic, and glycolic acids yield Co^{II} and a carbonyl compound to the extent of 50% of $[Co^{III}]_{initial}$; $[V^V]_{consumed}$ is 1.5—1.7 times $[Co^{III}]_{initial}$. The other product of the reaction, phenylglyoxylatocobalt(III) complex, obtained in 50% yield by a two-electron oxidation, is responsible for the 50% change in absorbance at 502 nm. The rate of the reaction is proportional to the concentration of a V^V–Co^{III} complex, observed spectrophotometrically. This is consistent with the one-electron route preferred by V^V, producing a radical which, by nearly synchronous C–C fission and one-electron transfer to Co^{III}, produces Co^{II}. Stoicheiometric studies made with V^V and mandelic acid (Co^{III}-free system) reveal that the yields of PhCHO and phenylglyoxylic acid are nearly equal. When coupled with the results of the induced electron transfer using V^V, this suggests that the one- and two-equivalent paths prevalent in the oxidation of α-hydroxy-acids by V^V are very nearly of equal importance.

The oxidation of alcohols, 2-hydroxy-acids, glycols, and keto-acids by V^V has been the subject of an intensive investigation by Waters and co-workers.[1] These studies provided evidence for the formation of a vanadium(V) complex, which, in a subsequent one-electron transfer step, forms V^{IV} and a radical, which then reacts with one more V^V to form the products. However, the oxidation of hydrazine by V^V proceeds by both one- and two-electron transfers, yielding N_2 and NH_3.[2]

The present communication describes an estimation of the one-equivalent and two-equivalent paths utilised by V^V during redox reactions, making use of induced electron transfers by V^V, *i.e.* reactions in which a net two-electron oxidation is initiated through an organic ligand bound to Co^{III}, yielding a radical-cation intermediate which, by an intramolecular electron transfer to Co^{III}, then forms products.[3] Earlier studies have involved the one-electron oxidants Ce^{IV} and Cr^{IV},[4] where the cobalt(III) centre is separated by a conjugated, as well as a saturated, fragment. The latter complexes, therefore, should suffer breakage of a carbon–carbon bond while Co^{III} is reduced to Co^{II}, if an induced electron transfer occurs. The cobalt(III) complexes employed in the present work are derived from α-hydroxy-acids. On treatment with vanadium(V) perchlorate, these complexes will form initially either a cobalt(III)–keto-acid complex and V^{III}, if the reaction involves two-electron transfer, or Co^{II}, V^{IV}, CO_2, and a carbonyl product if the reaction follows a one-electron path. From an estimate of the reaction products, coupled with a kinetic study, we can determine the fraction proceeding by each route.

Experimental

Solutions of vanadium(V) perchlorate were prepared by dissolving V_2O_5 in 1 mol dm^{-3} $HClO_4$ overnight, and the concentration of V^V was determined both spectrophotometrically[5] and by direct titration with Fe^{II} using diphenylamine as indicator.[6] The cobalt(III) complexes of lactic, mandelic (α-hydroxybenzeneacetic), benzilic, 2-hydroxy-2-ethylbutyric (heba), 2-hydroxy-2-methylbutyric (hmba), glycolic, and phenylglyoxylic acids were prepared as their perchlorates by the method of Fan and Gould.[7] The complex $[(NH_3)_3Co(OH)_3Co(NH_3)_3][ClO_4]_3$ and bridged mandelato- and glycolato-complexes were prepared following procedures available in the literature.[8] Cobalt analyses[9] of these complexes are in agreement with the assigned structures.

Rate Measurements.—Rates of reactions of cobalt(III) complexes were estimated from the observed decrease in absorbance at 502 nm using a Carl-Zeiss VSU2-P spectrophotometer. Ionic strength was maintained by addition of suitable quantities of $HClO_4$ and $LiClO_4$. The rate of disappearance of V^V was followed at 370 nm and the estimated rates compared with the above values. Whereas there was only a 50% change in absorbance for lactato-, mandelato-, and glycolato-penta-amminecobalt(III) complexes at 502 nm, the change in concentration † of V^V at 370 nm was 1.5—1.7 times the initial concentration of cobalt(III) complex in all these cases.

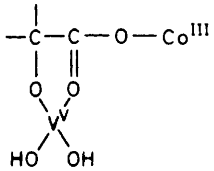
With V^V in excess, the rate of the reaction was first order in $[Co^{III}]$ but upon variation of $[V^V]$ kinetic saturation was observed indicative of intermediate complex formation. Although the ion VO_2^+ is formed on acidifying a solution of vanadate[10] [equation (1)], earlier kinetic evidence suggested

$$VO_3^- + 2H^+ \rightleftharpoons VO_2^+ + H_2O \qquad (1)$$

that in strong perchloric acid there is an equilibrium (2) and $[V(OH)_3]^{2+}$ is a better oxidant than VO_2^+.

$$VO_2^+ + H_3O^+ \rightleftharpoons [V(OH)_3]^{2+} \qquad (2)$$

The formation of a vanadium(V)-substrate complex observed spectrophotometrically in the present reaction is



possibly similar to the one reported by Waters and co-workers.[12] Rate constants from successive half-life values agree within ±7% and the average values do not differ from those obtained from a plot of the logarithmic change in absorbance against time. The values reported are averages of at least two runs and the temperature was kept at 28 ± 0.2 °C during the

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† $\Delta[V^V] = ([V^V]_{initial}/A_{initial}) \times$ change in absorbance (ΔA).

Table 1. Kinetic data for the reaction of $[Co(NH_3)_5L]^{2+}$ complexes with V^V [a]

L	$10^2[V^V]$	$[H^+]$	10^3k [b]/s^{-1}
	mol dm^{-3}		
Mandelate	4.2	0.40 [c]	0.44
	4.2	0.60 [c]	0.58
	4.2	1.0 [c]	0.84
	4.2	1.6 [c]	1.77
	1.85	1.6	0.68
	2.8	1.6	0.80
	3.9	1.6	1.11
	5.6	1.6	1.41
Lactate	1.64	1.6	0.157
	2.5	1.6	0.23
	3.7	1.6	0.50
	3.7	1.6	0.51 [d]
	5.6	1.6	0.68
Glycolate	2.5	1.6	0.084
	3.7	1.6	0.089
	4.9	1.6	0.148
	6.1	1.6	0.176
	3.7	1.6	0.114 [d]
	4.1	1.6	0.117 [d]

[a] Carried out at 28 °C with V^V in excess (ionic strength 1.6 mol dm^{-3}) unless otherwise mentioned. [b] The pseudo-first-order rate constant $k_1 = -d \ln [Co^{III}]/dt$. [c] At ionic strength 2.0 mol dm^{-3}, adjusted with $LiClO_4$. [d] Followed at 370 nm.

entire series of experiments. Under similar conditions, the oxidation of mandelic acid with V^V in excess was monitored at 370 nm and the rate of this reaction is twice that for the mandelatocobalt(III) complex.

Product Analysis.—Cobalt(II) was estimated in reaction mixtures having an excess or a deficiency of V^V after almost complete reaction of the original complex. The percentage of Co^{II} did not vary much after 5 h (see footnotes to Table 3). The reaction mixtures were then diluted 10-fold with concentrated HCl, allowing evolution of chlorine to cease, and then the absorbance of the chlorocobalt(II) complex was measured at 692 nm (ε = 560 dm^3 mol^{-1} cm^{-1}).[9] Optical density measurements on a vanadium(V) solution diluted 10 times with concentrated HCl in the absence of cobalt(III) complex were used as a blank and suitable corrections applied. The blank amounts to about 40% of the total absorbance when $[V^V] = 3.7 \times 10^{-2}$ mol dm^{-3}. From the change in absorbance at 370 nm, the V^V consumed was evaluated and optical density measurements at 502 nm used to calculate $[Co^{III}]_{reduced}$. The amount of the original Co^{III} or V^V consumed and of Co^{II} formed was less than 5% of $[Co^{III}]_{initial}$ when complexes of phenylglyoxylic acid or hmba or heba were used, even after several days. Under the same conditions, about 20% of Co^{II} was formed after 6 d in the reaction of V^V with the benzilatocobalt(III) complex, revealing that reaction does occur, but slowly. Due to the volatility and low absorbance of acetaldehyde, the product estimation in the reaction of V^V with the lactatocobalt(III) complex is hampered. However, at varying initial concentrations of the mandelatocobalt(III) complex or of V^V the amount of benzaldehyde formed was estimated after extraction with diethyl ether and measuring the absorbance at 250 nm (ε = 11 400 dm^3 mol^{-1} cm^{-1}).[13,14] In the above cases, the kinetics were followed at 370 and 502 nm to calculate the percentage of Co^{III} converted into Co^{II} and of V^V reacted so that these can be compared with the amount of benzaldehyde formed.

Table 2. Data on binuclear complex formed between V^V and $[Co(NH_3)_5L]^{2+}$ complexes *

L	$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})	K/dm^3 mol^{-1}	$10^3k_{lim}/s^{-1}$
Mandelate	495 (140)	7.5	4.5
Lactate	490 (135)	3.1	2.5

* Values refer to reaction in 0.040 mol dm^{-3} $HClO_4$. In the case of the glycolato-complex the intercept obtained from the double reciprocal plot is so low that further calculation based on this value is unwarranted.

Results and Discussion

Table 1 summarises kinetic data for the oxidation of pentaamminecobalt(III) complexes of mandelic, lactic, and glycolic acids at different $[H^+]$ or $[V^V]$. The rate of the reaction is first order in $[Co^{III}]$ and dependent on acidity within the range 0.40—1.60 mol dm^{-3},* in accord with kinetic data of Jones *et al.*,[12] indicating the existence of reactive species such as $[V(OH)_3]^{2+}$. With increasing $[V^V]$ the rate seems to approach a limiting value, possibly due to a dependence on the concentration of a V^V–Co^{III} complex which may dissociate at low $[V^V]$. Assuming a 1 : 1 V^V–Co^{III} complex, the rate law for the reaction can be expressed as in equation (3) where k_{lim} is the

$$\text{Rate} = \frac{k_{lim}[Co^{III}][V^V]}{K^{-1} + [V^V]} \qquad (3)$$

rate observed at higher $[V^V]/[Co^{III}]$ ratios and K is the association constant for the binuclear complex. The approximate limiting rate (from intercept) and association constant (from intercept/slope) may be evaluated from a plot $1/k_{obs.}$ ($= [Co^{III}]/$rate) *vs.* $1/[V^V]$ and these are listed in Table 2.

For each of the binuclear complexes † the visible absorption maximum lies close to the $\lambda_{max.}$ of the carboxylatocobalt(III) complexes (502 nm).[9] The absence of such an absorption maximum near 520 nm in the system containing V^V and mandelato- or glycolato-bridged dicobalt(III) complexes suggests that whereas in the case of monomeric cobalt(III) complexes the V^V–Co^{III} complex is stabilised through chelation this is not possible with dimeric cobalt(III) complexes.

The percentages of products formed in a number of representative vanadium(V) oxidations of $[Co(NH_3)_5L]^{2+}$ complexes are included in Table 3. The amount of Co^{III} reacted can be calculated from the change in absorbance at 502 nm, and the amount of V^V reacted from the change in absorbance at 370 nm. In the cases of the mandelato-, lactato-, and glycolato-cobalt(III) complexes, the amount of Co^{III} reduced is *ca.* 50% of $[Co^{III}]_{initial}$ (percentage ranges from 40 to 60%) as indicated by the amount of Co^{II} formed, which is equal to the amount of benzaldehyde formed, in the case of the mandelato-complex. However, the amount of V^V reacted is 1.5—1.7 times the initial concentration of cobalt(III) complex. Considering the reaction $V^V + V^{III} \longrightarrow 2V^{IV}$, along with the two-electron-transfer path, one would expect the ratio $[Co^{III}]_{initial}/\Delta[V^V]$ to be 1 : 1.5, which is close to the experimentally observed ratio of 1 : 1.5—1.7 in the present systems.

The above results can be explained by a reaction sequence (Scheme 1) in which V^V behaves both as a one- and a two-

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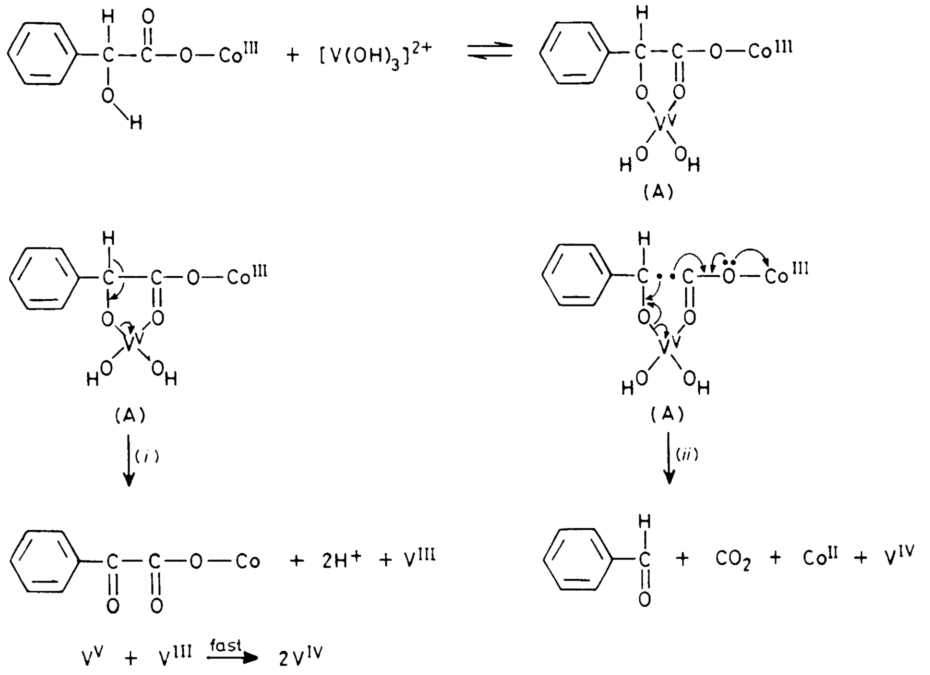
* In this range dimerisation of V^V seems to be negligible up to $[V^V]$ = 0.10 mol dm^{-3}.[10c]

† The absorbance measurements were made with $[V^V] = [Co^{III}] = 3.0 \times 10^{-3}$ mol dm^{-3} at which the redox reaction will be too slow to interfere with the determination of $\lambda_{max.}$ of the binuclear complex.

Table 3. Yield of products in oxidation of $[Co(NH_3)_5L]^{2+}$ complexes by V^V [a]

L	$[Co^{III}]_{initial}$ mmol dm^{-3}	$[V^V]_{initial}$ mmol dm^{-3}	$[Co^{III}]_{reduced}/[Co^{III}]_{initial}$ [b]	$\Delta[V^V]$ [c]/ mmol dm^{-3}	$[Co^{II}]$ [d]/ mmol dm^{-3} (%)	[PhCHO]/ mmol dm^{-3} (%)
Mandelate	2.5	37	0.53	4.2	1.07(47)	1.08(47)
	2.5	56	0.55	4.2	1.43(56)	—
	2.4	74	0.44	—	1.21(50)	1.18(49)
	2.4	46	0.48	—	—	1.09(45)
	3.5	37	0.46	5.4	1.54(45)	1.38(40)
	6.1	2.0	0.132	—	0.79(40) [e]	—
	2.1	42	0.45	—	1.05(50) [f]	—
	2.1	42	0.49	—	1.10(52) [g]	—
	2.1	42	0.49	—	1.07(51) [h]	—
	2.4	39	0.46	4.4 [i]	1.25(52)	—
Lactate	2.5	37	0.53	4.4 [i]	1.11(44)	—
	2.4	56	0.51	—	1.11(46)	—
Glycolate	2.5	25	0.54	—	1.50(60)	—
	2.5	37	0.53	—	1.34(54)	—
	2.5	49	0.55	—	1.54(62)	—
	2.5	61	0.48	—	1.39(56)	—
	2.5	37	0.53	4.8 [j]	1.46(59)	—

[a] At 28 °C in 1.6 mol dm^{-3} $HClO_4$ unless otherwise mentioned. One product of the reaction was identified by i.r. spectral studies as corresponding with the spectrum of the benzoylformatocobalt(III) complex. Quantitative estimation of this complex was hampered by the interference from V^V present even in traces after several precipitations. Due to volatility and low absorbance of acetaldehyde and formaldehyde, estimation of carbonyl compounds has been hampered. [b] $[Co^{III}]_{reduced} = [Co^{III}]_{initial} \times \Delta A/A$ at 502 nm. [c] $\Delta[V^V] = ([V^V]_{initial}/A$ at 370 nm) $\times \Delta A$. [d] Yield of Co^{II} calculated on the basis of $[Co^{III}]_{initial}$ and percentage (in parentheses) compared with $[Co^{III}{}_{reduced}]$. [e] Yield calculated on the basis of V^V taken. [f] At 0.40 mol dm^{-3} $HClO_4$ + 1.6 mol dm^{-3} $LiClO_4$. [g] At 0.60 mol dm^{-3} $HClO_4$ + 1.4 mol dm^{-3} $LiClO_4$. [h] At 1.0 mol dm^{-3} $HClO_4$ + 1.0 mol dm^{-3} $LiClO_4$. [i] Stoicheiometric studies made after 5 h. [j] Stoicheiometric studies made after 2 d. (The other stoicheiometric studies were made after 1.5 h when the absorbance at 370 nm was constant.) This value is probably due to consumption of V^V by the products of the reaction.



Scheme 1. (*i*) Two-equivalent path; (*ii*) slow one-equivalent path

equivalent oxidant. In the one-equivalent step the chelate formed between V^V and Co^{III} decomposes with a simultaneous one-electron transfer in opposite directions to V^V and Co^{III}, and breaking of a carbon–carbon bond leading to the formation of CO_2, V^{IV}, and Co^{II}. The two-electron-transfer step involves breaking of a C–H bond, resulting initially in the formation of a benzoylformatocobalt(III) complex and V^{III} which with V^V forms V^{IV} ultimately. As the benzoylformato-complex * does not undergo any reaction with V^V,

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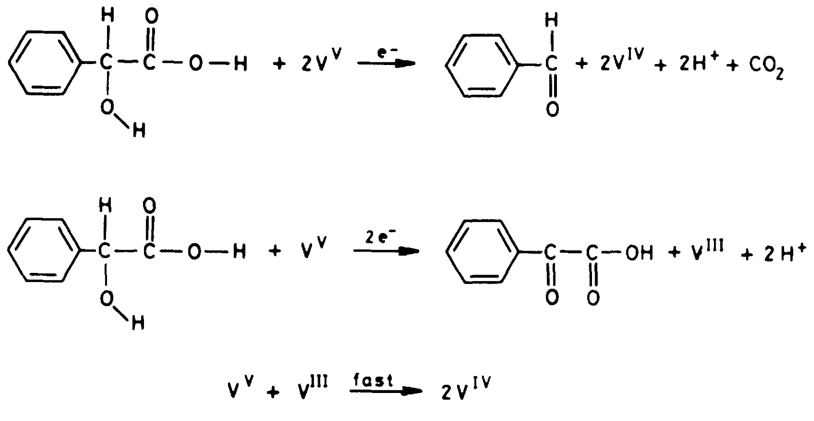
* Under similar conditions V^V oxidises neither phenylglyoxylic acid nor benzaldehyde at a significant rate.



Scheme 2.

the limiting absorbance observed in each run is nearly 50% of the initial optical density. Similar observations have also been made with the lactato- and glycolato-cobalt(III) complexes.

Of the two steps that which involves one-electron transfer seems to be slowest as the oxidation by V^{V} of the benzilato-, heba, and hmba complexes, which feature no α-C–H bond, are also very slow. The yield of Co^{II} in the reaction of V^{V} and the benzilatocobalt(III) complex is *ca.* 18% after 8 d (suitable blank correction made) and <10% in the corresponding oxidations of the heba, hmba, or dimeric mandelato- or glycolato-bridged complexes.

At this stage, it is worth mentioning that the amount of Co^{III} reduced to Co^{II} is very nearly 50% of $[Co^{III}]_{initial}$, at all concentrations of V^{V} whether in excess or in deficiency, as well as at different acid concentrations, indicating that the acid dependence is possibly due to a shift in the position of equilibrium involving the V^{V}–Co^{III} complex. Although earlier studies with cerium(IV) and cobalt(III) complexes [3a–c] pointed to two-electron transfer between the oxidant (two equivalents) and the ligand in conjugation with Co^{III}, in the present work Co^{III} is separated from the reaction site by a saturated fragment containing a carbon–carbon bond which must break to yield Co^{II}. Also if the radical $>\dot{C}-O-V^{V}$ is produced by C–H bond cleavage it will require one more equivalent of V^{V}, altering the stoicheiometry of the reaction. Hence the present duality of reaction paths can be attributed to V^{V} behaving as both a one- and two-equivalent oxidant with the same substrate. This is further corroborated by data on the stoicheiometry obtained by using a reaction mixture containing excess of V^{V} and the free ligand mandelic acid. The products of the reaction are benzaldehyde and phenylglyoxylic acid. The rates of oxidation of mandelic acid by V^{V} are about twice that for the mandelatocobalt(III) complex,* indicating that electrostatic effects are less pronounced in the oxidations of V^{V} compared with Ce^{IV}. Table 4 summarises the yield of benzaldehyde and phenylglyoxylic acid in the oxidation of mandelic acid by V^{V}. The ratio of $[V^{V}]_{consumed}$ to [mandelic acid] is nearly 1.9 : 1 suggesting that V^{V} behaves both as a one- and a two-equivalent oxidant, yielding benzaldehyde and phenylglyoxylic acid, according to the reaction sequence in Scheme 2.

Table 4. Yield of the products of reaction between V^{V} and mandelic acid [a]

[Mandelic acid]	$[V^{V}]$	[Benzaldehyde] [b]	[Phenylglyoxylic acid] [b]
mmol dm^{-3}		mmol dm^{-3}	
3.8	7.2	1.89(50)	1.79(47)
5.1	9.6	3.1(60)	1.62(32)

[a] At 28 °C in 1.6 mol dm^{-3} $HClO_4$. Yield of benzaldehyde estimated after checking that the reaction was complete (the absorbance at 370 nm for V^{V} was constant). [b] Percentages given in parentheses are based on $[\text{mandelic acid}]_{initial}$.

Although the earlier report [12] on the oxidation of α-hydroxy acids by V^{V} favours predominant carbon–carbon bond fission, Bakore and Shanker [15] are of the view that in the oxidation of glycolic acid by V^{V} the yield of HCO_2H is nearly 80%, formed by C–H fission in two-electron-transfer steps in $HClO_4$. However, subsequent work [16] on the latter reaction in H_2SO_4 led to a mechanism involving predominant C–C bond fission with V^{V} behaving as one-equivalent oxidant. The results of Roček and Radkwosky [17] on the oxidation of cyclobutanol by V^{V} in 1 mol dm^{-3} $HClO_4$ at 30 °C favour predominant C–C bond fission by one-electron transfer to V^{V} as the k_H/k_D value is close to one (1.22) and the carbonyl product is formed in *ca.* 84% yield.

The present work suggests that both one- and two-equivalent paths occur, with almost equal ease, yielding nearly equal amounts of Co^{II} and benzaldehyde and about 50% of the keto-acid complex of Co^{III}.

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* With Ce^{VI} as oxidant the rate of oxidation of mandelic acid is about 10^2—10^3 times greater than that of the corresponding penta-amminecobalt(III) complex.

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