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THE ROLE OF COMPLEXES IN METAL-ION OXIDATIONS IN SOLUTION

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CONTENTS

A. INTRODUCTION

The oxidation state of a metal ion must be referred to its immediate environment since the stability and reactivity of an ion in any oxidation state is known to be influenced by the presence of ligands. A particular oxidation state is stable as a result of thermodynamic or kinetic factors in that any associated redox reactions may be accompanied by

(*a*) unfavourable free energy changes or
(*b*) the activation energies for the intramolecular electron transfer processes involved are too large.

In the reactions involving two metal ions, redox processes generally involve a single electron transfer step and much work has been done on the elucidation

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of the mechanisms of such systems in solution. Detailed reviews on both the "inner"[1-3] and "outer"[4-6] sphere mechanism are available. The inner sphere route has been demonstrated mainly as the result of product studies[7], *cf.* the elegant investigations of Taube and his co-workers on the reactions of pentamminocobalt(III) complexes with Cr^{II}, and only in a few cases has the inner sphere mechanism been demonstrated unambiguously. In the reaction of Cr^{II} with V^{IV}[8], the pale blue solutions produce on mixing a bright green colour which slowly fades to the V^{III} and Cr^{III} ions. Characterisation of this binuclear intermediate has been achieved using a stopped-flow apparatus Also in the reaction of $Fe(CN)_6{}^{3-}$ with $[Co(CN)_5]^{3-}$, the product $[(NC)_5Fe(CN)Co(CN)_5]^{6-}$ has been isolated[9]. For outer sphere reactions, the interactions are substantially weaker and correlations between kinetic and overall thermodynamic parameters have been demonstrated[10,11].

The stability of a complex ion with respect to an intramolecular redox reaction will depend on several factors[12]. If the electron affinity of the ligand is not large, it will be oxidised; alternatively if its electronegativity is greater than that of the metal atom then oxidation of the latter may take place. In general, however, ligands tend to act as reducing agents and unlike metal ions which may undergo changes in oxidation state in single electron steps without the formation of highly reactive intermediates, ligands frequently require two-electron changes to reach a new stable state.

Reactions of the type

$$(H_2O)_nM^{a+} + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (H_2O)_{n-1}ML^{a+} \rightarrow M^{(a-1)+} + P$$

will proceed from left to right if there is a decrease in free energy. The energy profile diagram for the overall reaction may be represented by Fig 1. The magnitude of AB will define whether the reaction can be considered as a concerted process involving only the formation of ML^{a+} as a transient activated intermediate (when AB is small), or a two step reaction where an intermediate complex is formed (AB large) In the former, the equilibrium constant of the complex ion $ML^{a+}(K)$ is small and a rate study would exhibit strict second order kinetics In the latter case, however, the rate law will be modified to include a term in K, since there is now formed a thermodynamically unstable metal complex which has all its partition functions and which is in equilibrium with its precursors. Also this species should be distinguished from any activated complex in the reaction profile. A distinction must thus be made between complex species formed as a result of metal–ligand interaction prior to the oxidation process and those which may be postulated as intermediates in the electron transfer process. The question of intermediates in oxidation reactions has recently been discussed in detail by Halpern[139].

When AB is small (Fig. 1) the interaction between the reacting species is weak and an onter sphere type of mechanism might be considered as operating.

The theoretical approach for these reactions is much simpler than for the inner sphere. No metal–ligand bonds are made or broken in the electron transfer step and arbitrary parameters which occur in theoretical studies in chemical kinetics are therefore absent. A theory has been developed[13,5] which predicts the rates of outer sphere electron transfer reactions. A single wave function describes the state of the transferring electron,

$$\psi = (1-M)^{\frac{1}{2}}\phi_1 + M^{\frac{1}{2}}\phi_2$$

where ϕ_1 and ϕ_2 are the wave functions for the initial and final states at a distance where there is no interaction The mixing parameter, M, varies smoothly from zero to unity during the course of the reaction, M being the average fraction of the electron which is transferred. The transition state is at the top of the energy barrier A, and corresponds to that value of M which minimises the energy when the internuclear coordinates are fixed. The free energy of activation includes the Coulombic repulsion of the reactants, the changes in the inner hydration shell and the changes in the Born hydration energy in going from the reactants to the transition state. Thus the rate constant for the reaction may be calculated, and comparison of observed and calculated rate constants has been made[14]. No unambiguous cases of metal–ligand interactions of this type has however so far been identified. When AB is finite (Fig. 1) then the oxidation may take place via an inner sphere route. Theoretical investigation of such reactions is more difficult than in the previous case in that closer contact of the reactants results in greater orbital overlap and the lower symmetry makes calculation of the rearrangement free energy more difficult.

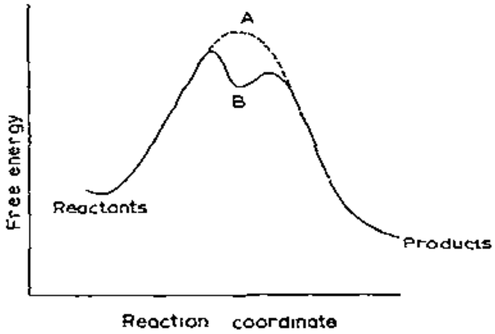


Fig 1. Free energy as a function of reaction coordinates.

Most electron transfer processes involving metal ions and ligands take place via this route and it is of importance that studies are made on the nature of intermediates which are involved If a transient complex ion is formed in the course of the reaction, there are three possible rate controlling factors: (*a*) the rate of formation of the intermediate, (*b*) the rate of electron transfer within the complex ion and (*c*) the rate of breakdown of the complex.

Although the nature and reactivity of metal-ion oxidants has been well documented previously[15-20] the use of fast reaction techniques is now providing greater detail in such reactions and in this Review the mechanism and nature of the complexes involved will be considered. Various metal ion oxidants are considered in the types of interaction with organic and inorganic substrates. In general, systems involving cations have been the more fully investigated but reference is made to anionic reactants where data are available.

B. COBALT(III)

The cobaltic ion to stable only in the form of complex salts, the fluoride chloride, sulphate and acetate species being solids all of which revert to the cobaltous state[21,22]. The aqueous cobalt(III) ion is extremely reactive, being known as a very powerful oxidant, the redox potential for the system

$$Co^{3+} \xrightarrow{+e} Co^{2+}$$

being 1.95 V at 25°[23]. In pure water at room temperature spontaneous reduction to the Co^{II} state takes place with evolution of oxygen. This reaction was first studied in detail by Bawn and White[21] who found a rate dependence which was first and second order in cobalt(III) concentration. Decrease in acidity increased the rate, due to reaction of both Co^{3+} and the hydrolysed species formed in the reaction:

$$(H_2O)_6Co^{3+} \rightarrow (H_2O)_5Co(OH)^{2+} + H^+$$

A later study failed to reproduce the earlier findings[24], the reaction order of Co^{III} being observed to be $^3/_2$ and the rate inversely proportional to $[H^+]^2$. The mechanism proposed in this case, involved the cobaltic ion present in the dimeric form, *e.g.*

$$2\,CoOH^{2+} \rightleftharpoons [Co{-}O{-}Co]^{4+} + H_2^{\cdot}O$$

with the rate determing step

$$CoOH^{2+} + [Co{-}O{-}Co]^{4+} \rightarrow 3\,Co^{2+} + HO_2^{\cdot}$$

followed by $CoOH^{2+} + HO_2^{\cdot} \rightarrow Co^{2+} + H_2O + O_2$. Recently the reaction has been studied using ^{18}O as a tracer[25] the results showing that the HO_2 is formed as a primary product and that the reaction proceeds *via* an inner sphere oxidation of the water bound to the metal ion. These experiments exclude the formation of an O–O bond in the intermediate since this would lead to hydrogen peroxide which was shown not to be a precursor of the oxygen evolved. The mechanism suggested is the attack of cobalt(III) on the dimeric aquo complex followed by formation of the HO_2 radical. The water exchange rate of cobalt(III) has been studied in 4M perchloric acid[26] and exchange was found to be complete before any measurements were made (~2 min at 10°). The solid complex $KCoF_3$ is known to be paramagnetic[27] and since water is close to fluoride in the spectrochemical series, it may be that the aquo cobaltic ion is high spin, with the loss of any crystal field energy associated with strong field d^6 systems. A solution of cobaltic ions in 6M perchloric acid at 0° was found to be diamagnetic[28]. In order to account for these findings, it has been suggested that either the exchange is Co^{II} catalysed or that the energy to promote an electron from a t_{2g} to an e_g level would contribute about 4 kcal/mol to the activation energy, allowing the cobalt(III) to react as in a high spin configuration. This route has been extended and the mode of substitution for cobalt(III) complexes involving a redox step has been proposed[29]. A series of papers of the cobaltic ion oxidation of organic substrates includes the reactions with phenols[30], *tert*-butanol[31], ketones[32], and carboxylic acids[33]. In general rate laws involved two terms, one hydrogen ion dependent suggesting the reaction of the aquo ion and its hydrolysed product. The proton dependence of the alcohols and aldehydes may confuse the interpretation of the acid dependence in these systems, however the same rate law is found in the oxidation of benzene[34] where protonation is too low to interfere.

In the latter reaction, the main products are *p*-benzoquinone, muconic acid and its lactone, via the oxidation sequence:

$$\begin{tikzcd}
\text{benzene} \arrow[r, "(1)"] & \text{phenol} \arrow[r, "(2)"] \arrow[d, "(4)"] & \text{hydroquinone} \arrow[r, "(3)"] & p\text{-benzoquinone} \\
& \text{catechol} \arrow[r, "(5)"] & o\text{-benzoquinone} \arrow[d, "(6)"] & \\
& & \text{muconic acid} + \text{lactone} &
\end{tikzcd}$$

Where each step requires two cobaltic ions and reaction (1) is rate determining. In the reactions with chlorine dioxide[34a] and hydrazoic acid[34b] no evidence is found for intermediate complex formation, and kinetic evaluations of the hydrogen ion dependence have been made using a Harned-type correction factor. In both cases, the reactive cobaltic species is considered to be $Co(OH)^{2+}$. In the case of propionic acid[33], the reaction is considered to take place via the formation of a complex intermediate, the equilibrium constant being sufficiently large to manifest itself in the rate law, Michaelis–Menten kinetics being exhibited:

$$\begin{tikzcd}
R.CO_2H + Co(H_2O)_6{}^{3+} \arrow[r, shift left, "K"] & \{R.CO_2.\,Co(H_2O)_5\}^{2+} + H^+ + H_2O \arrow[l, shift left] \arrow[d, "k_2"] \\
& R^{\cdot} + CO_2 + Co^{2+} + 5H_2O
\end{tikzcd}$$

$$\text{and } R^{\cdot} + Co^{3+} \xrightarrow{\text{fast}} R^+ + Co^{2+}$$

$$R^+ \xrightarrow{+\,H_2O} ROH + H^+$$

Indirect physical evidence has also been presented in the case of the corresponding reaction with H_2O_2[24]. Again although first order plots are linear, when extrapolated to zero reaction time the cobaltic ion concentration was lower than the known starting value, indicating involvement of the metal ion in some rapid initial reaction. The effect was more marked with increase in temperature, the observation being interpreted using the equilibrium:

$$Co^{3+} + H_2O_2 \rightleftharpoons Co(HO_2)^{2+} + H^+$$

The oxidation of chloride to yield chlorine has also been investigated[35,36]. In this case, however, using a stopped-flow device, it has been possible to demonstrate the existence of a complex, which subsequently decomposes in an intramolecular electron transfer step (e.g. Fig. 2). In the wavelength range 250–300 nm, the stopped-flow traces consisted of two parts, (*a*) an initial increase in absorbance associated with the formation of the transient species and (*b*) a much slower decrease when the electron transfer occurs. Similar studies on malic[37] and thiomalic[38] acids, and cysteine[36] indicate a route via a complex. The rate of formation of the species has been characterised using the following reaction scheme:

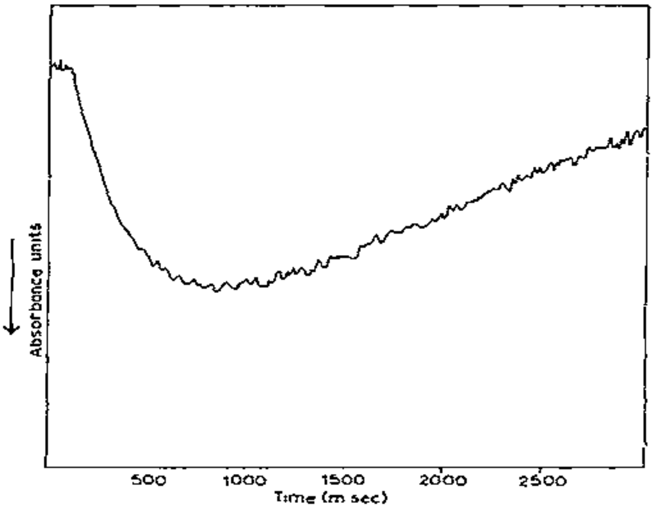


Fig. 2. Stopped-flow trace· reaction of cobalt(III) with L-cysteine, showing the formation of a complex followed by its slower decomposition; [L-cysteine] = 10×10^{-2} M, $[Co^{III}] = 1 \times 10^{-3}$ M, $[H^+] = 0.41$ M, $T = 18°$.

$$Co^{3+} + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoL^{3+} \tag{1}$$

$$CoOH^{2+} + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CoOHL^{2+} \tag{2}$$

$$(H_2O)_5Co(OH_2)^{3+} \overset{K_h}{\rightleftharpoons} (H_2O)_5CoOH^{2+} + H^+ \tag{3}$$

$$(H_2O)_5CoL^{3+} \overset{K_3}{\rightleftharpoons} (H_2O)_4Co(OH)L^{2+} + H^+ \tag{4}$$

Providing the protolytic reactions are sufficiently fast and the electron transfer step sufficiently slow, the first order rate of formation of the complex may be expressed as rate $= k_{\mathrm{obs}}[\mathrm{Co^{III}tot}]$ where k_{obs}, the observed rate constant may be written as

$$k_{\mathrm{obs}} = k_{-1} + \frac{k_{-2}K_3}{[\mathrm{H}^+]} + \frac{k_{-1}K_1[\mathrm{L}]}{[1+K_h/[\mathrm{H}^+]]} + \frac{k_{-2}K_3K_1[\mathrm{L}]}{\{[\mathrm{H}^+](1+K_h/[\mathrm{H}^+])\}} \tag{5}$$

Maintaining the hydrogen ion concentration constant Eqn. (5) may be written as:

$$k_{\mathrm{obs}} = k_a + k_b[\mathrm{L}] \tag{6}$$

where

$$k_a = k_{-1} + k_{-2}K_3/[\mathrm{H}^+] \tag{7}$$

and

$$k_b = \frac{K_1}{[1+K_h/[\mathrm{H}^+]]}\left\{k_{-1} + k_{-2}K_3/[\mathrm{H}^+]\right\} \tag{8}$$

Eqn. (8) involves the equilibrium constant K, corresponding to reaction (1) $(= k_1/k_{-1})$ and rearrangement of (7) and (8) yields

$$k_a/k_b = [K_h/K_1[\mathrm{H}^+]] + 1/K_1 \tag{9}$$

so that both K_1 and K_h may be evaluated from plots of k_a/k_b against $[\mathrm{H}^+\mathrm{J}]^{-1}$. Formation rates k_1 and k_2 $(= k_{-2}K_3K_1/K_h)$ have been evaluated for several systems and are listed in Table 1.

TABLE 1

KINETIC PARAMETERS[a] FOR FORMATION OF Co(III) INTERMEDIATES ($T = 8°$)

Ligand	k_1[b]	k_2[b]	$E_a(1)$[c]	$E_a(2)$[c]	K_1[d]	*Ref.*
Malic acid	5.4 ± 1.2	70 ± 10	—	—	34	37
Thiomalic acid	8.2 ± 2	320 ± 50	—	—	137 ±15	38
Chloride[e]	2	200 ± 100	—	—	26 ±3	35
Chloride	3 ± 2	100 ± 20	18 ± 4	22 ± 4	21 ±4	36
Bromide	4.5 ± 2	120 ± 40	24 ± 5	10 ± 4		36
Cysteine	2 ± 1	50 ± 15	—	—	18 ±4	36
Thiourea[f]	2.5 ± 0.5	180 ± 30	8.6 ± 4	9 ± 1	—	39
N,N'-Dimethylthiourea	15 ± 3	1300 ± 200	7.6 ± 4	9.8 ± 1	—	39
N,N'-Diethylthiourea	11 ± 3	820 ± 100	7.6 ± 4	10.6 ± 1	—	39
Ethylene thiourea	10 ± 2	150 ± 20	7.8 ± 4	10.9 ± 1	—	39

[a] k_1 and $E_a(1)$ correspond to equilibrium (1) and k_2 and $E_a(2)$ to equilibrium (2), see p. 250.
[b] L/mole sec. [c] Kcal/mol [d] L/mole. [e] $T = 25°$, $I = 3.0$ M [f] Derived assuming electron transfer reaction to be very fast, *i.e.* complex formation step is rate determining

In the case of the chloride oxidation[35] evidence was found for acceleration of the rate due to cobalt(II) ions present. In other studies[32,37] however, the rates of reaction are invariant with the concentration of cobalt(II) present, *e.g.* the redox state involving malic acid showed no effect on a six-fold variation of cobaltous ions.

It may be seen from Eqn. (9) that the equilibrium constant for complex formation may be derived. Values derived from temperature dependence studies using the Van't Hoff isochore may then yield the overall thermodynamic parameters ΔH_0 and ΔS_0 for equilibrium (I). The use of the stopped-flow procedure would appear to be one of the few methods by which such investigations may be made when highly oxidising species are involved. From detailed studies of the chloro, and L-cysteine complexes[36], the following thermodynamic data have been derived:

Ligand	$-\Delta G^\circ$ *(kcal/mol)*	ΔH° *(kcal/mol)*	ΔS° *(kcal/mol)*
Chloride	2.1 ± 0.5	3 ± 2	18 ± 10
L-Cysteine	1.9 ± 0.5	4.5 ± 2	22 ± 10

From these data it may be seen that the bonding involved in these complexes is predominantly electrostatic, the favourable free energy change being the result of a large positive entropy effect.

The behaviour of these ligands contrasts markedly with the more weakly coordinating thiourea and substituted thiourea of general formula[39] $R'NH \cdot C = S \cdot NH \cdot R''$. For these systems, although the reactions are still fast, there is no evidence for complex formation, the second order kinetics being first order with respect to each reactant. The rate determining steps are however considered to correspond to the formation of a complex but in this case the rate of the electron transfer step is substantially greater. An alternative mechanism for these reactions based on the "outer sphere" process using the Marcus[13] theory indicated marked curvature in the plots of free energy of reaction against free energy of activation, probably due to the large energies of interaction involved. It is of interest to note that in four of the five instances where there is no adherence to a Marcus treatment of this type, one of the reacting species is the cobaltic ion[10,40]. From the data in Table 1 it may be seen that the rate constant for the formation of the complex (k_1) varies little with the nature of the ligand L. Although the mechanism of formation of divalent metal complexes is well established as a first order process[41], involving the rate of loss of a coordinated water molecule from the primary coordination sphere of the metal ion as the rate determining step, the position with respect to trivalent metal ions is much less certain due to the greater tendency towards hydrolysis and also because many of these species are oxidants. It would appear from the data so far derived that Co(III) forms complexes via an S_N1 process. A possible exception to this may be the reaction with iodide[36].

The stopped-flow traces which show evidence for an intermediate complex have also been used to derive the spectra of these species[42]. Since the electron transfer is substantially slower than the rate of formation, the increase in absorbance at any wavelength is a measure of the concentration of the complex present and by maintaining the reagent concentrations constant and varying wavelength, it is possible to characterise the UV spectrum. Examples of spectra derived using this method are shown in Fig. 3. Unfortunately the low concentrations of cobaltic ion used precluded investigations in the visible region. Jørgensen[43] has discussed the charge-transfer peak in the spectra of metal-ion complexes in relation to the oxidising power of the ligand. For the same metal ion, the more reducing the ligand the nearer is the charge-transfer peak to the IR region. The spectra (Fig. 3) are in keeping with this observation, the reducing power of the mercaptan being greater than the oxygen analogue. The wavelength maxima are $\mathrm{CoCl^{2+}}$ 272 nm; $\mathrm{Co(cysteine)^{4+}}$ 290 nm; $\mathrm{Co\text{–}(thiomalic\ acid)^{3+}}$ 293 nm; $\mathrm{Co\text{–}(malic\ acid)^{3+}}$ 285 nm.

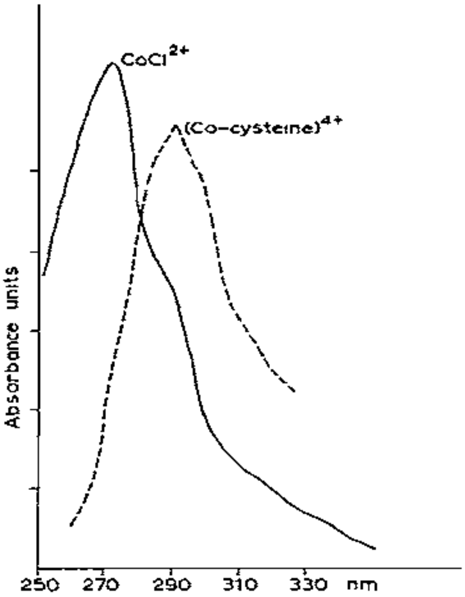
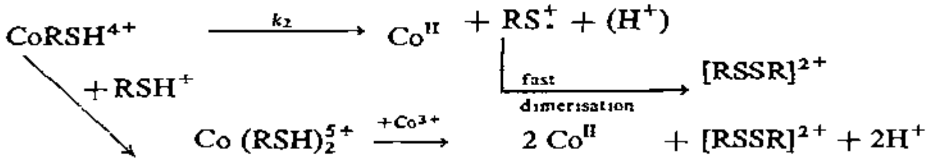


Fig 3. UV spectra of intermediates.

The oxidation–reduction step in cobaltic reactions has been found to be photo-catalysed in the UV region and most studies have been carried out at about 600 nm where there is no evidence for this behaviour. The mode of reaction would appear to vary markedly with ligand, *e.g.* for malic[37] and thiomalic acid[38] complexes, the process is unimolecular yielding $\mathrm{Co^{II}}$ and either the α-keto acid or the corresponding disulphide as product. In the case of L-cysteine, however, as well as the former path, a second route has been suggested from kinetic data[36], *e.g.* ($\mathrm{RSH^+}$ = cysteine$^+$)



A concerted mechanism has been postulated[33] in the redox step involving carboxylic acids. The case of oxidation of aliphatic acids follows the sequence.

$$\mathrm{Me\ \ CO_2H < MeCH_2CO_2H < Me_2CH\ \ CO_2H < Me_3C \cdot CO_2H}$$

The activation energy decreases by 4 kcal/mol for the replacement of each α-hydrogen by a methyl group. This would not be expected from a two stage mechanism of the type:

$$\mathrm{R.COO{-}Co^{III}} \overset{\text{(slow)}}{\rightarrow} \mathrm{R{-}COO^{\bullet}+Co^{II}}$$
$$\mathrm{R{-}COO^{\bullet}} \overset{\text{(fast)}}{\rightarrow} \mathrm{R^{\bullet}+CO_2}$$

In marked contrast to the studies in aqueous media where there are limitations in the use of the cobaltic ion, the formation and oxidation of alkyl radicals by $\mathrm{Co^{III}}$ have been examined in non-aqueous media[44] in order to obviate problems dealing with the stability of the products. Cobalt(III) acetate is soluble in a variety of carboxylic acids which were used as solvent. Thermal decompositions were carried out on primary, secondary and tertiary acids in the absence of air. The use of these media enabled the examination of catalytic effects due to strong acids which are unobservable in aqueous solutions. The rates both of the oxidation of alkyl radicals by $\mathrm{Co^{III}}$ and of the decarboxylation were catalysed markedly by acid in contrast with the observations in aqueous media.

C. CERIUM(IV)

The oxidation potential of the $\mathrm{Ce^{IV}{-}Ce^{III}}$ couple is markedly ligand dependent, *e.g.* the potentials are 1.70[45], 1.61[46], 1.44[47] and 1.28[48] volts in 1N perchloric, nitric, sulphuric and hydrochloric acids, respectively. Increasing the acid concentration from 1M to 8M increases the potential to 1.87 V whereas a decrease to 1.42 V is observed for sulphuric acid. This latter decrease has been attributed to the formation of sulphato complexes of cerium(IV), *e.g.* $\mathrm{CeSO_4{}^{2+}}$, $\mathrm{Ce(SO_4)_2}$, and $\mathrm{Ce(SO_4)_3{}^{2-}}$. The reason for the stability of the ceric ion in solution has been attributed to such complex formation[16].

Cerium(IV) oxidations in perchloric acid are generally fast whereas the sulphuric acid medium has been widely used to investigate the reactions with organic substrates, where the ceric species acts as a one electron oxidant. The primary products of such reactions are radicals which subsequently undergo rapid oxidations to stable species. Kinetic studies on the oxidation of lactic, malic[49], glycollic[50] and mandelic acids[51] indicate a first order dependence on both ceric ion and the organic substrate. While the oxidation of mandelic acid requires only two moles of cerium(IV) being oxidised to benzaldehyde, glycollic, malic and lactic acids require 4.0. 8.5 and 7.5 equivalents of ceric ion, respectively to produce mixtures of CO_2, formic and acetic acids. There is no evidence in these systems for cerium(IV) carboxylic acid complexes. The reaction with oxalic acid, which has analytical importance has been studied in detail[52,53]. In this case, a comparison of the actual cerium(IV) concentration at the start of the reaction with the apparent concentration obtained by extrapolation to zero time indicated the existence of a rapid pre-equilibrium step involving cerium(IV). The instanteous concentration of the intermediate is controlled by the bisulphate (or sulphate) concentration of the medium via the scheme

$$\mathrm{Ce(SO_4)_3}^{2-}+(\mathrm{H}^+) \overset{Kd}{\rightleftharpoons} \mathrm{Ce(SO_4)_2}+\mathrm{HSO_4}^-$$

and

$$\mathrm{Ce(SO_4)_2}+\mathrm{HC_2O_4}^- \overset{Kc}{\rightleftharpoons} [\mathrm{Ce(SO_4)_2(C_2O_4)}^{2-}]+\mathrm{H}^+$$

The decomposition of the intermediate has been investigated separately and has been shown to be independent of the bisulphate concentration of the medium. Since the same temperature dependence parameters are indicated for this step as for the overall reaction, the final products are considered to result from two consecutive one-electron transfer processes:

$$[\mathrm{Ce(SO_4)_2(C_2O_4)}^{2-}] \xrightarrow{k_1} \mathrm{Ce(SO_4)_2}^-+\mathrm{C_2O_4}^-$$

and

$$\mathrm{Ce(SO_4)_3}^{2-}+\mathrm{C_2O_4}^- \xrightarrow{\text{fast}} \mathrm{Ce(SO_4)_2}^-+\mathrm{SO_4}^{2-}+2\mathrm{CO_2}$$

In the reaction with bromide[54], it is considered the 1:1 and 1:2 complexes are formed as transient intermediates, the rate of disappearance of bromide being represented as

$$-\mathrm{d}(\mathrm{Ce^{IV}})/\mathrm{d}t = \{k_1[\mathrm{Br}^-]+k_2[\mathrm{Br}^-]^2\}\,[\mathrm{Ce^{IV}}]/[\mathrm{SO_4}^{2-}]$$

A mechanism consistent with the rate law may be written as

$$\begin{aligned}
&\mathrm{Ce(SO_4)_3}^{2-}+\mathrm{Br}^- \rightleftharpoons \mathrm{Ce(SO_4)_2Br}^-+\mathrm{SO_4}^{2-}\\
&\mathrm{Ce(SO_4)_2Br}^-+\mathrm{Br}^- \rightarrow \mathrm{Ce(SO_4)_2}^-+\mathrm{Br_2}^-\\
&\mathrm{Ce(SO_4)_2Br}^-+\mathrm{aq} \rightarrow \mathrm{Ce(SO_4)_2}^-+\mathrm{Br}^{\bullet}\,(\mathrm{aq})\\
&\mathrm{Br_2}^-+\mathrm{Br}^{\bullet} \rightarrow \mathrm{Br_2}+\mathrm{Br}^-
\end{aligned}$$

Complex formation has also been postulated in the ceric ion oxidations of methanol[55], ethanol[56] and mandelic[57] and malonic acids[58] in perchloric acid media. In the same medium, the oxidation of glycerol[59] also indicated the presence of a complex (using Michaelis–Menten kinetics) but in sulphuric acid, no such intermediate is formed. Similarly with methanol[55] in sulphuric acid no formation step is discernible. The activation parameters do not greatly differ in the two solutions and it is considered[60] that the reason for such observations lies in the relative complexing abilities of the ligand and the solvent anion. In non-complexing media like perchlorate, a complex between the organic substrate and the metal ion may be formed whereas in the presence of sulphate which itself complexes strongly with ceric ion, any transient species with the ligand is unlikely. Another interpretation[59] which has been advanced is that the reaction mechanism is dependent on the nature of the medium, the route in sulphate media involving free radical formation.

Recently the oxidation of sulphur containing systems has been investigated using fast reaction techniques[61,62]. Where the substrate is either an α-mercapto-carboxylic acid or a thiourea, the kinetics are shown to be strictly second order with no evidence for extensive complex formation, and in both cases the thermodynamic parameters are fairly similar. The reaction rates are substantially slower for the corresponding oxygen analogues, due to less favourable activation energy terms. If the *d* orbitals of the sulphur are involved in bonding to the sulphur in the course of the reaction, the activated complexes of this type would be more stable than for the oxygen substrates. A comparison of the thermodynamic data are included in Table 2. The values of ΔS^* in the range −20 to −34 e.u. in radical reaction have been ascribed to electron-pairing and unpairing processes and to the loss of degrees of freedom formerly available to the reactants on the formation of a rigid transition state[63].

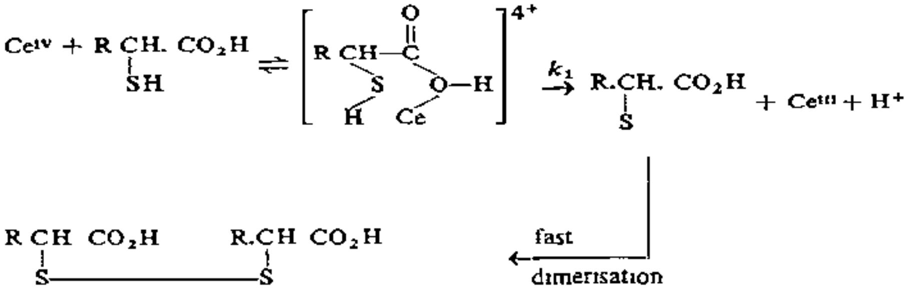
TABLE 2

THERMODYNAMIC PARAMETERS FOR CERIC OXIDATIONS AT 25°

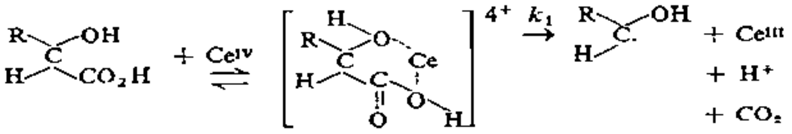
Substrate	E_a *(kcal/mol)*	ΔS^* *(e.u.)*	$\Delta H°$ *(kcal/mol)*	*Ref*
Glycollic acid	23 2	1	—	50
Lactic acid	22 8	3	—	64
Thioglycollic acid	7 9	−27		61,65
Thiolactic acid	6 8	−31		61,65
Thiomalic acid	7 6	−30		61,65
Thiourea	7 9	−33	26 4	62
N,*N′*-Dimethylthiourea	9.1	−29	24 8	62
N,*N′*-Diethylthiourea	8 9	−28	25 2	62
Ethylenethiourea	9 6	−25	22 3	62
Thiosemicarbazide (*N*-aminothiourea)	9 8	−29	—	62

The greater stability of the sulphur containing radicals is demonstrated by the fact that in all cases disulphides are formed as reaction products. In the oxygen analogues, however, delocalisation of the electron takes place throughout the entire radical which may now interact with another ceric ion with subsequent rapid decomposition of the intermediate involving decarboxylation and the formation of either a lower aldehyde or its corresponding acid. Another explanation of the differences in energy of activation in the systems may be that whereas in the sulphur systems an S–H bond is broken, it has been shown from the kinetic isotope effect, k_h/k_d, of 1.2 formed for the ceric ion oxidation of mandelic acid[66] that a C–C bond is broken in the rate determining step. The mechanistic differences in reactions of α-hydroxy- and α-mercapto-carboxylic acids may be represented as:

α-mercaptocarboxylic acids



α-hydroxycarboxylic acids



and

$$\text{R.CH (OH)} + Ce^{IV} \xrightarrow{\text{fast}} \text{RCHO} + Ce^{III} + H^+$$

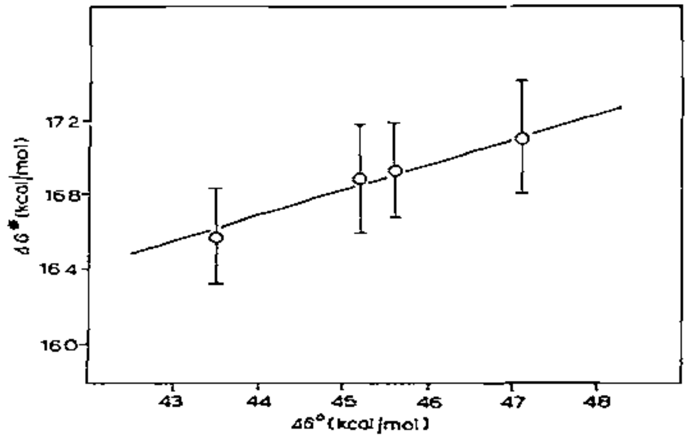


Fig 4 Cerium(IV) reaction with thioureas; plot of ΔG^* against $-\Delta G^\circ$.

For the thioureas, the oxidation of substrates follows the reactivity sequence. Dimethyl > diethyl > thiourea > ethylenethiourea which is in accord with the order of inductive effects found previously[67]. Attempts to correlate the data for these systems according to the Marcus theory have shown that whilst the plot of $-\Delta G^\circ$ (the overall free energy) against ΔG^* for the various reactions showed good linearity (Fig. 4) the slope of -0.14 is markedly different from the theoretical value of 0.5. As in the case of the cobalt(III) systems, it would appear that the energies of interaction are too great for the theory to be applicable. Table 2 includes the overall heats of reaction and making allowance for the heat of dimerisation, the enthalpies of radical formation ($\Delta H_{\text{rad}}{}^\circ$) would appear to be in the range 14–20 kcal/mol. It may be, however, that the large overall entropy changes and the heat of dimerisation are responsible for the observed free energy relationships[62].

D. IRON(III)

The ferric ion is shown as a fairly stable species which may be hydrolysed in solution. The redox potential for the Fe^{3+}/Fe^{2+} couple of 0.771 V[68] in M $HClO_4$ is lower than for the oxidants previously described. The corresponding values in M H_2SO_4 and HCl are 0.68 and 0.70 V, indicating that again the perchlorate ion shows least tendency to complex with the metal ion.

Oxidation reactions involving the ferric ion have been shown with few exceptions[69] to proceed via a mechanism involving the formation of a complex, although side reactions may complicate the overall picture. In the oxidations of thiosulphate[70,71], the rapid formation of a blue-purple intermediate is followed by decomposition to Fe^{II} and tetrathionate, following the overall reaction

$$2Fe^{III}+S_2O_3{}^{2-} \rightarrow 2Fe^{II}+S_4O_6{}^{2-}$$

The experimental rate may be represented by the expression

$$\text{rate} = k'_2[FeS_2O_3{}^+]^{\frac{1}{2}}[S_2O_3{}^{2-}]^{\frac{1}{2}}$$

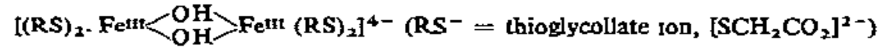
and is consistent with the reaction scheme:

$$Fe^{III}+S_2O_3{}^{2-} \overset{k_1}{\rightleftharpoons} FeS_2O_3{}^+$$

$$FeS_2O_3{}^+ + S_2O_3{}^{2-} \rightleftharpoons FeS_2O_3+S_2O_3{}^-$$

$$FeS_2O_3{}^+ + S_2O_3{}^- \rightarrow Fe^{II}+S_4O_6{}^{2-}$$

The intermediate complex has been studied in various media[71] where its composition has been determined using Job's methods of continuous variations. In aqueous acidic (perchloric) solutions, the complex is $FeS_2O_3{}^+$ but there is a gradual shift in alcoholic solutions towards higher complex formation and in 70% alcoholic solution there is evidence for the anionic complex[72] $Fe(S_2O_3)_2{}^{2-}$. A similar blue species is formed in the reaction of ferric ion with cysteine[73] and other thiols[74,75] the overall reaction order again being complex. The iron(III)–cysteine complexes have been further studied at low temperature[76] and the 1:1 ratio confirmed for the blue species. The coordination to the iron is considered to occur through the sulphydryl and carboxyl groups of the cysteine, the absorption spectrum being very similar to that of the blue ferric thioglycollate complex, having a maximum at 620 nm. The bonding between the cysteine and the iron has been considered to be weak as the 620-nm band is optically inactive. In the case of the blue iron(III) thioglycollate complex[74] anaerobic bleaching in acid ethanolic solution has been shown to follow first order kinetics, yielding iron(II). A postulate that the composition of the labile species is a hydroxy bridged dimer:



$$[(RS)_2\cdot Fe^{III}\overset{OH}{\underset{OH}{\lessgtr}}Fe^{III}(RS)_2]^{4-} \quad (RS^- = \text{thioglycollate ion, } [SCH_2CO_2]^{2-})$$

has been made[75] by analogy with the Co^{III}–cysteine systems.

In the oxidation of iodide to iodine[77] the reaction was found to be first order with respect to iron(III) and second order in iodide ion. A mechanism consistent with these findings is of the form

$$Fe^{III}+I^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} FeI^{2+}$$

$$FeI^{2+}+I^- \rightleftharpoons Fe^{II}+I_2{}^-$$

$$Fe^{III}+I_2{}^- \rightarrow Fe^{II}+I_2$$

In this case, the ferric iodide complex formed initially is considered to react with another iodide ion.

The oxidation of sulphite[78], hydrogen peroxide[79,80] and acetylacetonate[81,82] are likewise considered to involve intermediate complexes.

E. MANGANESE(III)

The manganese(III) ion has been used as an oxidant both as the aquated species[83] and complexed as its fluoride or pyrophosphate[84]. The estimated potential for the Mn^{3+}/Mn^{2+} couple is 1.5–1.6 V but the reaction

$$Mn^{3+}+2H_2O \rightarrow MnO_2+Mn^{2+}+4H^+$$

is extremely rapid and limits the usefulness of Mn^{III} reagent. This difficulty may however be overcome by the addition of Mn^{II} which in the presence of perchloric acid forces the equilibrium

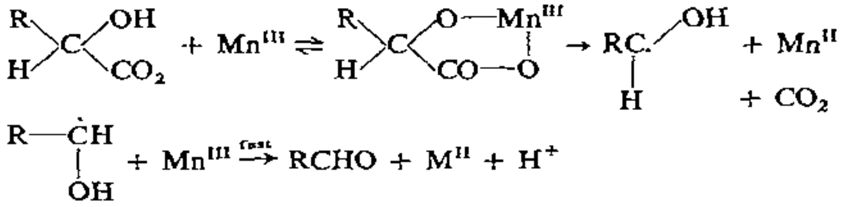
$$Mn^{II}+Mn^{IV} \rightleftharpoons 2Mn^{III}$$

well to the right. As expected, complexing with ligands lowers the redox potential, *e.g.* the value for the reaction

$$Mn(H_2P_2O_7)_3^{3-}+2H^++e^- \rightleftharpoons Mn(H_2P_2O_7)_2^{2-}+H_2P_2O_7^{2-}$$

is ~1.15 V. In the presence of ~7M sulphuric acid, the corresponding value[85] is 1.49 V. Some aspects of the chemistry of manganese(III) in aqueous solution have been the subject of a recent review by Davies[86]. The spectra of Mn^{III} aq and $MnOH^{2+}$ aq have been derived in perchlorate media[87] and are very similar both in the ultraviolet and visible regions, the absorption maximum at 470 nm being ascribed[87,88] to the $^5T_{2g} \leftarrow {}^5E_g$ transition which is the only spin-allowed transition in a spin-free d^4 system with octahedral symmetry. The hydrolytic equilibrium constant has been determined[87 89] the value of K_h being 0.93 ± 0.03M at an ionic strength of 4M at 25°, in a perchlorate medium.

The kinetics of the reaction of Mn^{III} with isopropyl alcohol[90] have been studied, the reaction being slow at room temperature with no evidence of an intermediate complex. A mechanism of oxidation of α-hydroxyacids by Mn^{III} has been postulated[66] which does not involve a C–H clearage as the rate determining step, *e g*.



$$R\dot{C}H(OH) + Mn^{III} \xrightarrow{\text{fast}} RCHO + M^{II} + H^+$$

The route, however, does involve the formation of a transient complex. In the case of the oxidation of oxalate[91] the overall stoichiometry is of the form:

$$2Mn^{III}+H_2C_2O_4 \rightarrow 2Mn^{II}+2H^++2CO_2$$

but the rate law indicates that the reaction involves 1:1, 1:2, and 1:3 complex formation, the mechanism being

$$Mn^{III}+C_2O_4^{2-} \rightleftharpoons MnC_2O_4^+ \xrightarrow{k_1} Mn^{2+}+C_2O_4^-$$
$$Mn(C_2O_4)^++C_2O_4^{2-} \rightleftharpoons Mn(C_2O_4)_2^- \xrightarrow{k_2} Mn(C_2O_4)+C_2O_4^-$$
$$Mn(C_2O_4)_2^-+C_2O_4^{2-} \rightleftharpoons Mn(C_2O_4)_3^{3-} \xrightarrow{k_3} Mn(C_2O_4)_2^{2-}+C_2O_4^-$$

with the fast secondary step

$$C_2O_4^-+Mn^{III} \rightarrow Mn^{II}+2CO_2$$

Complex formation has also been involved in the reaction with bromide[92] where the rate determining step is dependent on the concentration of bromide present. At low [Br⁻] the initial rate is first order in [Mn^{III}] and in [Br⁻] the reaction being considered inner sphere, *e.g.*

$$Mn^{3+}+Br^- \rightleftharpoons MnBr^{2+} \rightarrow Mn^{II}+Br^{\cdot}$$

At high [Br⁻], the mechanism involves another bromide ion in the outer sphere, the rate determining step

$$MnBr^{2+}\,aq + Br^- \rightarrow Mn^{II} + Br_2^{\cdot}$$

being followed by reaction with another Mn^{III} ion:

$$Mn^{III} + {}^{\cdot}Br_2 \rightarrow Mn^{II} + Br_2$$

Similarly in the case of the corresponding reaction with hydrazoic acid[93,94] the mechanism is dependent on the ligand concentration. On mixing Mn^{III} with hydrazoic acid, a pink colour develops which has been ascribed[94] to the formation of the monoazido–manganese(III) complex. At low azide concentrations, the reaction is first order in $[Mn^{III}]$ and second order in $[HN_3]$[93] the suggested mechanism being

$$\begin{aligned}
&Mn^{3+}aq + HN_3 \overset{K}{\rightleftharpoons} MnHN_3aq^{3+}\\
&MnHN_3{}^{3+}aq + HN_3 \xrightarrow{k_1} Mn^{II} + H_2N_6{}^+\\
&Mn^{3+}aq + H_2N_6{}^+ \xrightarrow{k_2} Mn^{II} + 3N_2 + 2H^+
\end{aligned}$$

with $k_2 \gg k_1$. Although $Mn(OH)^{2+}$ is present in these solutions it would appear to be unreactive under these conditions. Under conditions of a large excess of hydrazoic acid ($[HN_3]:[Mn^{III}] \sim 100:1$) the reaction stoichiometry is unaltered but the kinetic dependences become more complex, the mechanism proposed consistent with an observed second order rate in Mn^{III} being

$$2MnN_3{}^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mn^{2+} + Mn(N_3)_2{}^{2+} \tag{I}$$

$$Mn(N_3)_2{}^{2+} \xrightarrow{k_2} Mn^{2+} + 3N_2 \tag{II}$$

$$Mn(N_3)_2{}^{2+} \overset{k_3}{\rightleftharpoons} MnN_3{}^+ + N_3{}^+ \tag{III}$$

$$HN_3 + N_3^+ \xrightarrow{k_4} 3N_2 + H^+ \tag{IV}$$

the latter two steps providing the predominant route to nitrogen production[94]. Step (I) may be visualised as the transfer of an electron across an inner-sphere azide bridge with the formation of Mn^{2+} and a species which is *formally* a diazido complex of Mn^{IV}. The observed differences in this mechanism compared to the unimolecular decomposition of the cobalt(III) monoazide complex[34b] may be attributed to the failure of cobalt to attain a formal oxidation state of four. Values for equilibrium constant $K = [MnN_3aq^{2+}][H^+]/[Mnaq^{3+}][HN_3]$ have been obtained both from initial optical densities and by kinetic analysis. The values of 89 ± 18 and 74 ± 15 respectively are in good agreement. Using the stopped-flow method described earlier (p. 250), the absorption spectrum of the complex has been obtained in the wavelength range 440–570 nm, E_{max} being $\sim 7500\ M^{-1} \cdot cm^{-1}$ at 520 nm. The spectrum is shown in Fig. 5. It is of interest that the spectrum of the complex between Mn^{III} and *trans*-1,2-diaminocyclohexanetetraacetic acid has an absorption maximum[95] at ~515 nm in the pH range 2–7 and that of the pyrophosphate ion $Mn(H_2P_2O_7)_3{}^{3-}$ in 0.05M H_2SO_4 has a peak at 510 nm[11].

The kinetics of the reaction of Mn^{III} with H_2O_2 has been the subject of

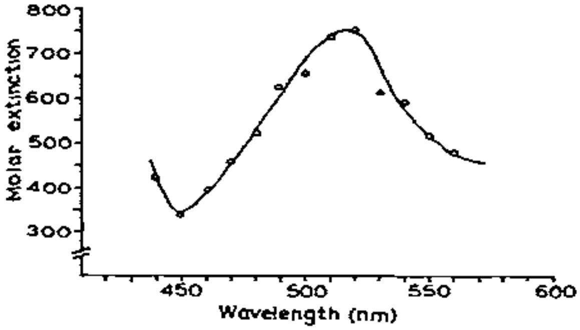


Fig 5. Visible spectrum of MnN_3^{2+} complex, for details of solution concentrations see Ref 94.

two studies[96,97], alternative mechanisms being proposed. The different conclusions reached have recently been discussed by Davies[86]. Wells[97] has also compared this reaction with the corresponding systems involving Co^{III} and Fe^{III}. It is of interest to note that whereas the order of redox potentials of the oxidising tripositive ions in the first transition series is[23,65]

$$Co^{III} > Mn^{III} > Fe^{III} > Cr^{III}$$

the order of reactivity with hydrogen peroxide is[98–100]

$$Mn^{III} > Co^{III} > Fe^{III} \gg Cr^{III}$$

In a recent study[101] the stoichiometries and kinetics of the Mn^{III} oxidations of hydroxylamine, *O*-methylhydroxylamine and nitrous acid have been investigated. In contrast to the complex reactions discussed above, these have been shown to be fast, second order processes. Also in general there is no spectrophotometric evidence for complex formation in these reactions. In the reaction with nitrous acid, the results are consistent with the mechanism:

$$Mn^{III}+HNO_2 \xrightarrow{k_1} Mn^{II}+NO_2+H^+$$
$$Mn(OH)^{2+}+HNO_2 \xrightarrow{k_2} Mn^{II}+NO_2$$
$$H_2O+Mn^{III}+NO_2 \xrightarrow{k_3} Mn^{II}+NO_3^-+2H^+$$

with $k_3 \gg k_1$ or k_2. The values of $k_1 = 2.2\times10^4$ $M^{-1}\cdot sec^{-1}$ and $k_2 = 4.9\times 10^4$ $M^{-1}\cdot sec^{-1}$, at 25° compare with those for hydroxylamine whereas methylation of the hydroxyl group causes a 500 fold decrease in rate constant.

In reactions involving Mn^{III} complexed to non-oxidisable ligands, *e.g.* pyrophosphate, it would appear that the reactions may proceed via an outer-sphere. Diebler and Sutin[11] have shown that reactions of $Mn(H_2P_2O_7)_3^{3-}$ with various substituted iron(II) phenanthroline complexes conform to the Marcus theory in their behaviour.

F. VANADIUM(V)

In aqueous acidic media, the vanadium(V) ion is formed from vanadate according to the equilibrium:

$$VO_3^- + 2H^+ \rightleftharpoons VO_2^+ + H_2O$$

The vanadium(V)/vanadium(IV) couple may be expressed as

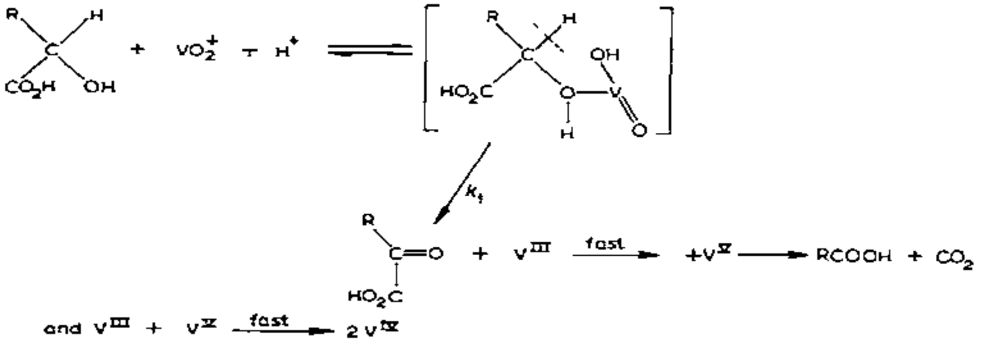
$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$$

the corresponding potential being 1.00 V. The solutions are stable over a limited pH range[102] and in strong sulphuric acid there may be complexing with the sulphate[16]. There is some evidence that in perchloric acid the equilibrium

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

exists[103].

Oxidation studies have been carried out on formic and malonic[104], glycollic[105], oxalic[106], mandelic[107], tartaric[108], and 2-hydroxy-2-methylpropanic acids[109] and pinacol[103]. In these reactions the mechanism postulated has been the formation of a transient complex between the vanadium and the organic substrate. No physical evidence for such complexes was obtained. The study of the kinetic isotope effect $k_h/k_d = 2.0$ for the oxidation of mandelic and α-deuteromandelic acids, indicates C–H bond fission is appreciable in these reactions, and a general mechanism may be postulated as:



A distinction may be made between on the basis of overall thermodynamic parameters between systems involving a C–H bond rupture and those where a C–C bond is broken. Table III summarises the thermodynamic parameters where it may be seen that a fairly large negative entropy of activation (~ −20 e.u.) is associated with C–H fission in the rate determining step.

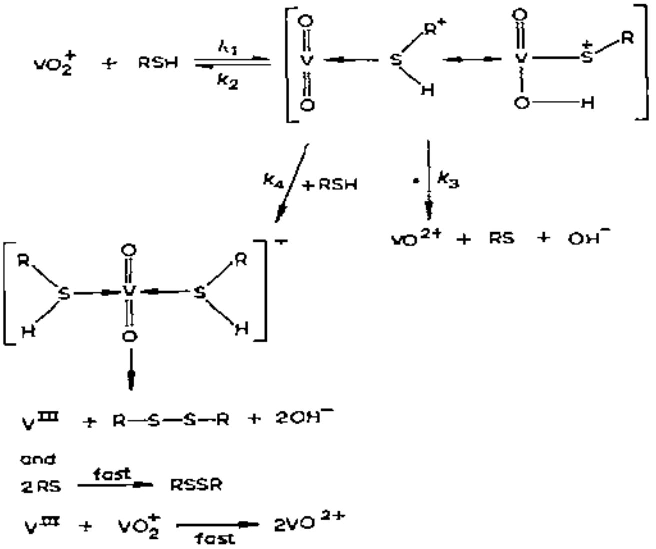
The vanadium(V) oxidation of thiomalic acid (2-mercaptosuccinic acid) has been studied[112] using fast reaction techniques and in this instance there is evidence for the formation of an intermediate complex. The spectrum of the purplish-

TABLE 3

THERMODYNAMIC DATA FOR OXIDATION OF ORGANIC ACIDS BY VANADIUM(V)

Acid	*E_a (kcal/mol)*	*ΔS^* (cal/deg/mol)*	*Ref.*
Glycollic	16.7	−16	105
Lactic	16.5	−20	110
Mandelic	14.0	−20	111
α-Hydroxyisobutyric	21.8	−0.4	105
Pinacol	22.8	+9.5	106
Oxalic	23.4	+6.5	107
Tartaric	22.8	+5.9	108
2-Hydroxy-2-methyl-propanoic	22.0	−1.0	109

brown intermediate was measured as described previously and is shown in Fig. 6. Product studies indicated that the overall reaction involved 1 mole of vanadate per 1.1 ± 0.1 moles of α-thiol, with the formation of the corresponding disulphide. The characteristic blue colour of vanadium(IV) was produced and 2 ± 0.3 moles of hydroxide ion released per mole of vanadium(V) reacted. Over the pH range 2.4–4.4 the rate constant for the formation of the intermediate remained constant. Calculations based on equilibrium data[113] indicate that the amount of VO_2^+ present decreases from over 70% to about 1% in this pH range. The change in relative proportions of vanadium(V) with pH did not appear to influence the kinetics so that the interconversion of the vanadium(V) species was considered to occur within the time of mixing the solvents. The kinetic data are consistent with the reaction scheme (RSH = 2-mercaptosuccinic acid).



The value of k_3 obtained is 5 ± 0.2 sec^{-1} whilst that of k_4 is 40 ± 3 mole^{-1} · sec^{-1}. The 1:2 complex has also been postulated in the cobaltic oxidation of cysteine[36].

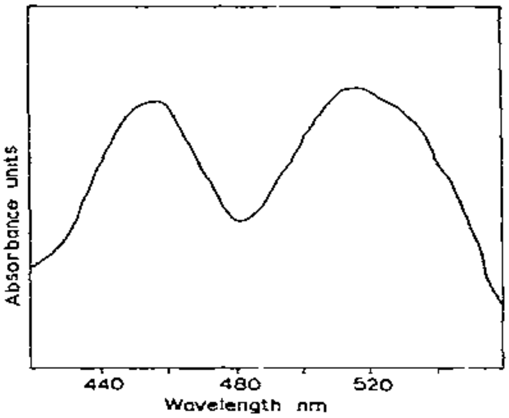
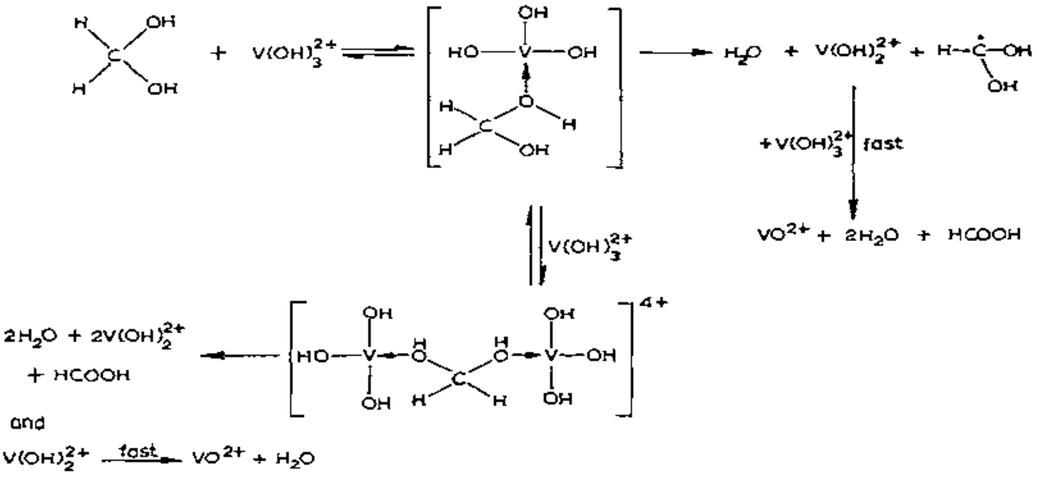


Fig 6 Visible spectrum of complex between vanadium(V) and 2-mercaptosuccinic acid, for details of solution concentrations see Ref. 112.

In the oxidation of formaldehyde[104], the initial oxidation rate showed both a first and second order dependence on the concentration of oxidant. As well as a 1:1 complex, a 2:1 complex is also considered to be formed:



The C–H bond fission is considered to be the rate determining step.

G. SILVER(II)

Silver(II) is one of the most powerful oxidants, the oxidation potential for the reaction

$$Ag^{II} + e^- \rightarrow Ag^I$$

being 1.98 volts[114]. Use has been made of its oxidising powers in analytical chemistry[60] although the fact that it is unstable with respect to water limits its effectiveness. In aqueous solutions, there is a tendency for the disproportionation reaction

$$2Ag^{II} \rightleftharpoons Ag^{I} + Ag^{III}$$

to take place followed by the rate determining decomposition of the silver(III) species to yield products. A change in the spectrum of the argentic ion in the range 350–750 nm with anion concentration (*e.g.* nitrate) has provided evidence for complex formation. Further confirmation of silver(II) complexes has been given by Rechnitz and Zamochnick[115] who observed an absorption maximum at 275 nm as well as at 475 nm for silver(II) perchlorate solutions. Using a kinetic extrapolation method, it was demonstrated that the argentic species in perchlorate media obeys Beer's Law and so must be the equilibrium species present in the reaction.

Recently, using a stopped-flow method, the silver(II)–hydrogen peroxide reaction has been examined[116], the observed first order rate constant being independent of the initial ratio of $[Ag^{II}]/[H_2O_2]$ or $[Ag^{I}]$ and of the acidity in the range 1.5–3.7 M $HClO_4$. In this latter respect the results are analogous to the corresponding manganese(III) oxidation[92]. The observation may be contrasted however with the rate of the silver(I)–silver(II) exchange[117] which increases rapidly with decreasing perchloric acid concentration suggesting the involvement of hydrolysed species. In the peroxide reaction, the rate determining step is an inner sphere electron transfer via the complex $(Ag\ HO_2^+)$ the formation constant of which has the remarkably high value of $\sim 5 \times 10^{16}$ l mole^{-1}. For first order kinetics

$$Ag^{2+} + HO_2^- \rightleftharpoons (AgHO_2^+)$$
$$AgHO_2^+ \xrightarrow{k} Ag^+ + HO_2^{\cdot}$$
$$HO_2^{\cdot} + Ag^{II} \xrightarrow{\text{fast}} Ag^+ + H^+ + O_2$$

$k \sim 11$ sec^{-1} at $I = 4.0$ M at 25 °C. The rate is insensitive to temperature variation; with $E_a \sim 0$ it is again analogous in this respect to the manganese(III) system. It is suggested that a high degree of sp^3d overlap exists in $AgHO_2^+$ due to the strong tendency for the $t_{2g}{}^6e_g{}^3$ arrangement of silver(II) to attain $t_{2g}{}^6e_g{}^4$ and the high polarisability of anionic oxygen compared with the oxygen atom in water.

In the reaction of silver(II) with thallium(I)[118], there is no acidity dependence in the concentration range 4.66–8.82 M. The mechanism is considered to involve in the first step the interaction of the anion with the oxidant,

$$Ag^{II} + NO_3^- \rightleftharpoons Ag^{I} + NO_3$$

followed by the rapid reactions of the radical:

$$NO_3 + Tl^{I} \rightleftharpoons NO_3^- + Tl^{II}$$

and

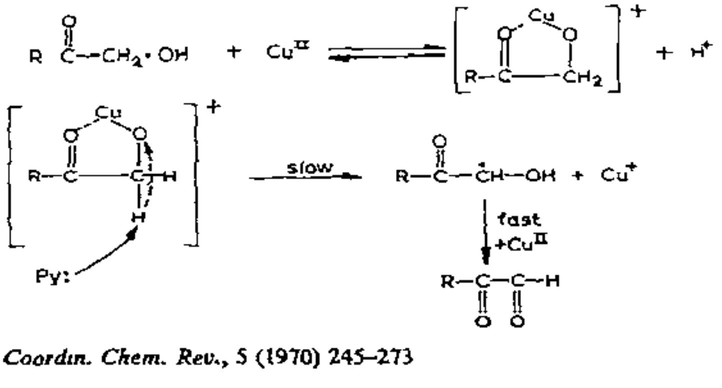
$$Ag^{II}+Tl^{II} \rightarrow Ag^{I}+Tl^{III}$$

In this respect, the mechanism is analogous to one of the pathways found for the cerium(IV) oxidation of thallium(I) in the same medium[119].

H. COPPER(II)

The oxidation states best characterised for copper are 1+ and 2+. The tervalent state has been shown to exist[15] (*e.g.* in the tellurate complex)[120] but only under very alkaline conditions. Although the second ionisation potential for copper is higher than that for any other element in the period, the much larger heat of hydration of copper(II) compared with copper(I) compensates for the ionisation potential, thus rendering the hydrated cupric ion the more stable in solution. Complexing is known to affect the redox potential and the difference in stereochemistry of the copper(I) and (II) states also appears to be important. This is illustrated in α,α′-dipyridyl complexes[121] where substituents in the 6 and 6′ positions increase the oxidation potential presumably reflecting a smaller sensitivity of tetrahedral copper(I) to steric interaction compared with the pseudo square planar copper(II).

Although the copper(II) ion is known to be very stable in solution and a relatively weak oxidant, it has been long known that solutions containing the cupric ion in a variety of conditions of pH and ligand concentration may be used to determine the concentration of reducing substrates. The first kinetic study of the oxidation of ketols by alkaline solutions of copper(II) was made in 1930[122] and copper acetate in acetic acid has been used in the reactions of monosaccharides. In an extensive series of papers, Singh and his co-workers[123] have reported studies on the reaction of copper(II) with sugars and α-hydroxycarbonyl compounds, the rate of oxidation being independent of copper(II) but approximately first order in reductant and hydroxide concentrations. A study of the oxidation of α-hydroxyacetophenone[124] has been made in buffered pyridine, which has the advantage of complexing with the copper(I) formed the system thus remaining homogeneous. A mechanism which interprets the data involves the initial formation of a ketol copper(II)chelate followed by a rate determining abstraction of a proton by the pyridine.



The oxidation of cyanide by copper(II) has been the subject of several investigations[125-127]. In the presence of ammonia[125] the reaction order was found to be first with respect to copper(II) and fourth in cyanide concentrations, suggesting a slow step involving the complex ion $Cu(CN)_4{}^{2-}$. At pH 4.7 in aqueous solutions[126], however, the reaction which was followed spectrophotometrically was considered to be the formation of the tricyanocuprate(I) the order with respect to copper(II) concentration being two and that of cyanide six. The formation of copper(II) cyanide complexes as intermediates has been postulated. In a low temperature study[127], however, Paterson and Bjerrum have confirmed the earlier findings of a second order dependence in copper(II) and have characterised in aqueous methanol a purple cupric cyanide complex which is a precursor to the redox step. EMF measurements have shown this species to be the $[Cu(CN)_4]^{2-}$ ion. The subsequent redox reaction may then be written as

$$2Cu(CN)_4{}^{2-} \rightarrow 2Cu(CN)_3{}^{2-} + (CN)_2$$

The oxidation of sulphite[128] and dithizone[129] have been studied, the corresponding copper(I) complex and a radical being produced. There is however a complex formation step prior to the redox reaction. The conditions of reaction in these systems play an important role in determining the nature of the final product. In the copper(II)–thiomalic acid reaction, the final products depend on the reagent in excess[130,131]. Under conditions of excess organic substrate[130] two redox reactions occur in the stopped-flow range, the first being a very rapid interaction (complete within ~100 m. sec) the second slower reaction yielding a copper(I)–thiomalic acid complex. Two reactions also occur in excess copper(II) where there is formed a violet coloured complex which has been investigated polarographically and spectrophotometrically[131]. From these considerations it is considered that this coloured species is a mixed valence Cu^{I}–Cu^{II} complex[131] but on isolating a salt from the solution it is found to be diamagnetic, the ESR spectrum also indicating no paramagnetism. A fuller study of this system is currently under investigation[130]. In all these copper–thiol systems, however, oxygen must be rigorously excluded since rapid side reactions yielding copper(II) are known to occur.

I. OTHER REDOX SYSTEMS

Reactions involving anionic oxidants have in general been well characterised and documented[18,20]. In the reaction of ferricyanide ion with ethylenediaminetetraacetatocobaltate(II)[132], however, Wilkins has demonstrated the existence of two intermediates using temperature-jump and stopped-flow methods. The kinetics of formation of the bridged-cyanide intermediate (A_1)

$$Co(EDTA)^{2-} + Fe(CN)_6{}^{3-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{(A_1)}{[(EDTA)Co^{III}\text{–}NC\text{–}Fe^{II}(CN)_5]^{5-}}$$

have been measured, the formation being controlled by the rate of water release from the cobalt(II) complex which is considered to react as the mono-aquo-ion $Co(EDTA)H_2O^{2-}$. The intermediate then decomposes in a slow step to yield the Co^{III} and Fe^{II} species. A second intermediate, A_2, has also been shown to exist when A_1 is mixed rapidly with ferricyanide, *e.g.*

$$A_1 + Fe(CN)_6^{3-} \rightleftharpoons \underset{(A_2)}{[(EDTA)Co^{III}\text{–}NC\text{–}Fe^{III}(CN)_5]^{4-}} + Fe(CN)_6^{4-}$$

The rate constants in this latter step closely resemble those for other outer-sphere oxidations involving $Fe(CN)_6^{3-}$ indicating that the bulkiness of A_2 appears to play a small role in the rate process.

The kinetics of the chromium(VI)–arsenic(III) reaction have been examined[133]. At low chromium concentrations, Michaelis–Menthen plots are linear demonstrating the existence of a pre-equilibrium step in the redox reaction. The mechanism is considered to involve:

$$\begin{tikzcd}
As^{III} + HCrO_4^- \arrow[r, phantom, "\rightleftharpoons"] & As^{III} \cdot HCrO_4^- \arrow[dl, "k_1"] & (K_1) \\
\text{products} & &
\end{tikzcd}$$

The rate determining step is k_1, the products being As^V and Cr^{III}. Other oxidations involving complex formation with chromium(VI) include tartaric acid[134], glycollic acid[135] and benzoyl alcohol[136].

J. CONCLUSION

In this Review, an attempt has been made to characterise the data for complex formation in terms of the nature of the metal ion involved. Although the coverage is by no means exhaustive with the advances in instrumentation in the fast reaction field, more detail will become available and patterns of behaviour of particular oxidants may develop. An area where further advances will be made is in the reactions of metal-ion–oxidant complexes as catalyst in other systems. It has been shown for example[18,137,138] that a copper(II) complex with hydrogen peroxide can interact with phenol to produce an intermediate which decomposes in a concerted cyclic two equivalent mechanism to yield *o*-hydroxyl phenol. Copper(II) catalysed oxidative de-aminations[15] are also considered to involve such intermediates. Metal ions are involved in biological processes where the nature of the linkage between the cation and the organic substrate is known to be of considerable importance. In haemocyanin, an oxygen carrying protein[131], for example, the available evidence suggests that a copper–sulphur interaction has substantial influence on the oxygen binding system. In these cases also, it would seem likely that intermediates are involved prior to the redox steps. Associated with these oxidation–reduction processes in enzymic systems is the high degree of specificity found where again the role of the interaction of the metal ion (usually iron or copper) with a particular substrate would appear to be important.

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