Coordination Chemistry Reviews, 22 (1977) 195—274

THE RADIATION CHEMISTRY OF METAL IONS IN AQUEOUS SOLUTION

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(Received 22 July 1976)

CONTENTS

A. INTRODUCTION

The discovery of the hydrated electron as a major product of the radiolysis of water and the development of pulse radiolysis have together resulted in the accumulation, in the last ten years, of a considerable amount of information on unusual valency states of metal ions in aqueous solution. For the most part attention has been focussed on hyper-reduced states produced in reaction (1),

$$e^{-}_{aq} + M^{n+} \rightarrow M^{(n-1)+} \qquad (1)$$

which affords a simple and often unique method of their formation. Reactions of hydroxyl radicals and hydrogen atoms, and of simple radicals derived, from them, with metal ions have been less commonly studied.

In this review we have tried to bring together a representative cross section of the information on metal ion chemistry in aqueous solution which has been gained in radiation chemical studies. We have set out this information within the framework of the Periodic Table. Certain areas, however, have received a good deal more attention than others for various reasons, and in these cases we have tended to adhere to the pattern of the original studies. The literature has been covered up to the end of 1975.

(i) The radiation chemistry of water

In the context of this review the radiation chemistry of water can be sum-

marised with sufficient accuracy by reaction (2) where the figures

$$4.0\ H_2O \xrightarrow{w} 2.6\ e^-_{aq} + 2.6\ OH + 0.6\ H + 2.6\ H^+ + 0.4\ H_2 + 0.7\ H_2O_2 \qquad (2)$$

express the number of each species destroyed or formed per 100 eV of energy absorbed by the water, and are called *G*-values.

The distinguishing feature of radiolysis is the formation of the products in isolated volume elements called spurs and tracks which may contain one or more pairs of reactive species which are e^-_{aq}, OH, H and H^+ in the case of water. These species diffuse and react with each other with the result that a fraction of them combine to form the molecular products H_2, H_2O_2 and H_2O, and the remainder escape into the bulk solution and become homogeneously distributed. This process can be regarded as complete after about 10^{-7} s whereas most of the experimental observations which we shall be concerned with here were made at 10^{-6} s or longer times.

Absorption of ionising radiation by matter is non-specific so that in aqueous solutions, for example, direct absorption of radiation by the solutes can be neglected when they constitute only a small fraction of the material present in the system. In practice direct effects can largely be ignored for solutions containing less than 1 mol dm^{-3} of a solute.

In reaction (2) roughly equal numbers of reducing and oxidising radicals are produced. It is often desirable to modify the system to be totally oxidising or totally reducing and this is achieved by adding solutes which react specifically with one of the primary products of reaction (2). For example, reaction (3) is commonly used to convert e^-_{aq} into OH, so that a totally oxidising system is obtained apart from the small number of hydrogen atoms also present.

$$e^-_{aq} + N_2O \rightarrow N_2 + O^- \left(\xrightarrow{H_2O} OH + OH^-\right) \qquad (3)$$

To achieve a totally reducing system solutes are added which react with H and OH to produce reducing radicals. Simple aliphatic alcohols or formate ion are generally used for this purpose (reactions (4) and (5)).

$$H \text{ or } OH + CH_3OH \rightarrow CH_2OH + H_2 \text{ or } H_2O \qquad (4)$$

$$H \text{ or } OH + HCO_2^- \rightarrow CO_2^- + H_2 \text{ or } H_2O \qquad (5)$$

(ii) Radiation chemical methods

These are divided into two types: (a) continuous, or steady-state radiolysis and (b) pulse radiolysis. In the former case radiation sources such as X-ray machines and Co^{60} γ-ray sources are commonly used and stable radiolysis products are analysed by conventional methods. In the latter case intense pulses of radiation generally of 10^{-6} s or less duration are delivered to the sample by, for example, an electron accelerator, and the immediate products, which are often transient, are detected by optical or ESR spectroscopy or

conductimetrically. As much as 10^{-4} mol dm^{-3} of a transient species can be generated by a single pulse. For further details of radiation chemical methods see refs. 1 and 2.

(iii) Reactivity of e^-_{aq}, OH and H with metal ions

Extensive studies have been made of the reactivity of the primary radicals of water radiolysis, e^-_{aq}, OH and H, since the advent of pulse radiolysis. Rate constants for many reactions have been measured, and compilations of them have been made by Anbar et al. [3] for e^-_{aq}, by Dorfman and Adams [4] for OH, and by Anbar et al. [5] for H. Table 1 shows a selection of these for reactions with some metal aquo ions, oxyanions and complexes.

In this section we discuss the general features of, and some possible mechanisms for, these reactions. The radicals CO_2^- and CH_2OH are also included because of their importance in totally reducing systems.

Hydrated electron reactions. The hydrated electron is a strong reducing agent with a redox potential estimated to be —2.7 V [6]. It is not surprising, therefore, that it reacts with aquo and complex ions of most metals except the alkali and alkaline earth metals, in many cases at a diffusion controlled rate (Table 1). These reactions all have a small activation energy of 15 ± 2 kJ mol^{-1}, and it has been suggested [7] that this is associated with the activation energy for the diffusion of e^-_{aq}. Transfer of the electron from the solvent to the metal ion may involve a transition state resulting from orbital overlap between e^-_{aq} and the ion. Alternatively, the ligands on the metal ion may act as bridges for electron transfer, in which case orbital overlap between e^-_{aq} and the ligand, and between the ligand and the metal, must occur. It seems more likely, however, that the electron tunnels through the potential energy barrier separating e^-_{aq} and the ion in view of the invariant activation energy [7]. Tunnelling certainly provides an explanation for the extremely high reaction rates observed in some cases in terms of large effective encounter distances [8].

In some cases complexation of the metal ion with ligands other than H_2O can produce a dramatic reduction in reaction rate (see Table 1) although the activation energy is unaffected [7]. Anbar [9] concluded that such kinetic behaviour is more consistent with the tunnelling transfer mechanism than with changes in the electron distribution in the *d* orbitals of the complexes as suggested earlier [10,11].

The product of these reactions is initially in a vibrationally or, in some cases, electronically excited state because of the Frank—Condon restriction. De-excitation of the vibrationally excited state occurs too rapidly ($<10^{-12}$ s) for it to be of any chemical significance, but an electronically excited product has been identified [12] when e^-_{aq} reduces $Ru(CN)_6^{3-}$. Claims for the detection of long-lived excited products of the reduction of Tl^+ [13] and $Co(dipy)_3^{2+}$ [14], however, are now recognised to be incorrect [15—17]. Excited

TABLE 1

Rate constants for reactions of e^-_{aq}, H and OH with metal ions

Metal ion	k(dm^3 mol^{-1} s^{-1}) [a]		
	e^-_{aq} [3]	H [5]	OH [4]
Aquo ions			
Ag^+	$3.6 \cdot 10^{10}$	$1.1 \cdot 10^{10}$	$\geq 3 \cdot 10^9$ [b]
Al^{3+}	$2.0 \cdot 10^9$		
Cd^{2+}	$5.6 \cdot 10^{10}$	$<10^5$	$<5 \cdot 10^5$ [36]
Ce^{3+}	$<10^9$		$7.2 \cdot 10^7$
Ce^{IV}		$3.4 \cdot 10^7$ [c]	
Co^{2+}	$1.1 \cdot 10^{10}$	$<10^3$ [d]	$8 \cdot 10^5$ [22]
Cr^{2+}	$4.2 \cdot 10^{10}$	$1.5 \cdot 10^9$ [29]	$1.2 \cdot 10^{10}$
Cr^{3+}	$6.0 \cdot 10^{10}$ [e]		$3.2 \cdot 10^8$
Cu^{2+}	$3.0 \cdot 10^{10}$	$6 \cdot 10^8$	$3.5 \cdot 10^8$
Dy^{3+}	$4.6 \cdot 10^8$		
Er^{3+}	$7 \cdot 10^7$		
Eu^{2+}			$1.3 \cdot 10^9$ [39]
Eu^{3+}	$6.1 \cdot 10^{10}$		
Fe^{2+}	$1.2 \cdot 10^8$	$1.6 \cdot 10^7$	$4.4 \cdot 10^8$
Fe^{3+}		$9.0 \cdot 10^7$	
Gd^{3+}	$5.5 \cdot 10^8$		
Hg^{2+}	[f]	$2.5 \cdot 10^{10}$	
Ho^{3+}	$6.6 \cdot 10^7$; $2.4 \cdot 10^9$		
In^{3+}	$5.6 \cdot 10^{10}$		
K^+	$3 \cdot 10^4$		
La^{3+}	$2.5 \cdot 10^8$		
Mn^{2+}	$5.7 \cdot 10^7$	$2.5 \cdot 10^7$	$\geq 1.4 \cdot 10^8$
Na^+	$<10^5$		
Nd^{3+}	$5.9 \cdot 10^8$		
Ni^{2+}	$2.2 \cdot 10^{10}$	$<10^5$	$<5 \cdot 10^5$ [36]
Np^V	$4 \cdot 10^9$ [40]		
Np^{VI}	$1.5 \cdot 10^{10}$ [40]		[f] (with O^-)
Np^{VII}	$1.8 \cdot 10^{10}$ [40]		
Pb^{2+}	$3.9 \cdot 10^{10}$		
Pr^{3+}	$1 \cdot 10^7$		$\leq 4 \cdot 10^6$ [39,41]
Pu^{VI}	$1.3 \cdot 10^{10}$ [40]		[f] (with O^-)
Pu^{VII}	$2.7 \cdot 10^{10}$ [40]		

TABLE 1 (continued)

Metal ion	k(dm^3 mol^{-1} s^{-1}) [a]		
	e^-_{aq} [3]	H [5]	OH [4]
Sc^{3+}	$<4 \cdot 10^8$ [42]		
Sm^{2+}			$6.2 \cdot 10^9$ [39]
Sm^{3+}	$2.5 \cdot 10^{10}$		
Sn^{2+}	$3.4 \cdot 10^9$ [c]	ca. $8 \cdot 10^{10}$	$2.5 \cdot 10^9$
Sn^{4+}	$6.3 \cdot 10^8$ [b]		
Tb^{3+}	$1.7 \cdot 10^7$		
Ti^{3+}	$<8 \cdot 10^9$ [42]	$4.2 \cdot 10^7$ [43]	$3.0 \cdot 10^9$ [44]
Tl^+	$3.0 \cdot 10^{10}$	$1.0 \cdot 10^8$	$7.6 \cdot 10^9$
Tl^{3+}		$3.9 \cdot 10^7$ [45]	
Tm^{2+}			$7 \cdot 10^9$ [39]
Tm^{3+}	$3 \cdot 10^9$		
UO_2^{2+}	$7.4 \cdot 10^{10}$		
VO^{2+}			$5.0 \cdot 10^8$
Y^{3+}	$2 \cdot 10^8$		
Yb^{2+}			$3.2 \cdot 10^9$ [39]
Yb^{3+}	$4.3 \cdot 10^{10}$		
Zn^{2+}	$1.0 \cdot 10^9$	$<10^5$	$<5 \cdot 10^5$ [36]
Oxy anions			
$Cr_2O_7^{2-}$	$3.3 \cdot 10^{10}$	$1.6 \cdot 10^{10}$	
CrO_4^{2-}	$5.4 \cdot 10^{10}$	$1.0 \cdot 10^{10}$	
MnO_4^-	$3.0 \cdot 10^{10}$	$2.4 \cdot 10^{10}$	
VO_3^-	$4.9 \cdot 10^9$		
Metal complexes			
$Ag(CN)_2^-$	$1.5 \cdot 10^9$		
$AgEDTA^{3-}$	$1.6 \cdot 10^9$		
$Ag(NH_3)_2^+$	$3.2 \cdot 10^{10}$		
$Au(CN)_2^-$	$4.2 \cdot 10^9$		
$Cd(CN)_4^{2-}$	$1.4 \cdot 10^8$	$>2 \cdot 10^9$	
$CdEDTA^{2-}$	$3.9 \cdot 10^8$		
$Cd(NH_3)_4^{2+}$	$3.1 \cdot 10^{10}$		
$Co(CN)_6^{3-}$	$3.6 \cdot 10^9$	$2.0 \cdot 10^7$	
$CoEDTA^-$	$2.9 \cdot 10^{10}$		

TABLE 1 (continued)

Metal ion	k(dm^3 mol^{-1} s^{-1}) [a]		
	e^-_{aq} [3]	H [5]	OH [4]
$Co(en)_3^{3+}$	$7.8 \cdot 10^{10}$		
$Co(NH_3)_6^{3+}$	$8.5 \cdot 10^{10}$	$1.6 \cdot 10^6$	
$FeEDTA^{2-}$	$<1.0 \cdot 10^9$		
$Fe(CN)_6^{4-}$	10^5	$4 \cdot 10^7$ [46]	$1.1 \cdot 10^{10}$
$Fe(CN)_6^{3-}$	$3.0 \cdot 10^9$	$4 \cdot 10^9$	
$Ni(CN)_4^{2-}$	$5.5 \cdot 10^9$	$1.8 \cdot 10^{10}$ [47]	$9.1 \cdot 10^9$ [47]
$NiEDTA^{2-}$	$1.0 \cdot 10^8$		
$Ni(en)_3^{2+}$	$\leq 2 \cdot 10^7$		
$Pt(CN)_4^{2-}$	$3.2 \cdot 10^9$		$1.0 \cdot 10^{10}$
$PtCl_4^{2-}$	$9.2 \cdot 10^9$		$8 \cdot 10^9$
$PtCl_6^{2-}$	$2.0 \cdot 10^{10}$		
$Ru(CN)_6^{4-}$	$<10^6$		
$Ru(NH_3)_6^{3+}$	$7.0 \cdot 10^{10}$	$1.8 \cdot 10^6$ [48]	
$Zn(CN)_4^{2-}$	$1.8 \cdot 10^8$		
$ZnEDTA^{2-}$	$<1.8 \cdot 10^6$		
$Zn(NH_3)_4^{2+}$	$6.5 \cdot 10^8$		

[a] Measured at ca. 25° C; see refs. for other conditions. [b] Estimated from data in ref. 35. [c] Calculated from data in ref. 37. [d] Estimated from data in ref. 38. [e] For $CrOH^{2+}$. [f] Reaction occurs. [g] For SnO_2^{2-}. [h] For SnO_3^{2-}.

states have also been invoked to explain the formation of $Fe(CN)_5H_2O^{3-}$ in the reduction of $Fe(CN)_6^{3-}$ [18], and Hart and Anbar [7] interpreted some observations of Buxton et al. [19] on the reduction of $Fe(CN)_5NO^{2-}$ by e^-_{aq} as evidence for excited states, although other explanations are possible (see Section C(vi) and Section K(i)).

Hydroxyl radical reactions. The hydroxyl radical is a strong oxidising agent (E^0 (OH/OH$^-$) = 1.9 V) and reacts with many metal ions. Several different mechanisms of oxidation have been characterised.

(a) Inner-sphere substitution. Here a ligand in the inner co-ordination sphere of the metal ion is displaced by OH and electron transfer then occurs as in reactions (6) and (7), either of which may be rate controlling.

$$M^{n+}(H_2O)_6 + OH \rightarrow (H_2O)_5M^{n+}OH + H_2O \quad (6)$$

$$(H_2O)_5M^{n+}OH \rightarrow (H_2O)_5M^{(n+1)+}OH^- \quad (7)$$

Reaction (6) is limited by the lability of the co-ordinated water molecule

which in many cases is too low to account for the rate of oxidation of M^{n+} by OH (Table 1). However, Berdnikov [20] suggested that inner-sphere substitution is likely for Sn^{2+} and Tl^{+} where the co-ordinated water is very labile, and in fact $TlOH^{+}$ has been identified [21] as the oxidation product in the latter case. Oxidation of Co^{2+} by OH is slow ($k = 8 \cdot 10^5$ dm^3 mol^{-1} s^{-1}) [22] and may also occur by an inner-sphere path.

(b) Hydrogen atom abstraction. In order to account for the absence of a correlation between the rate constants for oxidation by OH of metal ions and their ionisation potentials, Collinson et al. [23] proposed that the rate controlling step is abstraction of H from co-ordinated water as in (8), which would be followed by reaction (7).

$$OH + M^{n+}(H_2O)_6 \rightarrow (H_2O)_5M^{n+}OH + H_2O \qquad (8)$$

Berdnikov [20] pointed out that the rate constants for oxidation of several metal ions (e.g. Fe^{2+}, Mn^{2+}, Cu^{2+}, Ce^{3+}, Cr^{3+}) by OH are all approximately $3 \cdot 10^8$ dm^3 mol^{-1} s^{-1}, which he takes to be the upper limit of reaction (8). This value is to be compared with $k_9 \sim 10^4$ dm^3 mol^{-1} s^{-1}

$$OH + H_2O \rightarrow H_2O + OH \qquad (9)$$

which has been estimated [20] for free water and Berdnikov infers that the O—H bond strength in co-ordinated water is weaker by 40—80 kJ mol^{-1}.

(c) Outer-sphere electron transfer. Here electron transfer takes place across the co-ordination sphere as in (10).

$$M^{n+}(H_2O)_6 + OH \rightarrow M^{(n+1)+}(H_2O)_6 + OH^- \qquad (10)$$

This is undoubtedly the mechanism of the oxidation of substitution inert species such as Cr^{3+}_{aq} and $Fe(CN)^{4-}_6$. In the latter case it has been suggested [24 that the cyanide ligands play a significant role in view of the lower reactivity of the protonated complexes $Fe(CN)_6H^{3-}$ and $Fe(CN)_6H^{2-}_2$ with OH.

Jayson et al. [25] attempted to distinguish between mechanisms (b) and (c) by measuring the rates of oxidation of Fe^{2+}_{aq} by hydroxyl radicals in H_2O and D_2O. The rate constant is 2.7 times lower in D_2O which is consistent with either mechanism [25] and no definite distinction can be made between them.

(d) Other reactions. The reaction of OH with the square planar complex $PtCl^{2-}_4$ is believed to go by a novel mechanism involving addition of OH as a ligand at one of the vacant axial positions [26] (see also Sect. D(vii)).

Very recently it has been shown [27] that reaction of OH with $(NH_3)_5$-$Co^{III}py^{3+}$ results in addition of OH to the pyridine ligand to form a co-ordinated ligand radical which transfers an electron to the metal centre. This is an interesting example of OH inducing reduction of the complexed metal ion.

Reactions of hydrogen atoms. The reactions of hydrogen atoms with metal ions have not been studied as extensively as those of e^-_{aq} and OH. Mechanistic

details are lacking in most cases, but a number of different types of reaction have been proposed.

(a) Inner-sphere substitution. In its reactions with several metal ions which are reducing agents, e.g. Ti^{3+}, V^{2+}, Cr^{2+}, Fe^{2+} and Pu^{3+}, the hydrogen atom acts as an oxidising agent, itself being converted to molecular hydrogen. In the cases of Fe^{2+}_{aq} [28] and Cr^{2+}_{aq} [29] an intermediate hydrido complex has been identified which reacts with hydrogen ion so that oxidation occurs through reactions (11) and (12).

$$H + Fe^{2+}_{aq} \rightarrow Fe^{3+}_{aq}H^- \quad (11)$$

$$Fe^{3+}_{aq}H^- + H^+ \rightarrow Fe^{3+}_{aq} + H_2 \quad (12)$$

This mechanism probably operates in other cases too, rather than hydrogen atom abstraction from co-ordinated water.

(b) Outer-sphere electron transfer. The majority of reactions of H with metal ions probably fall into this category.

(c) Atom transfer. This has been suggested [30—32] for the reactions of H with complexes of the type $Co(NH_3)_5X^{n+}$, where X is a halogen or pseudo-halogen, based on the magnitudes of the reaction rate constants.

TABLE 2

Rate constants for reactions of CO_2^- and CH_2OH with metal ions

Metal ion	CO_2^-		CH_2OH	
	k(dm^3 mol^{-1} s^{-1})	Ref.	k(dm^3 mol^{-1} s^{-1})	Ref.
Cd^{2+}	ca. 10^5	36	$<10^2$	36
Co^{2+}	$10^2 < k < 10^5$	36	$<10^2$	36
Cr^{2+}	$1.1 \cdot 10^9$ [a]	42	$1.6 \cdot 10^8$ [a]	49
Cu^{2+}			$1.1 \cdot 10^8$ [a]	50
Eu^{3+}	$>7 \cdot 10^6$	42		
Ni^+	$6.6 \cdot 10^9$ [a]	51	$4.2 \cdot 10^9$ [a]	51
Ni^{2+}	$10^2 < k < 10^5$	36	$<10^2$	36
Ti^{3+}	ca. $5 \cdot 10^6$	42		
Zn^{2+}	$<10^2$	36	$<10^2$	36
$Co(bipy)_3^{3+}$	$7.6 \cdot 10^9$	52		
$Co(NH_3)_6^{3+}$	$1.1 \cdot 10^8$	52	$1.4 \cdot 10^8$	50
$Fe(CN)_5NO^{2-}$	$3.7 \cdot 10^8$	19		
Ferricytochrome-c	ca. $5 \cdot 10^8$	53		
$Ni(CN)_4^{2-}$	$1.2 \cdot 10^9$	47		
$Ru(NH_3)_6^{3+}$	$2.0 \cdot 10^9$	50	$4.1 \cdot 10^7$	50

[a] Metal radical complex formed.

(iv) Reactivity of the carboxyl and hydroxymethyl radicals

As noted in section (i) above, it is often desirable to remove radiolytically generated OH to achieve entirely reducing conditions, and formate ion (or formic acid) and methanol have been widely employed for this purpose. In both cases the radicals formed in reactions (4) and (5) have reducing properties, but they are much less reactive than the hydrated electron with metal ions. Some typical rate constants are shown in Table 2.

The high acid dissociation constant of CO_2H (pK_a = 1.4 [33]) means that CO_2^- can be employed as a reducing agent under conditions where e_{aq}^- reacts predominantly with H^+ (e.g. see Sect. C(ii)). CH_2OH (pK_a = 10.7 [34]) is a very much weaker acid than CO_2H.

In most cases the reactions of CO_2^- and CH_2OH with metal ions probably involve outer-sphere electron transfer, although a number of cases are known (e.g. Ni^+, Cd^+ and Cr^{2+}) where substitution occurs to form relatively long-lived metal—radical complexes.

B. GROUPS I AND II (ALKALI AND ALKALINE EARTH METALS)

These metal ions are generally considered to be unreactive towards the hydrated electron [3], and there is only circumstantial evidence for the species M^0 (for group I) and M^+ (for group II) in aqueous solutions. For instance, a transient species formed in continuously photolysed, H_2 saturated NaOH solutions at pH 11 has been tentatively attributed to an $Na^+—e_{aq}^-$ adduct [54]. A similar absorption with λ_{max} = 725 nm has been reported [55—57] in pulse irradiated or flash photolysed 14.5—16.0 M KOH and assigned [55—57] to $K^+—e_{aq}^-$. There is also a growing body of evidence for these $M^+—e_{aq}^-$ adducts in non-aqueous solvents [58—60], and Fisher et al. [58], in addition, found Na^0 as a transient species in tetrahydrofuran solutions. The formation of Mg^+ in γ-irradiated frozen Mg^{2+} solutions has been claimed by Moorthy and Weiss [61] from ESR measurements. Optical studies, however, show [62] that the trapped electron is quite stable in 4 mol dm^{-3} $Mg(ClO_4)_2$ glass at 77 K.

C. FIRST ROW TRANSITION ELEMENTS

(i) Scandium

The stable oxidation state for scandium is three. Attempts to produce divalent scandium by reduction with e_{aq}^-, H and CO_2^- have failed [42], although reaction of $ScEDTA^-$ with e_{aq}^- has been reported [3]. There is no evidence for oxidation of Sc^{III} by OH.

(ii) Titanium

Hexa-aquotitanium(III) is extensively hydrolysed in solution (pK_a = 2.7) [63], and in order to prevent precipitation of the metal it is necessary to work

at pH < 3. Under these conditions radiolysis of the solution results in little or no reduction to Ti^{II}, because the hydrated electrons react predominantly with H^+ [42]. In formic acid solutions where the reductant is CO_2H (pK_a = 1.4) or CO_2^- [33] reaction with Ti^{III} occurs ($k \sim 5 \cdot 10^6$ dm^3 mol^{-1} s^{-1}) [42], and the product, believed to be Ti^{2+}, has the absorption spectrum shown in Fig. 1. Complexation has been ruled out [42] on the grounds (i) that the reduction rate is appreciably faster than the water exchange rate for Ti^{III} ($\sim 10^5$ s^{-1} at 25°C) [64], and must therefore be outer sphere, and (ii) that no similar reaction with CH_2OH was observed [42]. Ti^{2+} is unstable under these conditions, and is believed to be rapidly oxidised by water [65].

Hydrogen atoms react with Ti^{III} [43,46], and the yields of molecular hydrogen (G = 3.0) and Ti^{IV} (G = ~7.0) produced indicate that Ti^{III} is oxidised with a stoichiometry given by eqn. (13).

$$H + Ti^{III} + H^+ = Ti^{IV} + H_2 \qquad (13)$$

A similar situation is found with ferrous ion, where pulse radiolysis experiments indicate that an intermediate hydride complex is found (see Sect. C(vi)). A similar mechanism is presumably operative in the present case. The radicals CH_3, $CH(CO_2H)_2$, CH_2CO_2H [66], Cl_2^- [42] and OH [42,44] also oxidise Ti^{III}.

(iii) Vanadium

The γ-radiolysis of deaerated acidic V^{2+} solution gives V^{3+} with G = 8.2, and of deaerated and aerated acidic solutions of V^{3+} gives VO^{2+} with G = 0.9 and 15.5 (cf. Fricke dosimeter, Sect. C(vi)) respectively [67]. These observations are consistent with the oxidation of V^{2+} by H and OH and oxidation of V^{3+} by OH, HO_2 and H_2O_2 and reduction by H. Some studies on the γ-radiolysis of acidic V^V solutions suggest that VO_2^+ is reduced by both H and HO_2, and that VO^{2+} is oxidised by OH with $k = 5.5 \cdot 10^8$ dm^3 mol^{-1} s^{-1} [68]. A similar

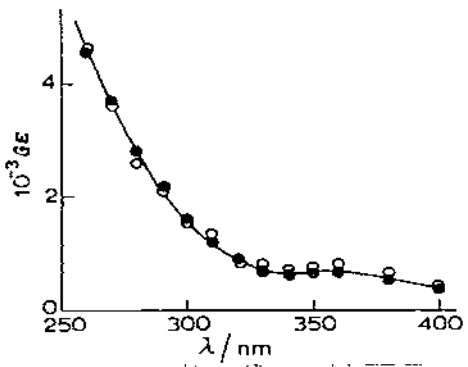

Fig. 1. Ultraviolet spectrum of titanium(II) at pH 1.4 in 1 M-formic acid (●), spectrum independent of initial titanium(III) concentration, and in 0.1 M-formic acid, (○). (From ref. 42. Reproduced by permission of the Chemical Society.)

rate constant has been found by pulse radiolysis methods [44]. Reduction of peroxyvanadate, VO_3^+, by OH has been suggested [68,69] (reaction 14), and Sigli et al. [69] estimated that the reaction is ca. 20 times faster than VO^{2+} + OH (i.e. $k_{14} \sim 10^{10}$ M^{-1} s^{-1}), although such a high rate constant for an oxygen atom transfer reaction seems unreasonable. This reaction deserves further study.

$$VO_3^+ + OH \rightarrow VO_2^+ + HO_2 \qquad (14)$$

(iv) Chromium

Reduction of Cr^{2+} by the hydrated electron results in a weakly absorbing species with absorption maxima at 300 nm and ~380 nm, and with a broad shoulder extending from 450 nm to 600 nm [29], believed to be Cr^+. The species decays rapidly by an approximately first order process, which is independent of pH. In these solutions $G(H_2) \sim 3.8$, which led Cohen and Meyerstein [29] to attribute the major decay to the two-electron oxidation of Cr^+ by water, reaction (15), with minor contributions from the dismutation of Cr^+ (16) and/or reaction with the molecular peroxide (17).

$$Cr^+ + H_2O \rightarrow Cr^{III} + H_2 \qquad (15)$$

$$Cr^+ + Cr^+ \rightarrow Cr^0 + Cr^{2+} \qquad (16)$$

$$Cr^+ + H_2O_2 \rightarrow Cr^{2+} + OH + OH^- \qquad (17)$$

The formation of Cr^{III} from Cr^+ suggests that Cr^+ is not involved in the dissolution of Cr metal in acidic solution since the latter results almost exclusively (ca. 95%) in Cr^{2+}.

Hydrogen atoms react with Cr^{2+} to give a hydride-complex (λ_{max} = 380 nm, ϵ_{380} = 190 dm^3 mol^{-1} cm^{-1}; λ_{max} = 260 nm, ϵ_{260} = 1000 dm^3 mol^{-1} cm^{-1}) [29]. This complex decays by a first order reaction dependent on $[H^+]$ with a specific second order rate constant of $1.8 \cdot 10^4$ dm^3 mol^{-1} s^{-1} [29]. Organic radicals, for instance those formed by OH attack on simple aliphatic alcohols or acids, react in a similar manner with rate constants of $(5—100) \cdot 10^7$ dm^3 mol^{-1} s^{-1} [49]. The complexes formed have two absorption bands, an intense one in the range 250—310 nm and a weaker one at 390—410 nm [42,49]. The rate constant for their decay is of the form

$$k_{obs} = a + b\,[H^+] \qquad (18)$$

which can be understood in terms of the reactions (19) and (20).

$$CrR^{2+} + H_2O \rightarrow Cr^{3+} + RH + OH^- \qquad (19)$$

$$CrR^{2+} + H^+ \rightarrow Cr^{3+} + RH \qquad (20)$$

Radiation induced oxidation of Cr^{II} in acidic solutions has been studied by Lykourezos et al. [67], and shown to result in a series of Cr^{III} products which depend on the conditions employed. This system is useful in identifying re-

action pathways because Cr^{III} is substitution inert, and can trap out in the form of readily recognisable complexes the products of the reaction of Cr^{II} with various radiation produced species.

Cr^{III} is reduced rapidly by e^-_{aq}, but is extremely unreactive with reducing radicals, probably because of the high reorganisation energy involved, and because of its inertness to substitution. This system is useful for studying reactions of Cr^{2+} which are too rapid to be detected by techniques such as stopped-flow. Sellers and Simic [70,71], for example, used the pulse radiolytic reduction of Cr^{III} to study the reaction $Cr^{2+} + O_2$. The reaction is rapid, $k_{21} = 1.6 \cdot 10^8$ dm^3 mol^{-1} s^{-1}, and was shown to result in the formation of a long-lived intermediate ($t_{1/2} \sim 1$ s), which absorbs with $\lambda_{max} = 245$ nm, $\epsilon_{245} = 7800$ dm^3 mol^{-1} cm^{-1}, $\lambda_{max} = 290$ nm, $\epsilon_{290} = 3200$ dm^3 mol^{-1} cm^{-1}, and is assigned to CrO_2^{2+}. Very similar results have been obtained by Ilan et al. [72], who also found evidence for oxidation of Cr^{2+} to chromic acid. Interestingly,

$$Cr^{2+} + O_2 \rightarrow CrO_2^{2+} \qquad (21)$$

CrO_2^+ had not been detected in previous studies [73] using conventional techniques, probably because these had always employed conditions where $[Cr^{2+}] >> [O_2]$, so that reaction (21) is rapidly followed by reaction (22).

$$CrO_2^{2+} + Cr^{2+} \rightarrow CrO_2Cr^{4+} \qquad (22)$$

Cr^{III} is oxidised by hydroxyl radicals, but this fact seems not to have been exploited pulse radiolytically to characterise Cr^{IV}, a valency state of chromium about which little is known. γ-radiolysis of aerated chromite solutions (Cr^{III} at pH 13.9) yields chromate with $G = 10.2$ (i.e. $2\,Ge^-_{aq} + 2\,G_H + G_{OH}$) [74]. It was suggested here that the superoxide radical anion oxidised chromite according to (23) [74]. Radiolysis of acidic Cr^{III} solutions results in no net change of valency state.

$$CrO_2^- + O_2^- \xrightarrow{H_2O} CrO_2 + OH^- + HO_2^- \qquad (23)$$

Chromate and dichromate are reduced by both e^-_{aq} and H to give Cr^V species (CrO_4^{3-} and $Cr_2O_7^{3-}$ respectively?). The ultimate product is Cr^{III} [75]. On pulse radiolysis of solutions of these oxyanions transient absorptions are produced which are found to be similar to those of the parents after making suitable corrections for the absorption due to the parent which is removed [76, 77]. In the chromate case the end of pulse absorption decays to a residual level by a second order process with $2k/\epsilon_{400} = (7 \pm 3) \cdot 10^6$ cm s^{-1} [77]. The large removal yield measured, G(—chromate) = 7.3 [78] or 5.8 [77] (in Ar saturated solutions), implies that not only H and e^-_{aq} are reacting with the chromate ion. A recent study [78] suggested that radiolytically produced protons are involved, and that the reactions occurring are

$$CrO_4^{2-} + H^+ \rightleftharpoons CrO_4H^- \qquad (24)$$

$$CrO_4H^- + CrO_4H^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad (25)$$

Little attention was paid in this investigation [78] to either the concomitant formation of Cr^{V} which may absorb appreciably in the wavelength range concerned, or the possibility that OH radicals may react with chromate.

Pulse radiolysis of dichromate is less complex [77], and only the reactions of e^-_{aq} and H need to be invoked. Many studies [79,80] of the γ-radiolysis of dichromate solutions have been made, mostly in 0.4 M H_2SO_4, to measure values of G_H, G_{OH} etc., but these provide little information on short-lived valency states of Cr.

(v) Manganese

Mn^{2+} is reduced by the hydrated electron to produce a weakly absorbing species with λ_{max} = 300 nm, thought to be Mn^{+}. It is oxidised by OH in neutral solutions to give another weakly absorbing species, which decays over a period of milliseconds to a permanent product [82]. The initial absorption is similar to that of manganic pyrophosphate in acidic solutions, conditions under which Mn^{III} is stable [83]. Permanganate ion is reduced to manganate by reaction with CO_2^-, H and e^-_{aq} [84].

(vi) Iron

The two stable oxidation states of iron, +2 and +3, are readily interconvertible by the primary radiation produced species; ferrous being oxidised by H and OH, whilst ferric is reduced by H and e^-_{aq} [3—5]. The oxidation of Fe^{2+} by H is an interesting reaction in that H atoms usually behave as reducing agents. The initial product has been identified as a hydrido complex, FeH^{2+}, which absorbs with λ_{max} = 325 nm and ϵ_{325} = 650 $dm^3\ mol^{-1}\ cm^{-1}$, by pulse radiolysis of ferrous perchlorate solutions [28]. The intermediate hydrido complex decays by reaction with H^+ with $k_{12} = 1.1 \cdot 10^4\ dm^3\ mol^{-1}\ s^{-1}$ [28]

$$Fe^{2+} + H \rightarrow FeH^{2+} \qquad (11)$$

$$FeH^{2+} + H^+ \rightarrow Fe^{3+} + H_2 \qquad (12)$$

The hydrated electron reduces Fe^{2+} but the product, presumed to be Fe^{+}, does not have any convenient absorption in the region 240—700 nm by which it may be characterised [76,85].

Without doubt the most important radiation chemical system containing iron is the Fricke dosimeter, which involves the radiolytic oxidation of Fe^{2+} to Fe^{3+} in aerated 0.4 $dm^3\ mol^{-1}$ H_2SO_4 solutions [84,86,87]. Ferric ion is produced with a yield given by eqn. (26). Equations (27)—(31) show how this stoichiometry arises.

$$G(Fe^{3+}) = 2\,G_{H_2O_2} + G_{OH} + 3\,G_H = 15.5 \qquad (26)$$

$$H_2O \text{ —}\sim\rightarrow H,\ OH,\ H_2O_2 \qquad (27)$$

$$H + O_2 \rightarrow HO_2 \qquad (28)$$

$$Fe^{2+} + HO_2 \xrightarrow{H^+} Fe^{3+} + H_2O_2 \quad (29)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^- \quad (30)$$

$$Fe^{2+} + OH \xrightarrow{H^+} Fe^{3+} + H_2O \quad (31$$

The actual reactions involved have been the subject of detailed study by puls. radiolysis, and are summarised in Table 3.

The primary product of reaction (29) is considered [88] to be the outer-sphere complex $Fe^{3+}(H_2O)_6HO_2^-$ on the grounds that its absorption spectrum does not contain a peak in the region 300—350 nm which characterises several inner-sphere complexes of ferric ion. On the other hand, the kinetic parameters for reaction (29), $k_{29} = 1.2 \cdot 10^6$ dm^3 mol^{-1} s^{-1} and $\Delta H^{\ddagger}_{29} = 39.6$ kJ mol^{-1} at 25° C, are not inconsistent with an inner-sphere substitution controlled mechanism operating [90].

When ferrous ion is replaced by the ion-pair $FeSO_4$, which occurs to a significant extent in the Fricke dosimeter, the rates of oxidation by OH and HO_2 are not significantly altered [25,89]. The sulphate ion, however, displaces HO_2^- from the ferric hydroperoxide complex and from the bridged complex which this complex forms with Fe^{2+} [88] (see Table 3). In the former case the inner-sphere sulphatoferric complex is formed, but at a rate faster than that of reaction (32) (see Table 3).

$$Fe^{3+} + SO_4^{2-} \rightarrow Fe^{3+}SO_4^{2-} \quad (32)$$

Oxidation of Fe^{2+} by other simple oxidising radicals has also been investigated [90—92]. Thornton and Laurence [90] studied the oxidation of Fe^{2+} by Br_2^- and Cl_2^-, generating these radicals by flash photolysis of X^- and FeX^{2+} (X = Br^- and Cl^-). The results, which are included in Table 3, were interpreted [90] in terms of an inner-sphere substitution controlled oxidation in each case. For Cl_2^-, however, it was evident [90] that outer-sphere oxidation also occurs. Jayson et al. [91] also investigated the reaction of Cl_2^- and Cl with Fe^{2+}, generating the radicals pulse radiolytically in reactions (33) and (34).

$$OH + Cl^- \xrightarrow{H^+} Cl + H_2O \quad (33)$$

$$Cl + Cl^- \rightarrow Cl_2^- \quad (34)$$

Their kinetic data are in good agreement with the photochemical study [90] (see Table 3), but they did not observe $FeCl^{2+}$ as a product and concluded that the reaction is predominantly an outer-sphere electron transfer process. Oxidation of Fe^{2+} by Cl is very rapid (see Table 3), and is also most likely to be an outer-sphere process.

Oxidation of Fe^{2+} by the azide radical, N_3, provides a clear demonstration of outer-sphere electron transfer [92]. In this case the rate of formation of the product azidoferric complex was independent of ferrous ion concentration and proportional to azide in concentration. On this basis it was concluded

TABLE 3

Rate constants and equilibrium constants for reactions of intermediates in the Fricke dosimeter

Reaction	k(dm^3 mol^{-1} s^{-1}) [a]	Ionic strength (mol dm^{-3})	$\Delta H^{\ddagger}$ [a] (kJ mol^{-1})	Ref.
$OH + Fe^{2+} \rightarrow Fe^{3+} + OH^-$	$2.3 \cdot 10^8$			25
$HO_2 + Fe^{2+} \rightarrow Fe^{3+}HO_2^-$ [b]	$1.2 \cdot 10^6$	1.0	39.6	88
$Cl_2^- + Fe^{2+} \rightarrow FeCl^{2+} + Cl^-$	$4 \cdot 10^6$	0.2	31.5	90
$Cl_2^- + Fe^{2+} \rightarrow Fe^{3+} + 2\,Cl^-$	10^7	0.2	22.7	90
$Cl_2^- + Fe^{2+} \rightarrow Fe^{3+} + 2\,Cl^-$	$1.4 \cdot 10^7$	0.1		91
$Cl + Fe^{2+} \rightarrow Fe^{3+} + Cl^-$	$5.9 \cdot 10^9$	0.1		91
$Br_2^- + Fe^{2+} \rightarrow FeBr^{2+} + Br^-$	$3.6 \cdot 10^6$	0.2	25.2	90
$SO_4^{2-} + Fe^{3+} \rightarrow FeSO_4^+$	$3.2 \cdot 10^3$	1.0	99	89
$Fe^{3+}HO_2^- \rightarrow Fe^{3+} + HO_2^-$	$1.8 \cdot 10^3$ [c]	1.0	8.8	88
$Fe^{3+}HO_2^-Fe^{2+} \rightarrow Fe^{3+} + Fe^{2+} + HO_2^-$	$2.5 \cdot 10^4$ [c]	1.0	45.5	88
$Fe^{3+}HO_2^-SO_4^{2-} \rightarrow FeSO_4^+ + HO_2^-$	ca. 10^4 [c]	0.5		89
$Fe^{3+}HO_2^-Fe^{2+}SO_4^{2-} \rightarrow Fe^{3+}SO_4^{2-}Fe^{2+} + HO_2^-$	ca. 10^4 [c]	0.5		89
Equilibrium	K(dm^3 mol^{-1})			
$Fe^{3+}HO_2^- + Fe^{2+} \rightleftharpoons Fe^{3+}HO_2^-Fe^{2+}$	27	1.0		88
$SO_4^{2-} + Fe^{3+}HO_2^- \rightleftharpoons Fe^{3+}HO_2^-SO_4^{2-}$	90	0.5		89
$SO_4^{2-} + Fe^{3+}HO_2^-Fe^{2+} \rightleftharpoons Fe^{3+}HO_2^-Fe^{2+}SO_4^{2-}$	100	0.5		89

[a] 25° C. [b] Considered to be $Fe^{3+}(H_2O)_6HO_2^-$ [88]. [c] Units of s^{-1}.

[92] that the mechanism is reactions (35) and (36).

$$\text{fast } N_3 + Fe^{2+} \rightarrow Fe^{3+} + N_3^- \quad (35)$$

$$\text{slow } N_3^- + Fe^{III} \rightarrow Fe^{III}N_3^- \quad (36)$$

The system was at pH 5.6 so that any iron(III) species will have been extensively hydrolysed. The rate constants obtained were $k_{35} > 1.7 \cdot 10^9$ dm^3 mol^{-1} s^{-1} and $k_{36} = 8.4 \cdot 10^5$ dm^3 mol^{-1} s^{-1}. This latter value is consistent with the much higher lability of co-ordinated water in hydroxy complexes of ferric ion [93].

The intermediate HO_2 is also capable of reducing Fe^{3+}, according to (37) and (38) [94]. The deprotonated form of FeO_2H^{3+} is probably the initial species produced in the oxidation of Fe^{2+} by molecular oxygen (reaction (39)) [95].

$$Fe^{3+} + HO_2 \rightarrow FeOH^{3+} \quad (37)$$

$$FeO_2H^{3+} \rightarrow Fe^{2+} + O_2 + H^+ \quad (38)$$

$$Fe^{2+} + O_2 \rightleftharpoons FeO_2^{2+} \quad (39)$$

Like the aquo-complexes, hexacyano ferrate (II) and (III) are readily interconverted in water radiolysis. In this case, however, only OH is capable of oxidising the divalent state [24]. Nitroprusside is reduced by e_{aq}^- and H to give ultimately $Fe(CN)_5NO^{3-}$ [19]. An intermediate has been observed in this reduction which possibly arises through electron addition to the nitroso group (see Sect. K(i)).

D. SECOND AND THIRD ROW TRANSITION ELEMENTS

(i) Zirconium, niobium and hafnium

The stable higher oxidation states of these metals, Zr^{IV}, Nb^V and Hf^{IV}, all form long-lived complexes with HO_2 [96—98]. The species, whose chemical composition is not fully known, have been detected using both in situ radiolysis and conventional flow system methods coupled with ESR spectroscopy. For Zr and Hf two complexed radicals have been distinguished [98], the differences possibly being due to hydrolysis effects or the state of polymerisation of the metal ions. The complexes can be formed either directly by the reaction of HO_2 with the metal ion (with the exception of Nb^V) or by reaction of OH or HO_2 with the metal ion—H_2O_2 complex [98]. The $Zr^{IV}O_2H$ species is also produced by the reversible reaction of Zr^{IV} with $U^{VI}O_2H$ (K = 18 dm^3 mol^{-1}) [99], and reacts reversibly with Th^{IV} to give $Th^{IV}O_2H$ (K = 3.6 dm^3 mol^{-1}) [99].

No other studies on the radiation chemistry of these metal ions have been reported.

(ii) Molybdenum

Very little work has been reported on the radiation chemistry of molybdenum compounds in solution. The complex ion, $Mo(CN)_8^{4-}$, is rapidly oxidised by OH radicals [100] to the stable $Mo(CN)_8^{3-}$ ion [101], and is reduced by e_{aq}^- [3]. Mo^{VI} is reported [97] to form a complex of uncertain composition following reaction with HO_2.

Baxendale et al. [102] observed reduction of molybdenum(II) trifluoroacetate by the solvated electron in methanol. An absorbing species is produced having λ_{max} at 780 nm and $\epsilon_{max} = 2.6 \cdot 10^3$ dm^3 mol^{-1} s^{-1} which is believed to be the product of reaction (40); and $k_{40} = 4 \cdot 10^9$ dm^3 mol^{-1} s^{-1} [102].

$$e_s^- + Mo_2(O_2CCF_3)_4 \rightarrow Mo_2(O_2CCF_3)_4^- \qquad (40)$$

ESR studies of this reaction in glassy methanol [102] indicate that $Mo_2(O_2CCF_3)_4^-$ is a molybdenum($1\frac{1}{2}$) species. In methanol solution it decays rapidly by two consecutive second-order processes with $k = 4.5 \cdot 10^9$ and $2.5 \cdot 10^8$ dm^3 mol^{-1} s^{-1} respectively. One of these processes is thought to be associated with reaction (41).

$$2\ Mo_2(O_2CCF_3)_4^- \rightarrow Mo_2(O_2CCF_3)_4 + Mo_2(O_2CCF_3)_4^{2-} \qquad (41)$$

As Baxendale et al. pointed out [102], this rapid decay indicates that the possibility of isolating the reduction products of molybdenum(II) carboxylates is unlikely. The decay of $Mo_2(O_2CCF_3)_4^-$ is accelerated by oxygen ($k = 5.9 \cdot 10$ dm^3 mol^{-1} s^{-1}) but does not result in its reoxidation to $Mo_2(O_2CCF_3)_4$. Presumably an oxygen adduct is formed.

Reduction of MoO_4^{2-} to Mo^V by mobile electrons in γ-irradiated sulphuric acid glasses at 77 K has been reported [103]. The Mo^V species has an absorption maximum at 300 nm under these conditions. When the irradiated glass is warmed above 190 K its colour changes from yellow to blue, indicating the formation of polymolybdate composed of Mo^V and Mo^{VI} oxides (molybdenum blue).

Papaconstantinou [104] studied the reduction of the heteropolyanions 18-molybdodiphosphate $[NH_4]_6[P_2Mo_{18}O_{62}]$, 18-tungstodiphosphate $[NH_4]_6[P_2W_{18}O_{62}]$ and 12-tungstophosphate $[Na_3][PW_{12}O_{40}]$ by organic free radicals derived from simple alcohols and formic acid (see e.g. reactions (4) and (5)). The heteropolyanions are reduced stepwise by addition of 1 to 6 electrons, and the extent of their reduction by the radicals was followed spectrophotometrically. From the extent of reduction of each heteropolyanion Papaconstantinou estimated the redox potentials of the radicals listed in Table 4. These are, of course, based on kinetic measurements, since the radicals are unstable, and must be viewed with caution.

(iii) Ruthenium

There is little evidence for simple aquo ions of ruthenium in aqueous solutions, and its chemistry is that of its complexes, a large number of which are known.

TABLE 4

Formal reduction potential range of some organic free radicals [104]

Radical	V vs. SCE
$(CH_3)_2\dot{C}H_2COH$	0.27 to 0.10
$\dot{C}H_2OH$	−0.42 to −0.65
$\dot{C}O_2H$	−0.42 to −0.65
$CH_3\dot{C}HOH$	< −0.65
$CH_3CH_2\dot{C}HOH$, $CH_3\dot{C}HCH_2OH$	< −0.65
$(CH_3)_2\dot{C}OH$	< −0.65
CO_2^-	< −0.65

Ru^{II} complexes. Irradiation of the divalent ruthenium complex, $Ru(NH_3)_5N_2^{2+}$, in neutral solutions containing methanol as an OH scavenger gives rise to a precipitate of ruthenium metal with the stoichiometry given by reaction (42) [105].

$$Ru(NH_3)_5N_2^{2+} + 2\ e_{aq}^- = Ru^0 + 5\ NH_3 + N_2 \qquad (42)$$

In solutions containing 0.1 mol dm^{-3} $HClO_4$ no precipitation of Ru metal or changes in the absorption of the parent complex take place [105], indicating that the CH_2OH radical, into which all the radiation produced radicals are converted at this pH, does not reduce the complex.

Pulse radiolysis of this complex shows [105] that the initial reaction is its reduction by the hydrated electron to an Ru^I complex, $Ru(NH_3)_5N_2^+$, which absorbs with λ_{max} = 300 nm (ϵ = 700 dm^3 mol^{-1} cm^{-1}). This species was found to decay by a second order reaction ($2k = 2.7 \cdot 10^9$ dm^3 mol^{-1} s^{-1}) [105] to produce another, weaker, absorption of similar shape to that of the Ru^I complex. It is suggested [105] that dismutation of the Ru^I according to (43) occurs, and that the weak absorption remaining is due to either Ru^0 or $Ru(NH_3)_5N_2$.

$$Ru(NH_3)_5N_2^+ + Ru(NH_3)_5N_2^+ \rightarrow Ru(NH_3)_5N_2^{2+} + Ru(NH_3)_5N_2 \ \text{(or } Ru^0 + 5\ NH_3) \qquad (43)$$

The $Ru(NH_3)_5N_2^{2+}$ complex also reacts with the OH radical [105]. In nitrous oxide solutions nitrogen is produced with G = 9.7 ± 0.3, of which G = 3.1 arises from the reaction of e_{aq}^- with N_2O (3). The reaction of OH with $Ru(NH_3)_5N_2^{2+}$ results therefore in $G(N_2)$ = 6.6 ± 0.3.

$$e_{aq}^- + N_2O \xrightarrow{H_2O} N_2 + OH + OH^- \qquad (3)$$

The optical absorption of these solutions also changes on γ-irradiation, giving rise to a species absorbing at λ_{max} = 297 nm, and identified as $Ru(NH_3)_5OH^{2+}$

[105]. These observations establish the stoichiometry to be eqn. (44). Pulse

$$Ru(NH_3)_5N_2^{2+} + OH = Ru(NH_3)_5OH^{2+} + N_2 \quad (44)$$

radiolysis of the complex indicates that reaction (44) proceeds by a two step mechanism. The initial reaction (45) gives rise to a species absorbing with λ_{max} = 430 nm, ϵ_{430} = 2250 dm^3 mol^{-1} cm^{-1}, attributed to $Ru(NH_3)_5N_2^{3+}$. This decays by a first order process with $k = 250 \pm 20$ s^{-1}, which is independent of $[Ru(NH_3)_5N_2^{2+}]$ and dose. Concurrently an absorption at 300 nm (the hydroxy Ru^{III}complex) grows in by a first order process with $k = 270 \pm 20$ s^{-1} [105], showing that aquation of the Ru^{III} intermediate (46) leads directly to the stable product.

$$Ru(NH_3)_5N_2^{2+} + OH \rightarrow Ru(NH_3)_5N_2^{3+} + OH^- \quad (45)$$

$$Ru(NH_3)_5N_2^{3+} + H_2O \rightarrow Ru(NH_3)_5OH^{2+} + H^+ + N_2 \quad (46)$$

The radiation chemistry of a number of other Ru^{II} complexes has been briefly reported. The bipyridyl complex, $Ru(bipy)_3^{2+}$, reacts with the hydrated electron [14,16,17], but the evidence is that the interaction is predominantly with the ligands [16,17]. This is dealt with more fully in Sect. K(i). The $Ru(CN)_6^{4-}$ complex is oxidised by OH to give the stable complex, $Ru(CN)_6^{3-}$ [100].

Ru^{III} complexes. The hexa-ammine Ru^{III} complex is reduced to the corresponding Ru^{II} complex not only by e_{aq}^- and H [48,106], but also by CO_2^- and several α-alcohol radicals [50]. Reaction of OH with $Ru(NH_3)_6^{3+}$ in neutral solutions results in the formation of a transient Ru^{IV} species, which absorbs with $\lambda_{max} \sim 400$ nm (ϵ = 350 dm^3 mol^{-1} cm^{-1}) and 280 nm (ϵ = 720 dm^3 mol^{-1} cm^{-1}) [106]. This absorption decays by a second order reaction ($2k = 4.5 \cdot 10^9$ dm^3 mol^{-1} s^{-1}) to another which changes over a period of seconds. Even then absorbing species (λ_{max} = 280 nm) remain in the solution [106]. The initial reactions can be written as

$$Ru(NH_3)_6^{3+} + OH \rightarrow Ru(NH_3)_6^{4+} + OH^- \quad (47)$$

$$Ru(NH_3)_6^{4+} + Ru(NH_3)_6^{4+} \rightarrow Ru(NH_3)_6^{3+} + Ru(NH_3)_6^{5+} \quad (48)$$

The chloropenta-ammino complex of Ru^{III} is also reduced rapidly by e_{aq}^- [106], but in contrast to the hexa-ammine, this results in a complex series of reactions. The initial product of the reaction (49) is an Ru^{II} complex, which aquates (reaction (50)) with $k = 4.7$ s^{-1} [106]. The aquo ion then reduces a further equivalent of $Ru(NH_3)_5Cl^{2+}$ according to (51) with $k = 1.0 \cdot 10^3$ dm^3 mol^{-1} s^{-1} [106]. In these solutions, then, one finds that even relatively small doses of radiation bring about the complete aquation of the chloropenta-ammine complex. Similar effects have been observed with other chloropenta-ammines under reducing conditions [107].

$$Ru(NH_3)_5Cl^{2+} + e_{aq}^- \rightarrow Ru(NH_3)_5Cl^+ \quad (49)$$

$$Ru(NH_3)_5Cl^+ + H_2O \rightarrow Ru(NH_3)_5H_2O^{2+} + Cl^- \quad (50)$$

$$Ru(NH_3)_5H_2O^{2+} + Ru(NH_3)_5Cl^{2+} \rightarrow Ru(NH_3)_5H_2O^{3+} + Ru(NH_3)_5Cl^+ \quad (51)$$

Ru^{VI}. A study of the γ-radiolysis of strongly alkaline solutions of the ruthenate ion has been made by Haissinsky and Dran [108]. In deaerated solutions a precipitate of RuO_2 was found, and values of $G(-Ru^{VI})$ of ca. 0.7 measured. This small yield was attributed to the difference between the yields of reducing species (Ge^-_{aq} = 3.3 *; $G_{HO_2^-}$ = 0.55) and oxidising species (G_{O^-} = 3.0). The reactions that occur are probably the following **

$$RuO_4^{2-} + O^- \xrightarrow{H_2O} Ru^{VII} + 2\ OH^- \quad (52)$$

$$RuO_4^{2-} + e^-_{aq} \rightarrow Ru^V \quad (53)$$

$$Ru^V + Ru^{VII} \rightarrow Ru^{VI} + Ru^{VI} \quad (54)$$

$$Ru^V + Ru^V \rightarrow Ru^{IV}(RuO_2) + Ru^{VI} \quad (55)$$

The HO_2^- present also brings about reduction. Two reactions were considered

$$RuO_4^{2-} + HO_2^- \xrightarrow{H_2O} RuO_2 + 3\ OH^- + O_2 \quad (56)$$

$$Ru^{VII} + HO_2^- \rightarrow Ru^V + H^+ + O_2 \quad (57)$$

In the absence of any information about the relative rates of (56) and (57) it is not possible to say which is the more important. Reactions (52)—(57) give

$$G(-RuO_4^{2-}) = \tfrac{1}{2}[2\ G_{HO_2^-} + Ge^-_{aq} - G_{O^-}] = 0.7$$

in good agreement with the experimental findings.

(iv) Palladium

Pulse radiolysis of deaerated Pd^{2+} solutions containing ethanol produces an absorption in the UV which increases towards shorter wavelengths, and which is probably due to Pd^+. A similar absorption was found following X-irradiation of Pd^{2+} doped metaphosphate glass [109], but could not be detected after γ-irradiation of sulphuric acid glasses containing $PdSO_4$ [110].

$PdCl_4^{2-}$ is reduced by e^-_{aq} and H to monovalent Pd which absorbs with λ_{max} = 340 nm (in solutions also containing 1 mol dm^{-3} NaCl) [111]. Reduction of $PdCl_4^{2-}$ has also been observed in irradiated solid K_2PdCl_4 and $(NH_4)_2PdCl_4$, and ESR measurements show $PdCl_4^{3-}$ to be the product [112,113]. The fate of the pulse radiolytically produced Pd^I is uncertain. Broszkiewicz [111] found

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* Under the conditions of Haissinsky and Dran's experiments [108] all H radicals are converted into e^-_{aq} via $H + OH^- \rightarrow e^-_{aq}$.

** In the mechanism proposed by Haissinsky and Dran reaction (54) is replaced by $Ru^{VII} + e^-_{aq} \rightarrow Ru^{VI}$. We feel that this reaction is unlikely to compete successfully with reaction (53).

that there were three consecutive first order reactions with half-lives of 6.0, 86 and 1840 μs in the presence of an OH scavenger, and that no metal precipitate was formed. In contrast, Spitsyn et al. [114] observed Pd^0 precipitation after γ-irradiating $PdCl_4^{2-}$ and Pd^{2+} solutions with $G(Pd^0) = G(-Pd^{II})$; and Philipp and Marsik [115] obtained palladium metal with $G(Pd^0) = 4.7$ on γ-irradiating $PdCl_4^{2-}$ solutions. $PdCl_4^{2-}$ is oxidised by OH, and the product, for which $\lambda_{max} = 320$ nm and $\epsilon_{320} = 4700$ dm^3 mol^{-1} cm^{-1}, decays by a rapid second order reaction, which is probably a dismutation (reaction (58)) [111].

$$Pd^{III} + Pd^{III} \rightarrow Pd^{II} + Pd^{IV} \qquad (58)$$

Another, quite different, transient Pd^{III} species with $\lambda_{max} \sim 340$ nm and $\epsilon_{340} = 1.8 \cdot 10^4$ dm^3 mol^{-1} cm^{-1} may also be produced by pulse radiolytic reduction of $PdCl_6^{2-}$. Broskiewicz [111] found that this decayed by a first order reaction ($t_{1/2} = 16$ μs), which he ascribed to reaction with ClO^-; it was necessary to have ClO^- in the solution to maintain the palladium as Pd^{IV}.

(v) Rhodium

The Rh^{III} complexes $Rh(NH_3)_5Cl^{2+}$, $Rh(NH_3)_5OH_2^{3+}$ and $Rh(NH_3)_4Br_2^+$ are rapidly reduced by reaction with e_{aq}^- [116]. Ligand exchange with water takes place within 1 μs to form an Rh^{II} complex, identified by conductivity measurements as $Rh(NH_3)_4(OH_2)_2^{2+}$ [116] (e.g. reactions (59) and (60)). Further hydrolysis reactions ensue ((61) and (62)) with $k_{61} = 350$ s^{-1} and $k_{62} = 40$ s^{-1} [116].

$$Rh(NH_3)_5Cl^{2+} + e_{aq}^- \rightarrow Rh(NH_3)_5Cl^+ \qquad (59)$$

$$Rh(NH_3)_5Cl^+ + 2\,H_2O \rightarrow Rh(NH_3)_4(OH_2)_2^{2+} + Cl^- + NH_3 \qquad (60)$$

$$Rh(NH_3)_4(OH_2)_2^{2+} + H_2O \rightarrow Rh(NH_3)_3(OH_2)_3^{2+} + NH_3 \qquad (61)$$

$$Rh(NH_3)_3(OH_2)_3^{2+} + H_2O \rightarrow Rh(NH_3)_2(OH_2)_4^{2+} + NH_3 \qquad (62)$$

In fact somewhat less than the stoichiometric 2 NH_3's per Rh^{II} ion are formed in reactions (61) and (62), which may be because reaction (62) is actually an equilibrium, or because some Rh^{II} is consumed in a side reaction (e.g. dismutation) without formation of NH_3. The intermediate $Rh(NH_3)_4(OH_2)_2^{2+}$ complex reacts rapidly with O_2 ($k = 3.1 \cdot 10^8$ dm^3 mol^{-1} s^{-1} [116]) to yield a long-lived species absorbing at $\lambda_{max} = 265$ nm, $\epsilon_{max} = 9600$ dm^3 mol^{-1} cm^{-1} [116]. This is thought to be $Rh(NH_3)_4(O_2)OH_2^{2+}$, the formation of which demonstrates the extreme lability of the axial positions of Rh^{II}.

In solutions where the tetra-ammino Rh^{II} complex is formed by radiolytic reduction of $Rh(NH_3)_4Br_2^+$ extremely large increases in conductivity are produced ($\Delta\Lambda = 10^6$ Ω^{-1} cm^2 mol^{-1}) [116]. It is suggested that this occurs by exchange of the Br^- ligands in the starting material for H_2O by a chain reaction. The propagating steps are

$$Rh(NH_3)_4(OH_2)_2^{2+} + Rh(NH_3)_4Br_2^+ \rightarrow Rh(NH_3)_4(OH_2)_2^{3+} + Rh(NH_3)_4Br_2 \qquad (63)$$

$$Rh(NH_3)_4Br_2 + 2\ H_2O \rightarrow Rh(NH_3)_4(OH_2)_2^{2+} + 2\ Br^- \quad (64)$$

The conductivity change showed [116] a strong, inverse dependence on the dose per pulse, indicating chain termination by a second order reaction, probably the dismutation or dimerization of the Rh^{II} intermediate.

(vi) Silver

Aquo ions. γ-Radiolysis of aqueous solutions of Ag^+ gives a precipitate of metallic silver with a yield equivalent to $G_{e^-_{aq}} + G_H - G_{OH}$ under optimum conditions [117]. Addition of ethanol as an OH scavenger increases this yield to ca. 5.5 ($G_{e^-_{aq}} + G_H + G_{OH}$), but only under conditions where $[C_2H_5OH]/[Ag^+]$ is large, indicating that Ag^+ is a good scavenger of OH. Addition of nitrite ion also gives high yields of Ag metal, but only when the ratio $[NO_2^-] : [Ag^+]$ is small. This interpreted as being due to the two electron reduction of Ag^{2+} by NO_2^- in reaction (65).

$$Ag^{2+} + NO_2^- \xrightarrow{H_2O} Ag^0 + NO_3^- + 2\ H^+ \quad (65)$$

Haissinsky [118] studied the radiolysis of Ag^+ solutions in detail and found

$$G(-Ag^+) + 2\ G(H_2) = 2\ G(H_2O_2) + 4\ G(O_2)$$

with

$$G(-Ag^+) = G(Ag^0) = 1.8$$

A mechanism comprising reactions (66)—(72) is consistent with these results.

$$Ag^+ + H \rightarrow Ag^0 + H^+ \quad (66)$$

$$Ag^+ + e^-_{aq} \rightarrow Ag^0 \quad (67)$$

$$Ag^+ + OH \rightarrow Ag^{2+} + OH^- \quad (68)$$

$$Ag^{2+} + Ag^0 \rightarrow 2\ Ag^+ \quad (69)$$

$$Ag^{2+} + H_2O_2 \rightarrow Ag^+ + H^+ + HO_2 \quad (70)$$

$$Ag^{2+} + HO_2 \rightarrow Ag^+ + H^+ + O_2 \quad (71)$$

and/or

$$Ag^+ + HO_2 \rightarrow Ag^0 + H^+ + HO_2 \quad (72)$$

Early pulse radiolysis studies [82,119,120] showed that several of the intermediates had intense absorptions in the UV region, although there was some confusion as to their assignment. A mechanism proposed by Pukies et al. [35] is now generally accepted [121,122], and has been substantiated in part by more recent work [121]. They found [35] that following the initial reduction of Ag^+ by e^-_{aq} and H to give Ag^0 (λ_{max} = 360 nm), (reactions (66)

and (67)), there was reaction with a further three equivalents of Ag^+ as follows

$$Ag^0 + Ag^+ \rightarrow Ag_2^+ \quad (73)$$

$$Ag_2^+ + Ag^+ \rightarrow Ag^{2+} + Ag_2 \quad (74)$$

$$Ag_2 + Ag^+ \rightarrow Ag_3^+ \quad (75)$$

Absorption maxima for the intermediates Ag_2^+, Ag_2 and Ag_3^+ were reported at 310 (charge transfer band [122]), 310 and 270 nm respectively [35]. These reactions describe the processes occurring within approximately the first millisecond after the pulse radiolysis of 10^{-4} mol dm^{-3} Ag^+ solutions. Subsequently there are complex optical changes leading to the formation of colloidal silver [35]. Irradiation of Ag^I in glassy media also gives rise to metallic silver. A number of intermediates such as Ag^0, Ag_2^+ and Ag_2^+ have been characterised by ESR methods [123], results which show a close parallel with the pulse radiolysis work described above. However the reduction of Ag^+ by H atoms in H_2SO_4 glasses apparently gives AgH^+ [124] rather than the Ag^0 produced in aqueous solution.

Ag^+ is oxidised by OH to Ag^{2+} which absorbs with $\lambda_{max} = 310$ nm [35]. This decays by a second order process producing a species absorbing with $\lambda_{max} = 260$ nm, believed to be Ag^{III} (Ag^{3+} ?) [35]. This is unstable, but its fate is unknown.

$$Ag^{2+} + Ag^{2+} \rightarrow Ag^+ + Ag^{3+} \quad (76)$$

The pulse radiolysis method has also been applied to a study of the reaction of $Ag^+ + Cl^-$ [125]. Here the chloride ion was generated in the presence of Ag^+ by the reaction of e_{aq}^- with chloroacetic acid (reaction (77)), so that immediately after the pulse the solution contained Ag^+ and Cl^-.

$$e_{aq}^- + ClCH_2CO_2H \rightarrow Cl^- + CH_2CO_2H \quad (77)$$

An absorption with a maximum at 325 nm was detected, and was thought to be due to $AgCl_2^-$ formed by the reactions (78) and (79)

$$Ag^+ + Cl^- \rightleftharpoons AgCl \quad (78)$$

$$AgCl + Cl^- \rightleftharpoons AgCl_2^- \quad (79)$$

By studying the rate of formation of the absorption and treating reaction (78) as a pre-equilibrium, Schiller and Ebert [125] were able to determine $k_{79} = 4.1 \cdot 10^8$ dm^3 mol^{-1} s^{-1}. Conversion of the AgCl to a precipitate took place over a period of tens of seconds, and could be described by an empirical equation of the form

$$\log t = -n \log c + \text{constant}$$

where t = incubation time, c = geometrical mean of ion concentrations and the constant n has a value of 8.9 ± 0.5.

In these solutions an absorbing species was also detected at 425 nm [125]. The intensity of this peak was at a maximum when the hydrated electrons were scavenged with equal probability by Ag^+ and chloroacetic acid, and it was formed in a first order reaction dependent on both $[Ag^+]$ and $[Cl^-]$. The absorption was tentatively assigned to some silver—chloroorganic compound. More work is required to characterise this species fully.

Ammino-complexes. The mechanism of the radiolytic reduction of Ag^I ammine complexes is very similar to that of the aquo complex described above. Reduction by the hydrated electron (reaction (80)) is followed by reaction with a further equivalent of Ag^I to give $Ag_2(NH_3)_n^+$ (reaction (81)) [126]. This may decay by two pathways depending on $[Ag^I]$. At low concentrations there is a dimerisation ($2k = 2.6 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1} [126]) possibly giving rise to $Ag_4(NH_3)_n^{2+}$, and then Ag_2^0.

$$e_{aq}^- + Ag(NH_3)_2^+ \rightarrow Ag^0 + 2\ NH_3 \quad (80)$$

$$Ag^0 + Ag(NH_3)_2^+ \rightarrow Ag_2(NH_3)_n^+ \quad (81)$$

$$Ag_2(NH_3)_n^+ + Ag_2(NH_3)_n^+ \rightarrow Ag_4(NH_3)_n^{2+}\ (?) \rightarrow Ag_2^0 + 2\ Ag(NH_3)_2^+ \quad (82)$$

$$Ag_2(NH_3)_n^+ + Ag(NH_3)_2^+ \rightarrow Ag_3(NH_3)_n^{2+} \rightarrow Ag_2^0 + Ag(NH_3)_n^{2+} \quad (83)$$

At higher concentrations of Ag^I, reaction of $Ag_2(NH_3)_n^+$ with the Ag^I predominates, although this also leads to the formation of Ag_2^0.

$Ag(NH_3)_2^+$ is oxidised by reaction with OH to give an ammoniated Ag^{II} species ($\lambda_{max} = 260$ nm) [126]. Note that in these transient valence states the number of coordinating ligands is unknown.

(vii) Osmium

Little work has been done on the radiation chemistry of osmium compounds. The osmium (II) ion $Os(CN)_6^{4-}$ is oxidised by OH to the stable $Os(CN)_6^{3-}$ ion [100]. Studies on the catalytic effect of OsO_4 in radiolytic oxidations have also been reported [127].

Like its ruthenium analogue, $Os(NH_3)_5N_2^{2+}$ reacts rapidly with OH ($k = 10^{10}$ dm^3 mol^{-1} s^{-1}) [128] to form a species which absorbs with λ_{max} at 380 nm. In N_2O saturated solution, however, $G(N_2) = 5.0 \pm 0.1$, so that less than one third of the expected yield of nitrogen is obtained on the basis that the complex decomposes according to the stoichiometry of eqn. (84), which holds for the ruthenium complex (see Sect. D(iii)). For this reason Venturi et al. [128] suggested that OH abstracts a hydrogen atom to form $Os(NH_3)_4NH_2N_2^{2+}$ (reaction (85)) and they identified the absorption at 380 nm with this species.

$$Os(NH_3)_5N_2^{2+} + OH = Os(NH_3)_5OH^{2+} + N_2 \quad (84)$$

$$Os(NH_3)_5N_2^{2+} + OH \rightarrow Os(NH_3)_4NH_2N_2^{2+} + H_2O \quad (85)$$

It is unlikely, however, that reaction (85) would have a rate constant of 10^{10} $dm^3\ mol^{-1}\ s^{-1}$, which is more typical of an electron transfer process. The decay of the 380 nm species is more complex and considerably slower than the aquation of $Ru(NH_3)_5N_2^{3+}$, and it is possible that, if it is $Os(NH_3)_5N_2^{3+}$, other reactions compete with aquation in this case and thereby lower the yield of nitrogen.

(viii) Iridium

$IrCl_6^{3-}$ is reduced by e_{aq}^-, H atoms and isopropanol radicals [129,130] to give an Ir^{II} species which absorbs with $\lambda_{max} = 280$ nm [129]. This decays by a second order process ($2k_{86} = 3.3 \cdot 10^9$ $dm^3\ mol^{-1}\ s^{-1}$ taking $\epsilon_{280} = 1740$ $dm^3\ mol^{-1}\ cm^{-1}$) thought to be dismutation.

$$Ir^{II} + Ir^{II} \rightarrow Ir^{III} + Ir^{I} \qquad (86)$$

The Ir^I produced has not been characterised, but no metallic iridium is detected in these solutions [129], and presumably, therefore, Ir^I is reoxidised by reaction with water. In agreement with this is the observation that the stable products of the γ-irradiation of $IrCl_3^{3-} + N_2O$ solutions give a good material balance [$G(Ir^{IV}) + G(O_2) = 2\ G(H_2) + 2\ G(N_2)$] [130]. Under the latter conditions a net oxidation occurs with $G(Ir^{IV}) = 4.0$ [130], indicating that oxidation by OH occurs.

$IrCl_6^{2-}$ is reduced by e_{aq}^-, H atoms and isopropanol radicals to give, it is believed [129], $IrCl_6^{3-}$, rather than the aquated complex, $IrCl_5H_2O^{2-}$, found in the photo-induced reduction [131]. No evidence for oxidation by OH to pentavalent iridium has been found [129], although stable complexes of this valency are known.

(ix) Platinum

Halo-complexes. In an early radiation chemical study Balandin et al. [132] reported that chloroplatinic acid (H_2PtCl_6) is resistant to radiation in aqueous solution. Haissinsky [133] showed that this is because reduction of Pt^{IV} by H atoms is balanced by oxidation of Pt^{II} by OH and H_2O_2. He also reported that in the radiolysis of $PtCl_4^{2-}$ solutions no appreciable net oxidation is observed in the absence of oxygen, due again to reduction of Pt^{IV} by H. In the presence of oxygen, however, $G(Pt^{IV}) = 7.8$ under optimal conditions, which is equated [133] with $\frac{1}{2}(G_{OH} + 3\ G_{HO_2} + 2\ G_{H_2O_2})$. The reaction mechanism can be summarised as follows

$$Pt^{II} + OH \rightarrow Pt^{III} \qquad (87)$$

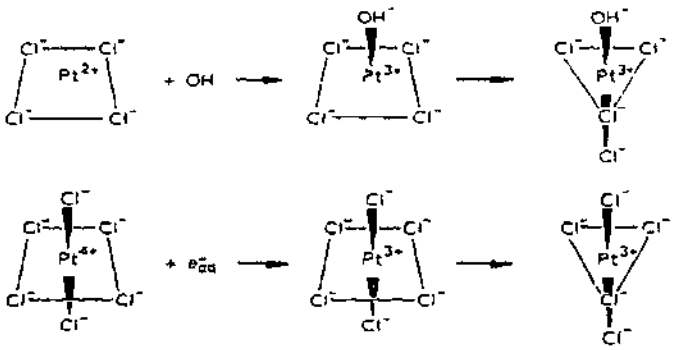
$$Pt^{II} + HO_2 \rightarrow Pt^{III} + H_2O_2 \qquad (88)$$

$$2\ Pt^{III} \rightarrow Pt^{II} + Pt^{IV} \qquad (89)$$

$$Pt^{II} + H_2O_2 \rightarrow Pt^{IV} \qquad (90)$$

It is now known that $PtCl_4^{2-}$ is rapidly reduced by reaction with e_{aq}^- and H to give the same transient species absorbing with λ_{max} = 310 nm [26,134]. The intensity of the peak is not influenced by the presence of methanol indicating that no reduction of the Pt^{II} by the CH_2OH radical occurs [26]. The platinum (I) species formed decays by a second order reaction resulting in the formation of colloidal platinum [26,134,135], although the processes involved have not been investigated.

Oxidation of $PtCl_4^{2-}$ occurs by reaction with OH [26,130,133,134,136], and results in the sequential formation of two short-lived complexes of Pt^{III} [26,134]. The initial product absorbs with λ_{max} = 450 nm and changes by a first order process ($k = 2.0 \cdot 10^5\ s^{-1}$) to another species absorbing with λ_{max} = 410 nm [26]. Interestingly, an absorption spectrum practically identical to the second of these is formed by a two step process following reduction of the $PtCl_6^{2-}$ complex [26]. Adams et al. [26] proposed the following mechanism to explain these observations



The novel feature is the suggestion of a change in stereochemistry from square pyramidal and octahedral to trigonal bipyramidal. Some doubt attaches to the number of chloride ligands involved in the transient complexes. It might be that the long-lived trigonal bipyramid complexes are in fact the same species, although substituting Cl^- by OH^- would probably produce only a small shift in the absorption spectrum. Ultimately these Pt^{III} complexes decay, probably by dismutation, to Pt^{II} and Pt^{IV} species. Thus γ-irradiation of $PtCl_4^{2-}$ + N_2O solutions gives Pt^{IV}, the yield depending on [N_2O] [130].

$PtCl_4^{2-}$ is also oxidised by Cl_2^- in acidic solution [137,138] and by Br_2^- [138] in neutral solution; the role of acid is merely to facilitate the production of Cl_2^- (see Sect. C(vi)). In each case the species which absorb at 450 nm and 410 nm are completely suppressed, and new absorptions are observed in the UV. Storer et al. [137] reported an absorption with λ_{max} = 260 nm and ϵ_{max} ~ 13000 $dm^3\ mol^{-1}\ cm^{-1}$ for the product of Cl_2^- oxidation, whilst Broszkiewicz and Grodowski [138] found λ_{max} to be 290 nm with ϵ_{max} ~ 7000 $dm^3\ mol^{-1}\ cm^{-1}$. The reason for the large discrepancy may be due to a small contribution from Pt^I species giving an apparent peak at 290 nm since Storer et al. observed a slight shoulder at ca. 300 nm. For the Br_2^- oxidation product λ_{max} is

at 310 nm and $\epsilon_{max} = 8.4 \cdot 10^3$ dm^3 mol^{-1} cm^{-1} [138].

Broszkiewicz and Grodowski [138] concluded that the most probable mechanism of oxidation of $PtCl_4^{2-}$ by Cl_2^- and Br_2^- is

$$PtCl_4^{2-} + Cl_2^- \rightarrow (PtCl_4^{2-} \cdot Cl_2^-) \rightarrow PtCl_4^- + 2\ Cl^- \quad (91)$$

$$PtCl_4^{2-} + Br_2^- \rightarrow (PtCl_4^{2-} \cdot Br_2^-) \rightarrow PtBr_nCl_{4-n}^- + 2\ X^- \quad (92)$$

where $n \leqslant 2$ and X^- is Cl^- or Br^-. Both reactions are rapid with $k_{91} = 1.6 \cdot 10^9$ and $k_{92} = 1.7 \cdot 10^9$ dm^3 mol^{-1} s^{-1} at an ionic strength of 0.1 dm^3 mol^{-1} [138].

The pulse radiolysis method has been applied to the study of the equilibrium between PtI_4^{2-} and PtI_6^{2-} (III) [139]. Following irradiation of solutions of $PtI_4^{2-} + I^-$, a small yield of I_3^- is formed via reactions (93)—(96) equivalent to $\frac{1}{2}(G_{e_{aq}^-} + G_{OH})$. By monitoring the decay of the absorption of I_3^-, or the growth of that of PtI_6^{2-}, Barkatt and Kobayashi [139] obtained values of $k_{93} = 2 \cdot 10^8$ dm^3 mol^{-1} s^{-1} and $k_{-93} = 1.4 \cdot 10^3$ dm^3 mol^{-1} s^{-1}.

$$PtI_4^{2-} + I_3^- \rightleftharpoons PtI_6^{2-} + I^- \quad (93)$$

$$e_{aq}^- + N_2O \xrightarrow{H^+} N_2 + OH + OH^- \quad (3)$$

$$OH + I^- \rightarrow OH^- + I \quad (94)$$

$$I + I^- \rightarrow I_2^- \quad (95)$$

$$I_2^- + I_2^- \rightarrow I_3^- + I^- \quad (96)$$

Amino-complexes. The platinum(II) amine complexes $Pt(en)_2^{2+}$, $Pt(dien)Cl^+$ and $Pt(Et_4dien)Cl^+$ have been investigated by pulse radiolysis of their aqueous solutions [137]. They react rapidly with e_{aq}^- and H ($k \sim 10^{10}$ dm^3 mol^{-1} s^{-1}) to form products which absorb in the region 240—450 nm. Their kinetic and spectral properties indicate that the products of reaction of e_{aq}^- and H with these complexes, unlike $PtCl_4^{2-}$, are different. Direct electron addition probably occurs with e_{aq}^-, but H may form an adduct or abstract a hydrogen atom from the ligands. In general, the absorbing products disappear by second-order kinetics, suggesting disproportionation, and no new absorbing species are formed. In the case of $Pt(dien)Cl^+$ substitution of Cl^- by H_2O ($k = (2.3 \pm 1.3) \cdot 10^5$ s^{-1}) is believed to occur [137].

Oxidation of the amine complexes by OH and Cl_2^- is rapid and, since Cl_2^- does not react with the free ligands, attack at the metal centre is implied. Transient species are formed which absorb in the UV. These react rapidly with Cu^{II} and are considered to be Pt^{III} species. Confirmatory evidence for this assignment was obtained [137] from a study of the reactions of the reducing radicals e_{aq}^-, H, $\cdot CH_2OH$ and $(CH_3)_2\dot{C}OH$ with the Pt^{IV} complex *trans*-$Pt(en)_2Cl_2^{2+}$. Absorbing products very similar to those obtained in the oxidation of the Pt^{II} complexes were observed, consistent with one electron reduction of the Pt^{IV} complex. Small differences in the spectra and kinetic properties of the Pt^{III} species were rationalised in terms of them having different structural forms [137] due to the high lability of the axial co-ordination sites.

Cyano-complexes. Tetracyano platinum(II) is reactive with e^-_{aq} and OH, giving rise to transient absorptions at 360 nm and 295 nm respectively. The Pt^I ion formed by reaction with e^-_{aq} has reducing properties, reacting rapidly with N_2O and O_2 for instance [128]. In the absence of oxidising solutes a complex decay is found. As with the amine complexes, a different Pt^I species having λ_{max} = 290 nm is formed by H atom attack on $Pt(CN)_4^{2-}$ [128].

(x) Gold

Reduction of the Au^I complex $Au(CN)_2^-$ by e^-_{aq} gives a transient species having an absorption maximum at 410 nm ($\epsilon_{410} = 7.5 \cdot 10^3$ dm^3 mol^{-1} cm^{-1}) [140]. Reduction of the same complex by hydrogen atoms produces a different absorbing species with λ_{max} at 270 nm and $\epsilon_{270} = 3.2 \cdot 10^3$ dm^3 mol^{-1} cm^{-1} [140]. Both transients decay by second order kinetics to produce metallic gold in the absence of reactive solutes. The 410 nm transient, however, reacts rapidly with N_2O ($k = 5.5 \cdot 10^3$ dm^3 mol^{-1} s^{-1}) [140] whereas the 270 nm transient is much less reactive. On the basis of these observations it was suggested [140] that the 410 nm is an electron adduct of $Au(CN)_2^-$ which can be written as $Au(CN)_2^- \cdots e^-_{aq}$, whilst the 270 nm transient is Au^0.

Transient Au^{II} species have been produced by oxidation of $Au(CN)_2^-$ by OH, and by reduction of $AuCl_4^-$ by H or e^-_{aq} [140,141]. The exact nature of these transient species is not known, but there is both spectral and kinetic evidence that the number of co-ordinating ligands is dependent on the concentration of free ligand in the solution [140,141].

A selection of rate constants for transient gold species is shown in Table 5.

(xi) Mercury

Mercury forms two stable ions in aqueous solution, Hg_2^{2+} and Hg^{2+}. Hg_2^{2+} is reduced by reaction with H atoms (97) to give a species absorbing with λ_{max} = 285 nm, ϵ_{285} = 9000 dm^3 mol^{-1} cm^{-1} [142]. It decays by a second order reaction with $2k = 1.4 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1} attributed to reaction (98).

$$Hg_2^{2+} + H \rightarrow Hg_2^+ + H^+ \qquad (97)$$

$$Hg_2^+ + Hg_2^+ \rightarrow 2\ Hg^0 + Hg_2^{2+} \qquad (98)$$

Hg^{2+} is also reduced radiolytically. In glassy media Hg^+ has been detected as the product by ESR [143—145] and optical methods [110,145]. Pulse radiolytic reduction of Hg^{2+} in acidic aqueous solution has been studied by two groups of workers, but there is little correspondence between their results. Faraggi and Amozig [142] observed a transient absorption at λ_{max} = 272 nm, ϵ_{272} = 7800 dm^3 mol^{-1} cm^{-1}, and found that it decayed by a second order process with $2k_{93} = 8.0 \cdot 10^9$ dm^3 mol^{-1} s^{-1}. These results were attributed to the dimerisation of Hg^+ ions (reaction (99)).

$$Hg^+ + Hg^+ \rightarrow Hg_2^{2+} \qquad (99)$$

TABLE 5

Rate constants of formation and decay of Au^{II} and Au^0 [140]

Reaction [a]	10^{-9} k/dm^3 mol^{-1} s^{-1}	pH
$Au^I + OH \rightarrow Au^{II} + OH^-$	4.7 ± 0.8	7
$Au^I + OH \rightarrow Au^{II} + OH^-$	2.6	2
$Au^{III} + H(e^-_{aq}) \rightarrow Au^{II} + H^+$	5.7 ± 1.5 [b]	4
$2\ Au^{II} \rightarrow Au^I + Au^{III}$	0.48 ± 0.12	4, 7
$2\ Au^{II} \rightarrow Au^I + Au^{III}$	~0.24	2
$Au^I + e^-_{aq} \rightarrow (Au^0)_{e^-_{aq}}$	8.0 ± 0.5	11
$2(Au^0)_{e^-_{aq}} \rightarrow$ product	3.2 ± 0.9	11
$2(Au^0)_{e^-_{aq}} \rightarrow$ product	2.9 ± 0.8	13
$2(Au^0)_H \rightarrow$ product	5.0 ± 1.0	2
$(Au^0)_{e^-_{aq}} + O_2 \rightarrow$ product	3.6	13
$(Au^0)_{e^-_{aq}} + N_2O \rightarrow$ product	0.55	13
$(Au^0)_{e^-_{aq}} + Fe(CN)_6^{3-} \rightarrow$ product	0.55	13

[a] Solute is $Au(CN)_2^-$. [b] Solute is $AuCl_4^-$.

In a more detailed study Fujita et al. [146] made the following observations:

(i) The initial product of the reaction H + Hg^+ absorbs in the UV with λ_{max} = 225 and 255 nm ($\epsilon_{255} = 1.4 \cdot 10^4$ dm^3 mol^{-1} cm^{-1}).

(ii) It decays by a second order reaction ($2k = 5.0 \cdot 10^9$ dm^3 mol^{-1} s^{-1}, μ = 0), which is independent of pH, but dependent on ionic strength as expected for a reaction between two singly charged cations.

(iii) Following this reaction there was a pseudo-first order growth of absorption in the region 220—250 nm resulting in a species with λ_{max} = 236 nm, $\epsilon_{236} = 2.4 \cdot 10^4$ dm^3 mol^{-1} cm^{-1}, identified as Hg_2^{2+}. The pseudo-first order growth rate of this species was proportional to [Hg^{II}] and increased sigmoidally (mid-point pH ca. 3.5) with increasing [H^+]. A novel sequence of reactions ((100) and (101)) was proposed to explain these observations.

$$Hg^+ + Hg^+ \rightarrow Hg^0 + Hg^{2+} \quad (100)$$

$$Hg^0 + Hg^{2+} \rightarrow Hg_2^{2+} \quad (101)$$

This mechanism suggests that the disproportionation reaction (100) is faster than the alternative dimerisation reaction which occurs with other Hg^I species (see below). Presumably ligand exchange by Hg^+ is too slow for dimerisation to compete with reaction (100). The differences in the spectra of the transient absorbing species reported by Faraggi and Amozig [142] and by Fujita et al. [146] has been attributed [146] to scattered light effects in the former case.

The reduction of $HgCl_2$ by e^-_{aq}, H or $(CH_3)_2\dot{C}OH$ results in a transient species absorbing with λ_{max} ca. 245 nm, $\epsilon_{245} = 7500\ dm^3\ mol^{-1}\ cm^{-1}$, $\lambda_{max} = 330$ nm, $\epsilon_{330} = 2300\ dm^3\ mol^{-1}\ cm^{-1}$ [147]. The product is believed to be HaCl on the basis of (i) the lack of effect of ionic strength on the decay and (ii) conductivity measurements [147]. In the presence of OH scavengers HgCl dimerises (reaction (102)) with $2k_{102} = 8.0 \cdot 10^9\ dm^3\ mol^{-1}\ s^{-1}$; in their absence reaction (102) competes with reoxidation by OH (reaction (103), $k_{103} \sim 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$). HgCl shows reducing properties, transferring an electron rapidly to such species as tetranitromethane and O_2 [147].

$$HgCl + HgCl \rightarrow Hg_2Cl_2 \qquad (102)$$

$$HgCl + OH \rightarrow HgCl^+ + OH^- \qquad (103)$$

The iodine analogue of HgCl has also been detected [148,149] following flash photolysis of HgI_2 solutions (reaction (104)) and absorbs at $\lambda_{max} = 340$ nm [148,149].

$$HgI_2 \xrightarrow{h\nu} HgI + I^{\cdot} \qquad (104)$$

Flash photolysis of mercury(II) chlorides and bromides gives rise to the respective radical anions, X_2^-, and gives no information on short-lived species of mercury [148].

There is some evidence [145] that an Hg^{III} ion is formed by OH oxidation of Hg^{2+}, for it has been observed that an absorption centred at 340 nm is formed when γ-irradiated H_2SO_4 or $NaClO_4$ glasses are warmed to ca. 130 K, approximately the temperature at which OH radicals disappear, in these glasses.

Mercuric oxide, HgO, is rapidly reduced by e^-_{aq} in neutral solution ($k = 2.3 \cdot 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$) to yield [150] a transient species the spectrum of which differs from that of Hg^+ in that it has a peak at 233 nm and a shoulder at 260—270 nm ($\epsilon_{260} = 5.3 \cdot 10^3\ dm^3\ mol^{-1}\ cm^{-1}$ [150]). The species decays by second order kinetics ($2k = 4.4 \cdot 10^9\ dm^3\ mol^{-1}\ s^{-1}$) and the decay rate is independent of ionic strength. Reactions (105)—(107) were proposed [150] to account for these observations.

$$e^-_{aq} + HgO \xrightarrow{H_2O} HgOH + OH^- \qquad (105)$$

$$HgOH + H^+ \rightleftharpoons Hg(H_2O)^+ \qquad (106)$$

$$2\ HgOH \rightarrow Hg_2O + H_2O \quad \text{or } Hg_2(OH)_2 \qquad (107)$$

From the effect of pH on the absorption spectrum pK_{106} was estimated [150] to be 5.1.

Fujita et al. [150] pointed out that the dimerisation of HgOH in neutral solution parallels that of HgCl [147] and is in contrast to the disproportionation which they reported for Hg^+ in acidic solution [146]. They suggest [150]

that the lack of charge on HgOH and HgCl facilitates the dimerisation reactions.

The product of reaction (107) decays by a slow first order process with $k = 2 \cdot 10^2$ min^{-1} [150] which is attributed to reaction (108).

$$Hg_2O \text{ or } Hg_2(OH)_2 \rightarrow Hg + HgO \text{ or } Hg(OH)_2 \quad (108)$$

At high [HgO] (>10^{-4} mol dm^{-3}) the decay is retarded, possibly due to the formation of long lived polynuclear species such as

$$Hg_2O + nHgO \rightarrow Hg_2O \cdot nHgO \quad (109)$$

Fujita et al. [151] also investigated the pulse radiolysis of $Hg(CN)_2$ solutions. Similarities with the $HgCl_2$ and HgO systems are observed. Thus, reduction of $Hg(CN)_2$ by e^-_{aq} ($k = 1.3 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1}) and CO_2^- ($k = 3.4 \cdot 10^9$ dm^3 mol^{-1} s^{-1}) produces a transient species, assigned as HgCN, which absorbs with λ_{max} at 285 nm and $\epsilon_{max} = 3.8 \cdot 10^3$ dm^3 mol^{-1} cm^{-1}. HgCN decays by second-order kinetics ($2k = 3.4 \cdot 10^9$ dm^3 mol^{-1} s^{-1}) to produce another species which absorbs at shorter wavelengths than HgCN. This is believed to be $(HgCN)_2$ which decays slowly (first half-life ~ 4 s) to produce a third species exhibiting a narrow absorption band with λ_{max} near 254 nm. On the basis that this species is Hg^0_{aq} formed in reaction (110), Fujita et al. [151] estimate $\epsilon_{254} = 2.8 \cdot 10^3$ dm^3 mol^{-1} cm^{-1} for Hg^0_{aq}.

$$(HgCN)_2 \rightarrow Hg^0_{aq} + Hg(CN)_2 \quad (110)$$

Alcohol radicals do not react with $Hg(CN)_2$, but they do react with HgCN ($k = 4$, 3.9, 2.4 and $1.6 \cdot 10^9$ dm^3 mol^{-1} s^{-1} for $\dot{C}H_2OH$, $CH_3\dot{C}HOH$, $(CH_3)_2\dot{C}OH$ and $\dot{C}H_2(CH_3)_2COH$ respectively). No evidence for the formation of any organomercury species was obtained, and in the case of the radical $(CH_3)_2\dot{C}OH$ acetone yields were consistent with the occurrence of reaction (111).

$$(CH_3)_2\dot{C}OH + HgCN \rightarrow (CH_3)_2CO + Hg^0 + H^+ + CN^- \quad (111)$$

E. LANTHANIDES

(i) Reduction of the trivalent ions

The stable valency state for the lanthanide elements is +3. Europium also forms a stable divalent ion in aqueous solution, whilst divalent samarium and ytterbium can be produced, but the ions are readily oxidised by water. Cerium forms also a stable tetravalent ion.

There is no known interaction between the hydrogen atom and the trivalent lanthanide ions, and only Ce^{III} and Pr^{III} are oxidised by OH (see Sect. E(ii) and E(iii) respectively). The hydrated electron reduces all the trivalent lanthanide ions[3] except Ce^{III} (see Sect. E(ii)) and Pm (no data available), but only in the case of Eu, Sm, Tm and Yb has the reaction been exploited to

characterise the divalent state. All four of these divalent ions have absorption spectra with maxima near 280 nm and secondary peaks at longer wavelengths (not Tm) in the UV—visible region [39,152] (Table 6). The spectra of Eu^{2+} and Yb^{2+} obtained by pulse radiolytic methods are very similar to those measured by conventional means. In the absence of OH scavengers and oxidising solutes the divalent ions (Ln^{2+}) are rapidly oxidised by reaction with OH (reaction (112)) [39,153]. In the presence of OH scavengers reaction (112) is prevented, and the divalent ions are quite long-lived [152] (Eu^{2+} is stable).

$$Ln^{2+} + OH \rightarrow Ln^{3+} + OH^- \quad (112)$$

When formic acid is present in Eu^{3+} solutions, an additional yield of Eu^{2+} is formed through reactions (5) and (113) ($k_{113} >> 7 \cdot 10^6$ dm^3 mol^{-1} s^{-1}) [42].

$$OH + HCO_2H \rightarrow H_2O + CO_2H \quad (5)$$

$$CO_2H/CO_2^- + Eu^{3+} \rightarrow CO_2 + H^+ + Eu^{2+} \quad (113)$$

No such reaction occurs with Yb^{3+} [42]. Eu^{2+}, Sm^{2+} and Yb^{2+} are powerful reducing agents and react rapidly with solutes such as oxyanions, O_2, H_2O_2, Co^{III} complexes etc. [39,152,154]. Some typical rate constants are shown in Table 7. The order of reactivity is Sm > Yb > Eu, which is also the order of the Ln^{III}/Ln^{II} redox potentials.

Tendler and Faraggi [155] examined the relationship between the oxidation potentials of lanthanide(II) ions and their rate of electron transfer to NO_2^- (reaction (114)) in more detail.

$$NO_2^- + Ln^{II} \rightarrow Ln^{III} \quad (114)$$

$$e_{aq}^- + Ln^{III} \rightarrow Ln^{II} \quad (115)$$

Ln^{II} was generated pulse radiolytically by reaction (115). By applying the

TABLE 6

Absorption spectra of divalent lanthanides

Metal	λ_{max}/nm	ϵ_{max}/dm^3 mol^{-1} cm^{-1}
Eu	260 [39,152,158] 320 [39,152]	1600 [152,158], 1650 [39] 800 [39,152]
Sm [a]	310 [152], 315 [39] 540 [39], 565 [152]	850 [39], 1000 [152] 300 [152], ca. 400 [39]
Tm	280 [39]	ca. 750 [39]
Yb	255 [39], 260 [152] 350 [152], 355 [39]	500 [152], 1100 [39], ca. 1300 [159] 500 [152], ca. 600 [159], 650 [39]

[a] Other bands at 425 (ϵ 600 dm^3 mol^{-1} cm^{-1}) and 480 (ϵ ca. 350 dm^3 mol^{-1} cm^{-1}) according to Pikaev et al. [39], but not observed by Faraggi and Tendler [152].

TABLE 7

Rate constants for reactions of divalent lanthanides [152]

Reactant	Eu^{2+}	Sm^{2+}	Tm^{2+}	Yb^{2+}
OH [39]	$1.3 \cdot 10^9$	$6.2 \cdot 10^9$	$7 \cdot 10^9$	$3.2 \cdot 10^9$
BrO_3^-	$<10^4$	$7.1 \cdot 10^6$	—	10^5
IO_3^-	$<10^4$	$4.9 \cdot 10^7$	—	$2.1 \cdot 10^6$
MnO_4^-	$6.5 \cdot 10^9$	$6.5 \cdot 10^9$	—	$8.3 \cdot 10^7$
NO_2^-	$6.2 \cdot 10^5$	$1.1 \cdot 10^9$	$1.7 \cdot 10^9$ [155]	$4.7 \cdot 10^7$
NO_3^-	$<10^4$	$2.0 \cdot 10^8$	—	$3.6 \cdot 10^6$
H_2O_2	$<10^4$	$3.5 \cdot 10^7$	—	$9.1 \cdot 10^6$
O_2	$<10^5$	$3.9 \cdot 10^8$	—	$6.5 \cdot 10^7$
N_2O	$<10^4$	$2.0 \cdot 10^5$	—	ca. 10^4
Yb^{3+}	—	$3.0 \cdot 10^6$	—	—
$Co(NH_3)_6^{3+}$	$2.0 \cdot 10^{-3}$ [160]	$5.0 \cdot 10^6$ [154]	—	$2.3 \cdot 10^3$ [159]
$Ru(NH_3)_6^{3+}$ [145]	ca. 10^3	$2.5 \cdot 10^7$	—	$5.0 \cdot 10^6$
$E^0(Ln^{III}/Ln^{II})/V$ [155]	0.43	1.55		1.15

Marcus theory for outer sphere electron transfer [156,157] to reaction (114) they obtained the relationship (116)

$$\log k_{act} = A + BE^0 \qquad (116)$$

where k_{act} is the activation controlled rate constant for (114), A and B are constants and E^0 is the redox potential of the Ln^{III}/Ln^{II} couple. Tendler and Faraggi showed that a plot of log k_{act} against the known values of E^0 for Eu, Yb and Sm was linear so that they were able to evaluate E^0 for other lanthanides knowing k_{act}. Values were obtained for Pr, Nd, Tb, Dy, Ho, Ev and Tm and in each case E^0 was close to 1.7 V.

(ii) Cerium

Cerium has two stable valency states in aqueous solutions, +3 and +4. Apparently Ce^{III} does not react with either e^-_{aq} or H [3,5], but it is oxidised to Ce^{IV} by OH [4], HSO_4 [161] and HO_2 [98,162,163]. The latter reaction is of interest because of its involvement in the $Ce^{IV} + H_2O_2$ reaction where a Ce^{III}—HO_2 complex is implicated [164]. This same complex has been detected by ESR when HO_2 oxidises Ce^{III} in perchloric acid [98,165,166]. The complex has not been observed, however, in sulphuric acid solution (Ce^{III} complexes strongly with SO_4^{2-}) [167] using either ESR [98,168] or spectrophotometric [162] detection methods. In the latter case a value of $k(Ce^{III} + HO_2) = 2.1 \cdot 10^5$ dm^3 mol^{-1} s^{-1} has been measured [162] from the rate of formation of the Ce^{IV} product. Further studies are needed to establish the reason for the dependence on the counter ion.

Radiation induced reduction of Ce^{IV} occurs in strongly acidic solutions containing small amounts of Ce^{III} with $G(-Ce^{IV}) = G(Ce^{III}) = G_{H_2O_2} + G_H - G_{OH}$, independent of whether the solutions are aerated or not [169,170]. This equation implies that reduction of Ce^{IV} occurs by reactions (117)—(119). Reaction (119) does not involve formation of an intermediate complex when either sulphate or perchlorate ions are present [98,168].

$$Ce^{IV} + H \rightarrow Ce^{III} + H^+ \qquad (117)$$

$$Ce^{IV} + H_2O_2 \rightarrow Ce^{III} + H^+ + HO_2 \qquad (118)$$

$$Ce^{IV} + HO_2 \rightarrow Ce^{III} + H^+ + O_2 \qquad (119)$$

(iii) Praesodymium

Hydroxyl radicals oxidise Pr^{3+} with a rate constant of $2 \cdot 10^6$ dm^3 mol^{-1} s^{-1} [39,41]. The species formed absorbs with $\lambda_{max} = 290$ nm, $\epsilon_{max} = 1050$ dm^3 mol^{-1} cm^{-1} [41] (possibly an *f*—*d* transition [41]) at pH 5.8, but at lower pH's the absorption is weaker [39,41]. This behaviour is thought to be due to the hydrolysis of the Pr^{IV} (possibly as in eqn. (120)), and from the variation of the absorption with pH, a value of $pK_{113} = 3.2$ has been measured [41].

$$Pr^{4+} + H_2O \rightleftharpoons PrOH^{3+} + H^+ \quad (120)$$

Pr^{IV} decays by a second order reaction at pH 5.8 with $2k = 8 \cdot 10^7$ dm^3 mol^{-1} s^{-1} [41], but by a first order reaction at $2 < pH < 3.8$ [41]. The latter is attributable to reaction (121), for which $k = 2 \cdot 10^6$ dm^3 mol^{-1} s^{-1} has been determined [41]. Pr^{IV} is a powerful oxidant, and its reactions with NO_2^-, H_2O_2 and Br^-.

$$Pr^{IV} + HSO_4^- \rightarrow Pr^{III} + HSO_4^{\cdot} \quad (121)$$

have been studied [41].

F. ACTINIDES

(i) General Remarks

The radiation chemistry of the actinide elements has received considerable attention, mainly because of its importance in nuclear reactor fuel technology. The elements of principal interest here, U, Np, Pu and Am, all form stable tri- and hexavalent ions, which in acidic aqueous solution can be represented as M^{3+} and MO_2^{2+} respectively. The tetra- and pentavalent ions (M^{4+} and MO_2^+ respectively) are also known, but, with the exception of U^{4+}, are subject to disproportionation, some rapidly (Am^{IV}), others only in strong acid (Am^V, Np^V). Heptavalent Np and Pu are known in strongly alkaline solution. The situation is complicated, however, by hydrolysis, complexation with anions other than perchlorate, and not least by autoradiolytic effects. Thorium, the other actinide considered here, is known only as the tetravalent ion.

(ii) Thorium

Little is known about the oxidation or reduction of Th^{IV} by OH, H or e_{aq}^-. The HO_2 radical is reported to react with Th^{IV} to give a complex written as $Th^{IV}O_2H$ (122) [98,99,162]. This intermediate has both an ESR signal (singlet line, $g = 2.01828$) [98], and an optical absorption ($\lambda_{max} < 270$ nm) [162].

$$Th^{IV} + HO_2 \rightleftharpoons Th^{IV}O_2H \quad (122)$$

The rate of formation of $Th^{IV}O_2H$ has been determined following pulse radiolysis of Th^{IV} solutions containing an excess of H_2O_2. It was found to be first order in both $[HO_2]$ and $[Th^{IV}]$ * giving $k = 1.8 \cdot 10^6$ dm^3 mol^{-1} s^{-1} [162]. The equilibrium constant for (122) was found to be $K_{122} = 4 \cdot 10^4$ dm^3 mol^{-1} by monitoring the absorption due to $Th^{IV}O_2H$ as a function of $[Th^{IV}]$ [162].

* A minor pathway independent of $[Th^{IV}]$ was detected, but because of the large errors involved in these experiments, no reliable rate constant could be estimated [162].

This value is ~4 times smaller than that estimated from ESR measurements in flow systems [99]. $Th^{IV}O_2H$ decays by a second order process *, probably due to reactions such as (123) and (124).

$$Th^{IV}O_2H + Th^{IV}O_2H \rightarrow 2\ Th^{IV} + H_2O_2 + O_2 \quad (123)$$

$$Th^{IV}O_2H + HO_2 \rightarrow Th^{IV} + H_2O_2 + O_2 \quad (124)$$

By monitoring the decay of the ESR signal of $Th^{IV}O_2H$ values of $2k_{123} = 5 \cdot 10^2\ dm^3\ mol^{-1}\ s^{-1}$ and $k_{124} = 8.0 \cdot 10^5\ dm^3\ mol^{-1}\ s^{-1}$ have been determined [171].

(iii) Uranium

Haissinsky [172] investigated the radiation induced oxidation of U^{IV} in sulphuric acid solutions in the absence and presence of oxygen. In the absence of oxygen the yields of U^{VI} are accounted for by the following mechanism

$$UOH^{3+} + OH \rightarrow UO_2^+ + 2\ H^+ + H_2O \quad (125)$$

$$UO_2^+ + OH \xrightarrow{H^+} UO_2^{2+} + H_2O \quad (126)$$

In the presence of oxygen $G(U^{VI})$ is as high as 18 depending on the conditions. From a study of the effects of dose rate and $[O_2]$, Haissinsky [172] deduced that U^{IV} is oxidised to U^{VI} by the chain reaction sequence

$$UOH^{3+} + OH \rightarrow UO_2^+ + 2\ H^+ + H_2O \quad (125)$$

$$UO_2^+ + O_2 \rightarrow UO_2^{2+} + O_2^- \ (\xrightarrow{H^+} HO_2) \quad (127)$$

$$UOH^{3+} + HO_2 \rightarrow UO_2^{2+} + OH + H^+ \quad (128)$$

$$UO_2^+ + OH \xrightarrow{H^+} UO_2^{2+} + H_2O \quad (126)$$

Other radiation chemical studies with uranium in aqueous solutions have been performed with U^{VI}, the most stable valency state. UO_2^{2+} is reduced by reaction with e_{aq}^- [3], but the product, U^V, has only a weak absorption spectrum [76,173]. The reaction of U^{VI} with HO_2 has also been studied [162]. The chemistry of the product, a complex written as $U^{VI}O_2H$, shows many similarities with the $Th^{IV}O_2H$ complex discussed in the previous section.

(iv) Neptunium

γ-Irradiation of NpO_2^{2+} in deaerated acidic solutions gives rise to a net reduction with $G(-NpO_2^+) = 5.0$ [174]. Oxygen is also formed with $G(O_2) = 1.5$, and arises through the reduction of NpO_2^{2+} by H_2O_2, a reaction which occurs with the stoichiometry given in eqn. (129) [175]. Since the measured yield

* A first order process is detected under certain circumstances [98], but this is probably due to reaction with impurity.

of O_2 is twice that of the molecular peroxide, $G_{H_2O_2} = 0.75$, there must be an additional source of H_2O_2.

$$2\ NpO_2^{2+} + H_2O_2 = 2\ NpO_2^{+} + 2\ H^{+} + O_2 \qquad (129)$$

This is most likely to be the combination of OH radicals (reaction (130)), which presumably occurs in competition with the reoxidation of NpO_2^+ (reaction (131)). NpO_2^{2+} is also reduced by H atoms [174].

$$OH + OH \rightarrow H_2O_2 \qquad (130)$$

$$OH + NpO_2^{+} \rightarrow OH^- + NpO_2^{2+} \qquad (131)$$

In alkaline solutions Np^V, Np^{VI} and Np^{VII} are all reduced by the hydrated electron [40], whilst O^- oxidises Np^{VI} [176].

Aerated solutions of Np^{IV} in H_2SO_4 are reported [177] to be oxidised radiolytically with yields identical to those in the Fe^{2+}/H_2SO_4 (Fricke dosimeter) system. The mechanism is presumably somewhat different since a Np^{IV} peroxide complex has been detected [177]. The known radiation induced redox reactions of Np can be summarised as follows

$$Np^{IV} \xrightarrow[e_{aq}^-,H]{OH,HO_2} Np^{V} \underset{e_{aq}^-,H}{\overset{OH}{\rightleftharpoons}} Np^{VI} \underset{e_{aq}^-}{\overset{O^-}{\rightleftharpoons}} Np^{VII}$$

(v) Plutonium

The principal isotopes of plutonium, ^{238}Pu, ^{239}Pu and ^{242}Pu all decay by emission of α-particles with energies of ca. 5.4, 5.1 and 4.9 MeV respectively [176], and in consequence autoradiolytic effects are an important aspect of plutonium solution chemistry. For instance solutions of Pu^{IV} are ultimately converted into a complex mixture of tri-, tetra-, penta- and hexavalent plutonium [178–180]. Molecular hydrogen is also formed, a fact which has received considerable attention [181,182] because of its significance in the commercial handling of plutonium solutions. There is, however, only a poor understanding of the mechanistic details and rates of these radiolytic reactions. The known radiation-induced redox reactions of plutonium can be summarised as follows

$$Pu^{III} \xrightarrow{OH,H,HO_2,Cl_2^-} Pu^{IV} \xrightarrow{OH} Pu^{V} \underset{e_{aq}^-,H,HO_2,}{\overset{OH}{\rightleftharpoons}} Pu^{VI} \underset{e_{aq}^-}{\overset{O^-}{\rightleftharpoons}} Pu^{VII}$$

The dismutation of Pu^{IV} and Pu^V, and their slow reactions with H_2O_2 are also important [178,179], and account for many of the post-irradiation changes that have been observed.

γ-Radiolysis of aerated acidic Pu^{III} solutions under conditions where α-radiolytic effects are negligible gives Pu^{IV} with $G(Pu^{IV}) = 6.6$ [183]. This

high yield indicates oxidation by both OH and HO_2, the latter, formed in reaction (28), being reduced to H_2O_2 ($G(H_2O_2) = 4.0$) [183]. There is also net oxidation with $G(Pu^{IV}) = 5.5$ in deaerated solutions. Here no HO_2 radicals are formed, so that oxidation by H atoms must occur (reaction (133)), and it is found that $G(H_2) = 3.6$ [183].

$$H + O_2 \rightarrow HO_2 \qquad (28)$$

$$Pu^{III} + HO_2 \xrightarrow{H^+} Pu^{IV} + H_2O_2 \qquad (132)$$

$$Pu^{III} + H^+ \xrightarrow{H^+} Pu^{IV} + H_2 \qquad (133)$$

The mechanism of the reaction has not been studied, but presumably involves the formation of a hydrido complex similar to that formed by reaction of H with Fe^{2+}, Cr^{2+} etc. (see Sect. C(vi)).

Pu^{VII} is unstable in acidic solutions [179], but is sufficiently long-lived in concentrated alkali ($t_{1/2}$ = 8 hr in 1 mol dm^{-3} NaOH) [184] for its reduction by e^-_{aq} to be studied by pulse radiolysis [40]. Pu^{VII} may be conveniently prepared by radiolytic oxidation of Pu^{VI} in N_2O saturated alkaline solutions, and is formed with $G(Pu^{VII}) = 5.4$ (i.e. $G_{e^-_{aq}} + G_H + G_{O^-} - 2\,G_{H_2O_2}$) [40]. No net oxidation occurs in oxygenated solutions [40]. γ-Radiolysis of alkaline deaerated Pu^{VII} solutions brings about reduction to Pu^{VI} with $G(-Pu^{VII}) = 2.35$ (i.e. $G_{e^-_{aq}} + G_H + 2\,G_{H_2O_2} - G_{O^-}$) [40].

(vi) Americium

Most studies with americium have employed ^{241}Am which decays by emission of an α-particle (energy ca. 5.4 MeV) [178]. Its half life is 458 yr [178], considerably shorter than that of the principle isotopes of either neptunium or plutonium, so that autoradiolytic effects are more significant for americium. Acidic solutions of both Am^V and Am^{VI} are ultimately reduced to Am^{III}, but little is known of the mechanistic details [177,178,185]. In a study of the rate of the auto-reduction of oxygenated Am^V and Am^{VI} solutions in the presence of $HNO_3 + S_2O_8^{2-}$ a mechanism has been proposed involving reduction of both valency states by HO_2, and oxidation of Am^V by OH and SO_4^- [185]. It has also been observed [186] that the rate of the autoradiolytic reduction of Am^V in HCl decreases with increasing [HCl], a result possibly due to the oxidation reaction $Am^V + Cl_2^-$. The known radiolytic redox reactions of Am can be summarised as follows

$$Am^{IV} \xrightarrow[HO_2]{} Am^V \underset{HO_2}{\overset{OH,SO_4^-,Cl_2^-}{\rightleftharpoons}} Am^{VI}$$

Am^{IV} is unstable in solution, and rapidly undergoes dismutation. No pulse radiolysis studies of americium have been reported.

G. GROUP IIIB METALS

(i) Aluminium, gallium and indium

For these three metals the only important stable aquo ions are trivalent. Going down the group there is an increase in the stability of the monovalent ion; In^+ can be formed for instance, but is slowly oxidised by H^+ [187], whilst for thallium, Tl^+ is the most important aquo ion. The trivalent ions are all reduced by reaction with the hydrated electron to give transient divalent ions. Al^{2+} has too weak an absorption in the range 250—500 nm ($\leqslant$300 $dm^3\ mol^{-1}\ cm^{-1}$ [188]) to be studied directly by pulse radiolysis. The only reactions of Al^{2+} reported are those with $ClCH_2CH_2OH$ and $BrCH_2CO_2^-$, which result in dehalogenation [189]. Ga^{2+} and In^{2+} both have large absorptions in the UV (for In^{2+} λ_{max} = 260 nm, ϵ_{260} = 9500 $dm^3\ mol^{-1}\ cm^{-1}$ [187,188]; Ga^{2+} has an absorption rising towards shorter wavelengths) [110]. Similar absorptions have been detected following γ-irradiation of Ga^{3+} or In^{3+} doped H_2SO_4 glasses at 77 K [110]. Ga^{2+} has also been identified by ESR in γ-irradiated $HClO_4$ glasses containing Ga^{3+} [143].

In solution In^{2+} disappears by a second order reaction. Taylor and Sykes [187] found this to be independent of the presence of an OH scavenger, but more recent results [188,190] suggest that the rate is ca. 3 times slower in the presence of the OH scavenger. This indicates that the disappearance is due principally to the reactions

$$In^{2+} + OH \rightarrow In^{3+} + OH^- \qquad (133)$$

$$In^{2+} + In^{2+} \rightarrow In^+ + In^{3+} \qquad (134a)$$

$$In^{2+} + In^{2+} \rightarrow In_2^{4+} \qquad (134b)$$

with rate constants of $k_{133} = 4.9 \cdot 10^5\ dm^3\ mol^{-1}\ s^{-1}$ and $k_{134} = 1.6 \cdot 10^9\ dm^3\ mol^{-1}\ s^{-1}$ [188]. Taylor and Sykes [187] were unable to find any absorption attributable to In^+ (λ_{max} = 209 nm [187]) following reaction (134), but this was probably because of the optical limitations of the apparatus employed (see also comments in ref. 33). With other metal ions, such as Cd^+, the dismutation is known to result in a binuclear ion, and this may be the fate of In^{2+}. No studies of the chemistry of Ga^{2+} or In^{2+} have been reported.

(ii) Thallium

Tl^+ is rapidly reduced by reaction with both e_{aq}^- [3] and H [5]. The immediate product of the reaction is undoubtedly Tl^0. However the intensity of the absorption of the transient species observed (λ_{max} = ca. 400 nm [15])

on pulse radiolysing $\geqslant 10^{-4}$ mol dm^{-3} Tl^+ solutions shows a marked dependence on $[Tl^+]$, and it is suggested [15] that the Tl^0 complexes with Tl^+ to form the ion Tl_2^+ (reaction (135)). The same species has been detected in solid KCl/TlCl [191]. Tl^0 also absorbs [122,192], apparently at shorter wavelengths than Tl_2^+.

$$Tl^0 + Tl^+ \rightleftharpoons Tl_2^+ \qquad (135)$$

Flash photolysis of Tl^0 at ca. 300 nm yields Tl^+ and e_{aq}^- (reaction (136)) [119], and it is concluded that the absorption is due to a charge transfer to solvent band [122]. Both Tl^0 and Tl_2^+ show reducing properties and a selection of their reaction rate constants is shown in Table 8.

$$Tl^0 + h\nu \rightarrow Tl^+ + e_{aq}^- \qquad (136)$$

Tl^+ is oxidised by OH to Tl^{II} [4]. Some difference of opinion exists regarding the absorption spectrum of Tl^{II} in solution. Three groups of workers, investigating wavelengths $\geqslant 240$ nm have found λ_{max} ca. 260 nm, $\epsilon_{max} = 5400$ dm^3 mol^{-1} cm^{-1} at $[H^+] = 0.01$—1 mol dm^{-3} [15,193,194]. Schwarz et al. [45] reported an absorption rising towards shorter wavelengths in the range 225—400 nm, $[H^+] = 1$ mol dm^{-3}, with a shoulder at ca. 280 nm, $\epsilon_{280} = 3000$ dm^3 mol^{-1} cm^{-1}, and suggested that earlier work was complicated by scattered light effects. In Schwarz et al's. [45] experiments, however, calculations indicate that significant amounts of the hydrogen atoms were scavenged by the Tl^+ present. Since the products of that reaction, Tl^0/Tl_2^+, may absorb appreciably below 300 nm (definitive studies have not been reported) we tentatively conclude that the earlier work of Cercek et al. [15], of Burchill and Wolodarsky [193] and that done more recently by Falcinella et al. [194] is the more precise. Furthermore, two of these groups [193,194] used a flash photolytic method of generating Tl^{II}, which is free from complications arising from the presence of hydrogen atoms. Some of the differences may also be due to the equilibrium (137) for which $pK_{128} = 4.6 \pm 0.2$ m dm^{-3} [21] which may also account for the wide variation in estimates of $2k_{138}$.

$$Tl^{2+} + H_2O \rightleftharpoons TlOH^+ + H^+ \qquad (137)$$

$$Tl^{II} + Tl^{II} \rightarrow Tl^+ + Tl^{3+} \qquad (138)$$

Tl^{II} has long been recognised as an intermediate in Tl^+/Tl^{3+} redox chemistry. The reduction of Tl^{3+} by Fe^{2+}, for instance, is retarded by addition of Fe^{3+}, the mechanism being [195]

$$Tl^{3+} + Fe^{2+} \rightleftharpoons Tl^{2+} + Fe^{3+} \qquad (139)$$

$$Tl^{2+} + Fe^{2+} \rightarrow Tl^+ + Fe^{3+} \qquad (140)$$

Studies of the reaction by conventional means gives values for k_{139} and k_{-139}/k_{140}. Measurements of k_{-139} and k_{140} have been made by fast reaction techniques, so that a value of K_{139} can be found. Since the redox potential

TABLE 8

Rate and equilibrium constants for some reactions of zero and divalent thallium

Reaction	Rate [a] or equilibrium constant	Ref.
$Tl^0 + Tl^+ \rightleftharpoons Tl_2^+$	$K = 2.3 \cdot 10^3$ dm^3 mol^{-1}	16
$Tl^0 + H_2O_2 \rightarrow Tl^+ + OH + OH^-$	$7 \cdot 10^6$	192
$Tl^0 + O_2 \rightarrow Tl^+ + O_2^-$	$1.0 \cdot 10^7$	192
$Tl^0 + Tl^{2+} \rightarrow 2\,Tl^+$	$\geq 4.5 \cdot 10^9$	192
$Tl_2^+ + H_2O_2 \rightarrow 2\,Tl^+ + OH + OH^-$	$7 \cdot 10^6$	192
$Tl_2^+ + N_2O \xrightarrow{H^+}$ products [b]	$1.4 \cdot 10^7$	77
$Tl_2^+ + O_2 \rightarrow 2\,Tl^+ + O_2$	$1.0 \cdot 10^7$	192
$Tl_2^+ + Tl^{2+} \rightarrow 3\,Tl^+$	$7.5 \cdot 10^9$	192
$Tl^{2+} + H_2O_2 \rightarrow Tl^+ + H^+ + HO_2$	$2.8 \cdot 10^7$	15
$Tl^{2+} + Tl^{2+} \rightarrow Tl^+ + Tl^{3+}$	$(2\text{–}23) \cdot 10^8$	15,45,193,194
$Tl^{2+} + Co^{2+} \rightarrow Tl^+ + Co^{3+}$	$6.2 \cdot 10^3$	194
$Tl^{2+} + Fe^{2+} \rightarrow Tl^+ + Fe^{3+}$	$6.7 \cdot 10^6$	45
$Tl^{2+} + Fe^{3+} \rightarrow Tl^{3+} + Fe^{2+}$	$1.1 \cdot 10^6$	194
$Tl^{2+} + CH_3CHOHCH_3 \rightarrow Tl^+ + CH_3\dot{C}OHCH_3 + H^+$	$2.8 \cdot 10^4$	198
$Tl^{2+} + Cl^- \rightleftharpoons TlCl^+$	$K = 6.2 \cdot 10^4$ dm^3 mol^{-1}	200
$TlCl^+ + Cl^- \rightleftharpoons TlCl_2$	$K = 1.9 \cdot 10^3$ dm^3 mol^{-1}	200
$TlCl_2 + Cl^- \rightleftharpoons TlCl_3^-$	$K = 13$ dm^3 mol^{-1}	200
$Tl^{2+} + H_2O \rightarrow TlOH^+ + H^+$	$3.5 \cdot 10^5$ s^{-1}	21
$H^+ + TlOH^+ \rightarrow Tl^{2+} + H_2O$	$1.4 \cdot 10^{10}$	21

[a] dm^3 mol^{-1} s^{-1}. [b] Products other than N_2 unidentified.

TABLE 9

Standard reduction potentials involving Tl^{2+}

	E^0/V
$Tl^{3+} + e^- \rightleftharpoons Tl^{2+}$	0.31 [a], 0.30 [b]
$Tl^{2+} + e^- \rightleftharpoons Tl^+$	2.22 [a]
$Tl^{3+} + 2\,e^- \rightleftharpoons Tl^+$	1.25 [c]

[a] From ref. 194. [b] From ref. 45. [c] From W.M. Latimer, Oxidation Potentials, 2nd Ed., Prentice-Hall, New York, 1952.

for the Fe^{3+}/Fe^{2+} couple is known, that for Tl^{3+}/Tl^{2+} can be calculated. Two recent estimates using this method are shown in Table 9. Similarly using data for the $Tl^+ + Co^{3+}$ reaction, for which the mechanism is [196]

$$Tl^+ + Co^{3+} \rightleftharpoons Tl^{2+} + Co^{2+} \quad (141)$$

$$Tl^{2+} + Co^{3+} \rightarrow Tl^{3+} + Co^{2+} \quad (142)$$

and a value for k_{-141} measured by flash photolysis, Falcinella et al. [194] were able to find $E^0(Tl^{2+}/Tl^+)$ (see Table 9).

These measurements of the redox potentials have important implications for the mechanism of the thermal Tl^+/Tl^{3+} exchange reaction. One proposed mechanism involves reaction (143) [197]. The data in Table 9 may be used to estimate the equilibrium constant for this, and since k_{-143} is known (Table 8), k_{143} can be deduced. The value found, ca. 10^{-25} dm^3 mol^{-1} s^{-1} [45,194],

$$Tl^+ + Tl^{3+} \rightleftharpoons Tl^{2+} + Tl^{2+} \quad (143)$$

is extremely small, completely ruling out reaction (143) in the exchange reaction.

γ-Irradiation of acidic, deaerated Tl^{3+} solutions containing simple aliphatic alcohols such as ethanol or isopropanol leads to reduction of Tl^{3+} by a chain reaction [198]. The mechanism proposed involves reactions (144) and (145) as the propagation steps. The second of these is of particular interest, and illustrates the powerful oxidising nature of Tl^{2+}. Rate constants for the reaction are ca. $3 \cdot 10^4$ dm^3 mol^{-1} s^{-1} [198].

$$R^1R^2\dot{C}OH + Tl^{3+} \rightarrow R^1R^2CO + Tl^{2+} \quad (144)$$

$$Tl^{2+} + R^1R^2CHOH \rightarrow Tl^+ + R^1R^2\dot{C}OH \quad (145)$$

Tl^{2+} also oxidises methoxylated benzenes rapidly ($k \sim 5 \cdot 10^8$ dm^3 mol^{-1} s^{-1}) to produce radical cations [199], e.g. reaction (146).

(146)

Since OH generally adds to the benzene ring, Tl^+ can be used to catalyse the electron transfer process through reactions (147) and (146)

$$OH + Tl^+ \rightarrow Tl^{2+} + OH^- \quad (147)$$

The pulse radiolysis method has also been used to study the equilibria between Tl^{2+} and Cl^- [200]. A summary of the stability constants measured is given in Table 8. The same work [200] indicates that the preferred path for reduction of Tl^{III}-chloro complexes by H atoms is ligand abstraction, e.g.

$$H + TlCl^{2+} \rightarrow Tl^{2+} + HCl \qquad (148)$$

H. GROUP IVB METALS

(i) Lead

Pulse radiolysis of deaerated Pb^{2+} solutions gives rise to a transient species absorbing with $\lambda_{max} = 300$ nm [76,77]. This is identified as Pb^+ produced by hydrated electron reduction of Pb^{2+} (149).

$$Pb^{2+} + e^-_{aq} \rightarrow Pb^+ \qquad (149)$$

The absorption disappears by an approximately second order process [201], which by analogy with other divalent ions (see section J) is probably due to reoxidation by OH and/or dismutation. In neutral deaerated solutions containing 1 mol dm^{-3} methanol, metallic lead is produced with $G(Pb^0) = 1.2$ [115]. This implies that the dismutation (or its equivalent) is the major reaction pathway for the decay of Pb^+ in the absence of OH, and that the hydroxymethyl radical (formed in reaction (4)) does not effect reduction. However, Pb^{2+} is reduced by Cd^+ and Zn^+ [201] (see Sect. J(i)(b)). Pb^+ shows reducing properties, reacting rapidly ($k \sim 4 \cdot 10^9$ dm^3 mol^{-1} s^{-1}) with O_2 [201], quinones and similar compounds [202,203].

There appears to be no report of any reaction between either the hydrogen atom or the hydroxyl radical and Pb^{2+}. The possibility of the occurrence of the latter reaction merits attention, particularly in view of the formation of Pb^{3+} centres in a series of γ-irradiated Pb^{II} and Pb^{IV} salts or doped glasses [144].

(ii) Tin

The hydrogen atom and the hydrated electron both reduce Sn^{II} [3], and pulse radiolysis studies have shown [188] that the Sn^I formed has a spectrum consisting of an absorption rising towards shorter wavelengths ($\epsilon_{260} = 3800$ dm^3 mol^{-1} cm^{-1} at pH 3.2) with a shoulder or minor peak at 320 nm ($\epsilon_{320} = 2300$ dm^3 mol^{-1} cm^{-1} at pH = 3.2). Hydroxyl radicals react [4] to produce an Sn^{III} species with a featureless absorption rising towards shorter wavelengths ($\epsilon_{260} = 4500$ dm^3 mol^{-1} cm^{-1} at pH 3.2 [188]). Both transients were found [188] to decay by reactions which were approximately second order.

A number of reports on the steady state radiolysis of Sn^{II} solutions have been published. Boyle et al. [204], in a study of the γ-radiolysis of Sn^{II} in 0.4 mol dm^{-3} H_2SO_4, reported a net oxidation to Sn^{IV} with a yield equal to G_{H_2}. Reactions (150)—(156) are in keeping with this, and Boyle et al. [204]

were able to confirm their occurrence by studying the effect of additions of Fe^{2+} and Fe^{3+}.

$$H + Sn^{II} \rightarrow H^+ + Sn^{I} \quad (150)$$

$$OH + Sn^{II} \rightarrow OH^- + Sn^{III} \quad (151)$$

$$Sn^{I} + Sn^{III} \rightarrow Sn^{II} + Sn^{II} \quad (152)$$

$$Sn^{III} + Sn^{III} \rightarrow Sn^{II} + Sn^{IV} \quad (153)$$

$$Sn^{I} + Sn^{IV} \rightarrow Sn^{II} + Sn^{III} \quad (154)$$

$$Sn^{I} + H_2O_2 \rightarrow Sn^{II} + OH + OH^- \quad (155)$$

$$Sn^{III} + H_2O_2 \rightarrow Sn^{IV} + OH + OH^- \quad (156)$$

Stepenuck [205] has reported that $G(-Sn^{II}) = 0.51$ in 0.4 mol dm^{-3} H_2SO_4, in agreement with the results of Boyle et al. [204], but that in 1—3 mol dm^{-3} HBr and at low doses $G(-Sn^{II}) = 2.5$ and $G(H_2) = 2.0$. Similar results were obtained [205] in 1 mol dm^{-3} HCl, whilst in more dilute HCl (just enough to effect solution of the Sn^{II}) containing 1 mol dm^{-3} methanol Philipp and Marsik [115] found a very small yield (0.1) of metallic tin. The high yields of H_2 in the presence of the concentrated halogen acids indicate inefficient scavenging of H by Sn^{II}, and can be equated with $G_{H_2} + \frac{1}{2} G_H$. The oxidising species, in this case H_2O_2 and X_2^- (X = Br or Cl) must, therefore, be responsible for the removal of Sn^{II}. Likely reactions are (156) and (157) followed by (153), which predict $G(-Sn^{II}) = \frac{1}{2} G_{OH} + G_{H_2O_2}$ = ca. 2.2) *, close to the value measured.

$$Sn^{II} + X_2^- \rightarrow Sn^{III} + 2\,X^- \quad (157)$$

The lack of reactivity of H atoms with Sn species in the halogen acids is probably due to extensive complexation of the tin ions by halide ions. The metallic tin formed in the more dilute HCl solutions probably arises via reactions (158) and (159), the small yield being due to the fact that the hydrated electrons are scavenged by Sn^{II} in competition with the reaction with $H^\cdot$.

$$Sn^{II} + e^-_{aq} \rightarrow Sn^{I} \quad (158)$$

$$Sn^{I} + Sn^{I} \rightarrow Sn^{0} + Sn^{II} \quad (159)$$

I. COPPER

(i) Reduction of Cu^{2+} by free radicals

Cu^{2+} is rapidly reduced to Cu^+ by e^-_{aq} [3] and H [5], and pulse radiolysis provides a very convenient way of generating Cu^+ in aqueous solution.

The absorption spectrum of Cu^+ consists of a weak band rising into the UV

* Yields taken from Fig. 4.1, p. 47 of A.O. Allen, The Radiation Chemistry of Water and Aqueous Solutions, Van Nostrand, Princeton, 1961.

[77,206] ($\epsilon_{240} \sim 600$ dm^3 mol^{-1} cm^{-1}) so that its reactions can only be followed conveniently by observing the other reactants or the products. Cu^+ forms relatively stable complexes with olefinic compounds (reaction (160)) and these show characteristic and fairly intense absorption bands in the near UV [207–210]. Rates of formation and stability constants of a number of these complexes have been measured by pulse radiolysis [209,210] and the data are given in Table 10. The high values of k_{160} are not unexpected since the water exchange rate by Cu^+_{aq}, a d^{10} cation, is likely to be rapid.

$$Cu^+ + \text{olefin} \rightleftharpoons (Cu\text{—olefin})^+ \qquad (160)$$

Cu^{2+} is also rapidly reduced by organic free radicals. The rates of these reductions can be measured by direct observation of the decay of the radicals or, more conveniently, by observing the rate of formation of $(Cu\text{—olefin})^+$ under conditions where reaction (161) is rate controlling (R = free radical).

$$R + Cu^{2+} \rightarrow R^+ + Cu^+ \qquad (161)$$

Rates of reduction of Cu^{2+} by simple hydroxyalkyl radicals have been measured in this way and they agree well with data obtained from direct observation of the decay of the radical (see Table 11). In each case the reaction rate is proportional to $[Cu^{2+}]$. Kochi [211] showed that reaction (161) generally proceeds via the formation of a radical—Cu^{II} complex (reaction (162)) which can then undergo either β-proton elimination (reaction (163)) or electron transfer (reaction (164)) (R = H or alkyl group).

$$HCR^1R^2\text{—}\underset{\displaystyle OH}{\underset{|}{\dot{C}R^3}} + Cu^{II} \rightarrow HCR^1R^2\text{—}\underset{\displaystyle OH}{\underset{|}{CR^3}}\text{—}Cu^{II} \qquad (162)$$

$$HCR^1R^2\text{—}CR^3\text{—}Cu^{II} \rightarrow CR^1R^2{=}\underset{\displaystyle OH}{\underset{|}{CR^3}} + Cu^I + H^+ \qquad (163)$$

$$HCR^1R^2\text{—}CR^3\text{—}Cu^{II} \rightarrow HCR^1R^2\text{—}\underset{\displaystyle OH}{\underset{|}{\dot{C}R^3}} + Cu^I \qquad (164)$$

Since the values of k obtained by both methods of measurement are the same (Table 11), reaction (162) must be the rate determining step of the reduction

TABLE 10

Values of k_{160} and k_{-160} for the formation of Cu^I—olefin complexes

Olefin	k_{160} (dm^3 mol^{-1} s^{-1})	k_{-160} (s^{-1})	Ref.
Acrylamide	$2 \cdot 10^9$	$1.1 \cdot 10^5$	213
Maleic acid	$2 \cdot 10^9$	$1.8 \cdot 10^5$	210
Fumaric acid	$1.7 \cdot 10^9$	$2.4 \cdot 10^5$	210

TABLE 11

Specific rates of reduction of Cu^{2+} by some organic radicals [213]

Radical	10^{-8} k (dm^3 mol^{-1} s^{-1})	
	a	b
$\cdot CH_2OH$	1.9 1.1 [50]	1.6
$CH_3\dot{C}HOH$	0.74 [50]	0.94
$(CH_3)_2\dot{C}OH$	0.5 0.45 [50]	0.52
$\dot{C}H_2C(CH_3)_2OH$	—	0.032
$\dot{C}H_2CH_2OH$	—	0.22

[a] From rate of decay of the radical. [b] From rate of formation of (Cu—acrylamide)$^+$.

as Kochi has suggested. Further evidence for the formation of an organocopper intermediate in the reduction of Cu^{II} by organic radicals is provided by the observation that when the radical contains a β-hydroxyl group the product is the corresponding epoxide [212], presumably formed through reaction (165).

$$\underset{\underset{OH}{|}}{HCR^1—CR^2R^3—Cu^{II}} \rightarrow \underset{\diagdown\,\diagup\ O}{HCR^1—CR^2R^3} + H^+ + Cu^I \qquad (165)$$

The reactivities of α-hydroxyalkyl radicals with Cu^{2+} (Table 11) decrease in the order primary > secondary > tertiary. This suggests that the transition state cannot have a high degree of carbonium ion character because the carbonium ion stability is in the reverse order. A similar order of radical reactivity occurs with Cr^{2+} [49] and Ni^+ [51] where organometallic intermediates are formed in each case.

(ii) Reaction of Cu^+ with free radicals

When aqueous solutions of Cu^{2+} are pulse irradiated under conditions where reactions (162)—(164) occur, secondary reactions become evident if the solution is repeatedly pulsed. These are manifested by the appearance of species which absorb strongly in the region 400—500 nm and which are believed to be complexes between Cu^+ and the organic radicals [213]. The formation and decay of these complexes has been interpreted in terms of the following reactions [213] (R = free radical)

$$R + Cu^{2+} \rightarrow Cu^+ + H^+ + \text{products} \qquad (166)$$

$$R + Cu^+ \rightleftharpoons CuR^+ \qquad (167)$$

$$CuR^+ + H^+ \rightarrow \text{products} \qquad (168)$$

TABLE 12

Rate constants for the formation and decomposition of CuR^+

R	k_{167} ($dm^3\ mol^{-1}\ s^{-1}$)	k_{-167} (s^{-1})	k_{168} ($dm^3\ mol^{-1}\ s^{-1}$)
$\dot{C}H_2OH$	$1 \cdot 10^{10}$	10^6	—
$(CH_3)_2\dot{C}OH$	$6 \cdot 10^9$	$6 \cdot 10^4$	$3.2 \cdot 10^7$
$\dot{C}H_2C(CH_3)_2OH$	$2.6 \cdot 10^9$	—	—
$\dot{C}H_2CH_2OH$	$1.9 \cdot 10^{10}$	—	—

Data for these reactions are given in Table 12. The organic radicals react much more rapidly with Cu^+ than with Cu^{2+} (c.f. Table 11).

The CuR^+ complexes are very short-lived and may decay via reactions (169) and (170), e.g. for R = $(CH_3)_2\dot{C}OH$,

$$Cu{-}C(CH_3)_2OH^+ \rightarrow Cu^0 + (CH_3)_2C{=}O + H^+ \quad (169)$$

$$Cu{-}C(CH_3)_2OH^+ \xrightarrow{H^+} Cu^{2+} + (CH_3)_2CHOH \quad (170)$$

Of these the latter seems to be the more likely since the decay of CuR^+ in this case is accelerated by increasing $[H^+]$. Although some Cu^0 is produced in these systems it may arise from the disproportionation of Cu^+.

Reactions similar to (166)—(170) may be responsible for the enhanced disproportionation of hydroxymethyl radicals which is observed when Cu^{2+} is present in methanol under irradiation [214].

No metallic copper is formed when R is a β-hydroxyalkyl radical such as $\dot{C}H_2C(CH_3)_2OH$ or $\dot{C}H_2CH_2OH$ [213], and in the former case isobutene is a product, showing that reaction (171) occurs

$$Cu^+ + \dot{C}H_2C(CH_3)_2OH \rightarrow CH_2{=}C(CH_3)_2 + Cu^{2+} + OH^- \quad (171)$$

This reaction also occurs when the radical reacts with Cr^{2+} [49], Ni^+ [51] and Cd^+ [215] or is reduced polarographically [216].

(iii) Copper—oxygen systems

The chemistry of copper—oxygen systems is of considerable interest in relation to the catalytic activity of copper in oxidation—reduction processes, both chemical and biochemical. In recent years the investigation of the copper enzyme bovine superoxide dismutase (see Sect. K(ii)) has prompted pulse radiolysis studies of the reactions between copper ions and O_2^-, HO_2 and O_2. Rabani et al. [217] have shown that the catalytic effect of Cu^{2+} in enhancing the dismutation of O_2^- and HO_2 involves alternate reduction and oxidation in reactions (172) and (173)

$$Cu^{2+} + O_2^- \text{ (or } HO_2) \rightarrow Cu^+ + O_2\ (+H^+) \quad (172)$$

$$Cu^+ + O_2^- \text{ (or } HO_2) \xrightarrow{2\,H_2O} Cu^{2+} + H_2O_2 + 2\,OH^-\ (+H^+) \quad (173)$$

They obtained $k_{172} = 8 \cdot 10^9$ and $\sim 10^8$ dm^3 mol^{-1} s^{-1}, and $k_{173} \sim 10^{10}$ and $> 10^9$ dm^3 mol^{-1} s^{-1} for O_2^- and HO_2 respectively.

Rabani et al. [217] suggested that the complexes CuO_2^+ and CuO_2H^{2+} may be intermediates in reaction (172), depending on the pH, but that the lifetime of CuO_2^+ must be shorter than that of CuO_2H^{2+}. Subsequently, Meisel et al. [218] obtained evidence for equilibrium (174) followed by reaction (175) in 0.1 mol dm^{-3} $HClO_4$ solution.

$$Cu^{2+} + HO_2 \rightleftharpoons CuO_2H^{2+} \quad (174)$$

$$CuO_2H^{2+} \rightarrow Cu^+ + O_2 + H^+ \quad (175)$$

They reported $K_{174} = (5.1 \pm 1) \cdot 10^7$ dm^3 mol^{-1} and $k_{175} = 30 \pm 5$ s^{-1}, and pointed out that CuO_2H^{2+} might resemble complexes of Cu^+ with O_2 which have been suggested as intermediates in the oxidation of Cu^+ by O_2 [219–222].

In an investigation of the oxidation of (Cu—olefin)$^+$ complexes by O_2 Buxton et al. [209] found it necessary to invoke equilibrium (176), (177) and (174) to account for the observed kinetics, and they estimated $K_{176} \cdot K_{177} \geqslant 10^5$ dm^6 mol^{-2}.

$$Cu^+ + O_2 \rightleftharpoons CuO_2^+ \quad (176)$$

$$CuO_2^+ + H^+ \rightleftharpoons CuO_2H^{2+} \quad (177)$$

Although solutions of Cu^+ are sensitive to oxygen, the reaction of Cu^+ with O_2 is apparently relatively slow since Rabani et al. [217] observed an absorbing product of reaction (172) in the presence of O_2 which they attributed to Cu^+. It showed no decay in 400 μs, which means that equilibrium (176) lies well to the left, or that Cu^+ and CuO_2^+ have similar spectra.

(iv) Cu^{III}

Hydroxyl radicals oxidise Cu^{2+} to Cu^{III} [5]. Some early pulse radiolysis studies by Baxendale et al. [119] showed this species to have an absorption spectrum with $\lambda_{max} = 300$ nm, the intensity of which increased with increasing pH in the range 2—7. Subsequent studies [77,223,224] have confirmed these observations, but indicate the situation to be quite complex. Meyerstein [223] reported that the intensity of the absorption of Cu^{III}, and its decay are dependent on both pH and $[Cu^{2+}]$. This behaviour was suggested to arise because of the Cu^{III} acid—base equilibrium, and the reversibility of the OH + Cu^{2+} reaction. Evidence for the latter was also claimed from measurements of the reaction of Cu^{III} with Br^-, H_2O_2, CH_3OH etc., in acidic solutions, where it was found that the ratio of the rate constants was very similar to those for the reactions with OH, but the absolute rate constants were about a factor of 10 less.

Buxton and Sellers [224] investigated the $Cu^{III} + Br^-$ reaction in some detail, and from the dependence of the pseudo-first order decay of Cu^{III} on pH,

[Br^-] and [Cu^{2+}] found that the following mechanism agrees with the data most closely

$$Cu^{III} + Br^- \rightleftharpoons Cu^{III}Br \quad (178)$$

$$Cu^{III}Br \rightarrow Cu^{II} + Br \quad (179)$$

$$Br + Br^- \rightarrow Br_2^- \quad (180)$$

where reaction (179) is the rate determining step. Also the dependence of the spectrum of Cu^{III} on pH was found [77,224] to show two steps giving pK = 2.4 and >6, and all previous data [119,223] can be normalised within experimental error to a titration curve drawn using these values regardless of the [Cu^{2+}] used. Conductivity measurements [224,225] indicate that approximately 2 protons are formed in the reaction of OH with Cu^{2+} at pH ~ 5, so that acid-base equilibria can be written

$$CuOH^{2+} \rightleftharpoons Cu(OH)_2^+ + H^+ \qquad pK = 2.4 \quad (181)$$

$$Cu(OH)_2^+ \rightleftharpoons Cu(OH)_3 + H^+ \qquad pK \geqslant 6 \quad (182)$$

Copper(III) complexes with NH_3, ethylenediamine, and various amino acids have also been characterised by pulse radiolysis [226] (see also Sect. K(i)).

J. CADMIUM, COBALT, NICKEL AND ZINC

The monovalent states Cd^+, Co^+, Ni^+ and Zn^+ were among the first hyperreduced metal ions to be studied by radiation chemical methods in a series of experiments by Baxendale and co-workers [76,81,227]. Subsequent studies by others have tended to follow the pattern of comparing the properties of these monovalent metal ions, largely because they all absorb strongly in the near UV, which makes their reactions easy to follow by optical spectroscopy.

(i) Cd^+, Co^+, Ni^+ and Zn^+

Formation. The monovalent ions (M^+) are readily formed by reaction (1),

$$e_{aq}^- + M^{2+} \rightarrow M^+ \quad (1)$$

Rate constants are listed in Table 1. The radical ion CO_2^- reduces Cd^{2+}, Co^{2+} and Ni^{2+}, but not Zn^{2+}, by reaction (183) [36,38],

$$CO_2^- + M^{2+} \rightarrow M^+ + CO_2 \quad (183)$$

but only for Cd^{2+} is the reaction fast enough ($k_{183} \sim 10^5$ dm^3 mol^{-1} s^{-1}) [36] to be measured by pulse radiolysis. Other reducing radicals such as the hydrogen atom and simple hydroxyalkyl radicals do not react with any of the divalent ions.

Reaction (1) results in the formation of intense optical absorption bands in the near UV, as shown in Fig. 2, which have been assigned to the corre-

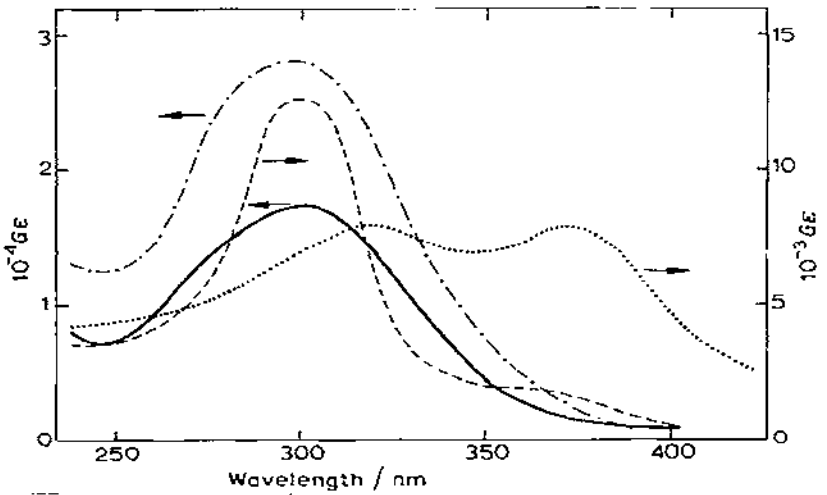


Fig. 2. The spectra of M^+. End of pulse spectra from the pulse radiolysis of deaerated 10^{-2} or 10^{-1} mol dm^{-3} M^{2+} solutions and corrected for absorption due to OH and H_2O_2. ·—·—, Cd^+; ·····, Co^+; - - - - -, Ni^+; ———, Zn^+. (From ref. 36. Reproduced by permission of the Chemical Society.)

sponding M^+ ions [36,76,81]. That the absorbing species carry unit positive charge has been demonstrated by ionic strength effects [22,228] and conductivity measurements [225]. Flash photolysis experiments have demonstrated [229] that the absorption bands are only partly due to a charge-transfer-to-solvent process. The long wavelength edge is mainly due to other transitions. This is particularly evident for Co^+ where the band at 370 nm (see Fig. 2) is not due to CTTS [229].

Absorption bands similar to those in Fig. 2 have been observed in γ-irradiated sulphuric acid glasses at 77 K and metaphosphate glasses at room temperature, which contained M^{2+} ions [110,230]. ESR studies of γ-irradiated glasses or single crystals containing M^{2+} reveal a single line spectrum in many cases [61,230,231], but for Cd^{2+} doped glasses and crystals Cd^+ and Cd_2^{3+} have been identified [232—234] from the hyperfine interactions of the isotopes ^{111}Cd and ^{113}Cd.

Reactivities. The redox potentials of the couples M^{2+}/M^+ have been estimated [235] (see Table 13) and they indicate that Cd^+, Co^+, Ni^+ and Zn^+ should be powerful reductants. In a systematic study of the reduction of inorganic substrates by M^+, Meyerstein and Mulac [228] found that the order of reactivity was generally $Zn^+ \geqslant Cd^+ > Ni^+$. They correlated this order with the electronic structure of M^+, pointing out that the extra electron is likely to be located in an exposed *s* orbital in Zn^+ and Cd^+, whereas in Ni^+ it may be in a less accessible 3*d* orbital. Subsequently, it has been shown [22] that Co^+ has the same reactivity as Zn^+ although its electronic structure is likely to be sim-

TABLE 13

Estimated values of the reduction potentials of M^{2+}/M^{+} couples

Redox couple	$-E^0$ (V)		
	a	b	c
Cd^{+}/Cd^{2+}	1.9—2.5	1.8 ± 0.4	~0.5
Co^{+}/Co^{2+}	3.1	—	
Ni^{+}/Ni^{2+}	2.7	0.7 ± 0.4	~0.7
Zn^{+}/Zn^{2+}	2.5—3.2	2.0 ± 0.4	~1.0

[a] Thermodynamic values [235]. [b] Calculated on the basis of the Marcus theory [48]. [c] Based on the Marcus theory [9].

ilar to that of Ni^{+}. The relative stability of the M^{+} oxidation state probably also influences its reactivity. That Zn^{+} is generally more reactive than Cd^{+} accords with the expected trend in stability of the +1 oxidation state of the group IIB metals. Typical rate constants of M^{+} with inorganic oxidants are listed in Table 14.

In an attempt to clarify the mechanism of reduction by M^{+}, Meyerstein and Mulac [236] measured the rates of reaction of Cd^{+}, Ni^{+}, Zn^{+} and e^{-}_{aq} with

TABLE 14

Specific rates of reaction of Cd^{+}, Co^{+}, Ni^{+} and Zn^{+} with some inorganic oxidants

Oxidant	$10^{-9}\,k$ (dm^3 mol^{-1} s^{-1})			
	Co^{+} [a]	Zn^{+} [b]	Cd^{+} [b]	Ni^{+} [b]
BrO_3^-	4.8	2.1	0.125	⩽0.0084
IO_3^-	4.3	3.6	2.3	0.22
NO_2^-	—	2.2	2.0	0.15
NO_3^-	1.8	2.1	0.35	⩽0.0014
$S_2O_8^{2-}$	2.8	1.3 [a]	2.4 [a]	0.15 [a]
CrO_4^{2-}	—	—	9.8 [a]	—
$Cr_2O_7^{2-}$	—	16 [a]	16 [a]	—
Cu^{2+}	0.41	0.25	0.12	⩽0.024
H_2O_2	1.6	1.8, 2.3 [a]	1.55, 2.2 [a]	0.043, 0.032 [a]
O_2	6.0	2.4	2.4, 3.6 [a]	1.4, 2.2 [a]
N_2O	1.0	0.013, 0.037 [a]	⩽0.002, 0.0035 [a]	⩽0.0063, 0.0091 [a]

[a] From ref. 22, ionic strength = 0.019 mol dm^{-3}. [b] From ref. 228, ionic strength ⩾0.08 mol dm^{-3}.

a series of complexes $Co^{III}(NH_3)_5X$ and $Co^{III}(en)_2YZ$, where X, Y and Z are typically NH_3, H_2O, halides or pseudo-halides. For the $Co^{III}(NH_3)_5X$ complexes the order of reactivity is $Zn^+ \geqslant Cd^+ > Ni^+$ (see Table 15) as above, but for the $Co^{III}(en)_2XY$ complexes the order is $Cd^+ \geqslant Zn^+ > Ni^+$, suggesting that the two series of complexes are reduced by different mechanisms. The effect of changing X, Y and Z was quite small for Cd^+ and Zn^+, but much larger for Ni^+, and it was concluded [236] that Zn^+ is mainly an outer-sphere reducing agent, Ni^+ is mainly inner-sphere, and Cd^+ reacts via both mechanisms.

In a similar study of $Ru(NH_3)_6^+$ [48] the rates of reaction of M^+ were found to be faster and more similar (see Table 15). Navon and Meyerstein [48] suggested that the difference is due to the transferred electron entering a t_{2g} orbital on Ru to form low spin Ru^{II}, whereas it enters an e_g orbital on Co, which involves a change from low spin Co^{III} to high spin Co^{II}. In addition, considerable reorganisation energy is involved because of the antibonding nature of the e_g orbitals.

On the assumption that the reactions of M^+ with Ru^{III} are outer-sphere, Navon and Meyerstein applied the Marcus theory [156,157] and estimated the reduction potentials of the M^{2+}/M^+ couples shown in Table 13. The values are to be compared with those estimated from thermodynamic data [235]. When the Marcus theory is applied to reaction (1), the reduction potentials obtained are quite different (see Table 13), probably because the theory is not applicable in this case. For example, e_{aq}^- may react by bridged transfer or by tunnelling [9].

Baxendale et al. [201] measured the rate of reaction of M^+ with M^{2+} in an attempt to place the redox potentials of M^{2+}/M^+ in order. They found that Zn^+ reacted with Cd^{2+}, Pb^{2+} and Ni^{2+}, Cd^+ reacted with Pb^{2+}, and that no mea-

TABLE 15

Specific rates of reaction of Cd^+, Ni^+ and Zn^+ with some transition metal complexes

Oxidant	$10^{-9}\ k$ (dm^3 mol^{-1} s^{-1}) [a]		
	Cd^+	Ni^+	Zn^+
$Ru(NH_3)_6^{3+}$	2.2 [b]	0.4 [b]	2.2 [b]
$Co(NH_3)_6^{3+}$	0.17	<0.005	0.84
$Co(NH_3)_5H_2O^{3+}$	0.62	<0.005	1.56
$Co(NH_3)_5OH^{2+}$	0.9	0.013	1.1
$Co(NH_3)_5Cl^{2+}$	2.2	0.65	2.2
cis-$Co(en)_2NH_3Cl^{2+}$	1.75	0.47	1.47
cis-$Co(en)_2Cl_2^+$	2.3	0.59	1.91

[a] From ref. 236. [b] From ref. 48.

surable reaction occurred in the case of Co^+ and Pb^+. On this basis they concluded that the reduction potentials of M^{2+}/M^+ are in the order $Zn^{2+}/Zn^+ > Cd^{2+}/Cd^+ > Pb^{2+}/Pb^+$ and $Zn^{2+}/Zn^+ > Ni^{2+}/Ni^+$. No reaction of Co^+ with these M^{2+} was observed [201]. Meyerstein and Mulac could not detect a reaction of Zn^+ with Cd^{2+} or Ni^{2+} in their experiments [228].

Rao and Hayon [237] claimed that the efficiency with which free radicals transfer an electron to acceptors is apparently related to the two electron redox potentials of the acceptors. They postulate a kinetic potential, $E_K^{0\prime}$, which is the redox potential of the acceptor for which 50% of the reaction is electron transfer, the remainder being assumed to be addition of the radicals to the acceptor. They have applied the same treatment to the reactions of M^+ with electron acceptors [203] and, on this basis, the values of $E_K^{0\prime}$ obtained are in the order $Zn^+ \sim Co^+ \sim Cd^+ > Pb^+ > Ni^+$. However, there is no reason why there should be any correlation between the rate of electron transfer to an acceptor and the acceptor's two-electron redox potential, and this should be borne in mind when extrapolating the correlation to predict the reactivities of M^+ with other acceptors.

Although many of the reactions of M^+ with oxidants probably involve simple electron transfer, in some instances other mechanisms operate. For example, Buxton et al. [22,38] showed that the following reactions occur

$$M^+ + N_2O \rightarrow MO^+ + N_2 \qquad (184)$$

$$M^+ + O_2 \rightarrow MO_2^+ \qquad (185)$$

$$M^+ + \text{olefin} \rightarrow (M\text{—olefin})^+ \qquad (186)$$

Reaction (184) is interesting since it involves O atom transfer and formation of the +3 oxidation state of the metal. This reaction, therefore, provides a way of obtaining this little known oxidation state of Cd, Ni and Zn in solution.

The properties of MO^+ have not been studied in any detail. They all absorb weakly in the UV and oxidise Br^- and I^- but not Cl^- [22]. Evidence from kinetic studies [38] of a radiation induced chain reaction between M^{2+} (Cd, Co, Ni), N_2O and HCO_2^- indicates that NiO^+ and CdO^+ react with water to form OH (reaction (187)), and the chain reaction mechanism is reaction (184) followed by

$$MO^+ + H_2O \rightarrow M^{2+} + OH + OH^- \qquad (187)$$

$$OH + HCO_2^- \rightarrow CO_2^- + H_2O \qquad (5)$$

$$CO_2^- + M^{2+} \rightarrow M^+ + CO_2 \qquad (183)$$

$$CO_2^- + MO^+ \rightarrow CO_2 + MO \qquad (188)$$

For Co reaction (187) does not occur. Instead, it appears from spectral changes that CoO^+ is converted to more stable Co^{III} species [22,38], which are undoubtedly hydrolysed and may be polynuclear.

Evidence for reaction (185) is based on (a) the difference between the ab-

sorption spectra and decay kinetics of MO_2^+ and the alternative product O_2^- (reaction (189)), and (b) the ability of O_2^- to transfer an electron to benzoquinone [238].

$$M^+ + O_2 \rightarrow M^{2+} + O_2^- \qquad (189)$$

Ni is the only case where it is certain that reaction (189) does not occur [22, 238]; and it has been suggested [238] that NiO_2^+ may be an inner-sphere complex. If so, water exchange by Ni^+_{aq} must be faster than $3 \cdot 10^5\ s^{-1}$ since NiO_2^+ is formed in less than 2 μs in oxygen saturated solution.

Investigation of the reaction of NiO_2^+ with tetranitromethane [238] revealed (a) that NiO_2^+ protonates ($pK = 3.2 \pm 0.3$), and (b) that the protonated and unprotonated forms decompose unimolecularly to give HO_2 and O_2^- respectively. The latter accords with the observation that the ultimate product of reaction (185) is H_2O_2 [22].

There is no evidence for the reverse of reaction (189) which occurs with Cu^{2+} (see Sect. I(ii)), which may be associated with the much slower water exchange by Ni^{2+}_{aq} ($k = 2.7 \cdot 10^4\ s^{-1}$) [239] compared to Cu^{2+}_{aq} ($k = 2 \cdot 10^8\ s^{-1}$) [239].

Reaction (186) is characterised by the formation of a long-lived ($t_{1/2} >> 10^{-4}$ s) absorbing product [22] which has been attributed to a 1 : 1 complex between M^+ and the olefin (allyl alcohol). Thus M^+ shows an interesting similarity to Cu^I and Ag^I which also form 1 : 1 complexes with olefins [207,240].

Reaction between M^+ and halogen substituted aliphatic acids has also been observed [189], and is exemplified by reaction (190). It is thought to involve halogen atom transfer to M^+ rather than dissociative electron transfer to the acid [189]. In this respect M^+ resembles H rather than e^-_{aq}. Co^+ and Zn^+ react rapidly with $ClCH_2CO_2^-$, whereas Cd^+ and Ni^+ do so slowly.

$$M^+ + BrCH_2CO_2^- \rightarrow M^{2+} + Br^- + \cdot CH_2CO_2^- \qquad (190)$$

Reactions of M^+ with free radicals. A number of studies have been made of the reactions of M^+ with inorganic and organic free radicals, and of the reaction of M^+ with itself. Such reactions occur when M^+ is generated by radiolysis of aqueous solutions containing no oxidising solutes. Under these conditions the major reactions of M^+ have been shown [36] to be reactions (191) and (192), with the former being approximately diffusion controlled and the

$$M^+ + OH \rightarrow M^{2+} + OH^- \qquad (191)$$

$$M^+ + M^+ \rightarrow M_2^{2+} \text{ or } M^0 + M^{2+} \qquad (192)$$

latter a good deal slower. When organic compounds (RH), such as simple aliphatic alcohols and formate ion, are present to scavenge OH (reaction (193)), the organic radical R in many cases reacts rapidly with M^+ and results

$$OH + RH \rightarrow R + H_2O \qquad (193)$$

in precipitation of the metal [36,51,115]. In fact, the yield of precipitated metal is generally only significant when R is present, suggesting that reaction (194) may be much more efficient than (192)

$$M^{+} + R \rightarrow M^{0} + \text{products} \qquad (194)$$

For Ni^{+} Kelm et al. [51] showed that reaction (194) proceeds via the formation of organonickel compounds, NiR^{+}, and they proposed that the reduction to Ni^{0} occurs through reactions (195) and/or (196) (for example when R is $(CH_3)_2\dot{C}OH$)

$$(CH_3)_2\dot{C}OH + NiC(CH_3)_2OH^{+} \rightarrow H^{+} + Ni^{0} + (CH_3)_2\dot{C}OH + (CH_3)_2CO \qquad (195)$$

$$Ni^{+} + NiC(CH_3)_2OH^{+} \rightarrow Ni^{2+} + Ni^{0} + (CH_3)_2\dot{C}OH \qquad (196)$$

They also found that NiR^{+} reacts with H_2O_2 and is slowly hydrolysed by water. Rate constants for these reactions are given in Table 16. Both reactions will occur more readily as the reducing power of R is increased, and the yields of Ni obtained [51] followed this trend.

In a similar study of Cd^{+}, Kelm et al. [215] found no correlation between the reducing power of R and the yield of Cd. In this case reaction (192) competes strongly with (194) and Cd_2^{2+} is formed as a precursor to Cd.

Reaction of Ni^{+} and Cd^{+} with the radical from *tert*-butanol results in oxidation of M^{+} and isobutene is formed,

$$M^{+} + (CH_3)_2C(\dot{C}H_2)OH \rightarrow M^{2+} + (CH_3)_2C{=}CH_2 + OH^{-} \qquad (197)$$

A similar reaction occurs with Cu^{+} (see Sect. I(ii)).

(ii) Formation and reactivity of complexes of M^{+}

M^{+} complexes are readily produced by radiolytic reduction of the corresponding M^{2+} complex, but relatively few have been studied.

Meyerstein and Mulac [241] investigated Cd^{II} complexed with glycine,

TABLE 16

Rate constants for reactions of Ni^{+} with R and of NiR^{+} [a]

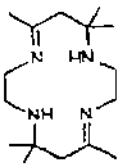
R	$k(Ni^{+} + R)$ ($dm^3\ mol^{-1}\ s^{-1}$)	$k(NiR^{+} + H_2O_2)$ ($dm^3\ mol^{-1}\ s^{-1}$)	$k(NiR^{+} + H_2O)$ (s^{-1})
$\cdot CH_2OH$	$4.2 \cdot 10^9$	$7.3 \cdot 10^3$	7
$CH_3\dot{C}HOH$	$2.3 \cdot 10^9$	$2.3 \cdot 10^3$	5
$(CH_3)_2\dot{C}OH$	$1.4 \cdot 10^9$	$1.1 \cdot 10^6$	<1
$C_2H_5O\dot{C}_2H_4$	—	$1.3 \cdot 10^3$	<1
CO_2^{-}	$6.6 \cdot 10^9$	—	<1
$c\text{-}\dot{C}_5H_9$	$2.8 \cdot 10^9$	$<5 \cdot 10^5$	49

[a] From ref. 51.

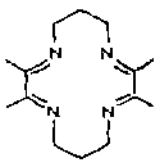
ethylene diamine, EDTA and nitrilotriacetic acid (NTA). Each complex is rapidly reduced by e^-_{aq} to produce species which all have similar absorption spectra with λ_{max} at 320—330 nm. These are assigned [241] to Cd^I complexes, but they are red shifted by about 25 nm from λ_{max} for Cd^+_{aq}, suggesting that the long wavelength side of the Cd^+_{aq} spectrum is not due to a CTTS transition [229] as noted above in section (i).

The Cd^I complexes react rapidly with oxidants and the effects of ligands are relatively small (see Table 17), which implies that the mechanism is generally the same. An exception is the reaction between Cd^I and NO_2^- which is the most strongly affected by changing the ligand. It was suggested [241] that when NO_2^- reacts with Cd^+_{aq} it penetrates the inner co-ordination sphere of the metal, whereas reaction with Cd^I—EDTA proceeds via an outer-sphere mechanism.

Of particular interest are cobalt complexes containing macrocyclic or tetradentate ligands because they can serve as models for the reactions of vitamin B12 in biochemical processes [242]. Co^{II} complexes containing macrocyclic ligands such as the following are rapidly reduced by e^-_{aq} ($k \sim 5 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1}) to the corresponding Co^I species [243]. The latter are powerful reducing agents, transferring an electron rapidly to a variety of organic and inorganic acceptors [243] (see Table 18). They also react rapidly with N_2O and O_2, but



$Me_6[14]4,11$-diene N_4



$Me_4[14]1,3,8,10$-tetraene N_4

TABLE 17

Specific rates of reaction of some Cd^I complexes with inorganic oxidants [a]

Matrix [b]	pH	μ [c]	10^{-8} k (dm^3 mol^{-1} s^{-1})			
			BrO_3^-	IO_3^-	NO_2^-	NO_3^-
0.02 $CdSO_4$	4.5	0.08	1.25	23	20	3.5
0.01 $CdSO_4$ 0.2 $enSO_4$	11.4	0.64	1.28	25	11.2	4.5
0.01 $CdSO_4$ 0.2 glycine	10.5	0.21	0.61	18	8.5	2.4
0.01 $CdSO_4$ 0.02 NTA	10.7	0.1	0.10	6.1	0.42	0.45
0.01 $CdSO_4$ 0.02 EDTA	11.3	0.16	0.089	2.7	0.032	0.166

[a] From ref. 241. [b] Concentrations in mol dm^{-3}. [c] Ionic strength.

TABLE 18

Rate constants for reaction of macrocyclic complexes of Co^I with oxidants [a]

Oxidant	k ($dm^3\ mol^{-1}\ s^{-1}$)	
	Co^I(4,11-diene N_4) pH = 9.2	Co^I(1,3,8,10-tetraene N_4) pH = 6.5
Organic [b]		
Menaquinone	$4.6 \cdot 10^9$	—
Indigosulphonate	—	$4.9 \cdot 10^9$
9,10-Anthraquinone-2,6-disulphonate	—	$3.8 \cdot 10^9$
Riboflavin	—	$1.0 \cdot 10^9$
9,10-Anthraquinone-2-sulphonate	$4.4 \cdot 10^9$	—
Fluorenone	$4.3 \cdot 10^9$	—
3-Benzoylpyridine	$4.6 \cdot 10^8$	—
Metal complexes [c]		
$Cr(bpy)_3^{3+}$	$1.2 \cdot 10^9$	$1.6 \cdot 10^8$
$Co(bpy)_3^{3+}$	$1.2 \cdot 10^9$	$8.5 \cdot 10^7$
$Fe(bpy)_3^{3+}$	$2.3 \cdot 10^7$	—
$Ru(NH_3)_6^{3+}$	$4.0 \cdot 10^8$	—
$Ru(NH_3)_5NO^{3+}$	$3.9 \cdot 10^7$	—
$Co(en)_3^{3+}$	$7.9 \cdot 10^6$	—
$Co(NH_3)_6^{3+}$	$7.5 \cdot 10^6$	—
[Co(4,11-diene N_4)$(OH)_2$]$^+$	$4.0 \cdot 10^6$	—
[Co(1,3,8,10-tetraene N_4)$(OH)_2$]$^+$	$6.7 \cdot 10^6$	—
Others		
O_2	$1.7 \cdot 10^9$	$1.1 \cdot 10^9$
N_2O	$3.9 \cdot 10^7$	—
CH_3I	$4.7 \cdot 10^8$	$<10^5$

[a] From ref. 243. [b] Ionic strength = 0.004 mol dm^{-3}. [c] Ionic strength = 0.016—0.028 and 0.002 mol dm^{-3} for diene and tetraene compounds respectively.

the spectra of the original Co^{II} species are not regenerated [243], which suggests that reactions corresponding to (184) and (185) occur.

Pratt and co-workers [244] showed that a number of relatively stable Co^I complexes and vitamin B12s react rapidly with N_2O with the overall stoichiometry of reactions (198) and (199). This provides another indication of the occurrence of reaction (184) for Co^I complexes.

$$Co^I + N_2O \rightarrow Co^{III} + N_2 \qquad (198)$$

$$Co^I + Co^{III} \rightarrow 2\ Co^{II} \qquad (199)$$

Reduction of $Ni(CN)_4^{2-}$ to $Ni_2(CN)_6^{4-}$ by CO_2^- has been studied [47] and the observations are consistent with the following mechanism

$$CO_2^- + Ni(CN)_4^{2-} \rightarrow Ni(CN)_4^{3-} + CO_2 \quad (200)$$

$$Ni(CN)_4^{3-} \rightarrow Ni(CN)_3^{2-} + CN^- \quad (201)$$

$$2\ Ni(CN)_3^{2-} \rightarrow Ni_2(CN)_6^{4-} \quad (202)$$

Reaction (200) ($k_{200} = 1.2 \cdot 10^9$ dm^3 mol^{-1} s^{-1}) is very much faster than the corresponding reaction of Ni^{2+} for which $10^2 < k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} < 10^5$ has been estimated [36], and probably reflects the greater ease with which CO_2^- can approach the metal centre in the square planar $Ni(CN)_4^{2-}$. The intermediate $Ni(CN)_4^{3-}$ absorbs with λ_{max} at 360 nm and $\epsilon_{max} = 4.8 \cdot 10^3$ dm^3 mol^{-1} cm^{-1} [47]; $k_{201} = 8.1 \cdot 10^3$ s^{-1} and $2k_{202} = 1.5 \cdot 10^8$ dm^3 mol^{-1} s^{-1}.

Hydrogen atoms also reduce $Ni(CN)_4^{2-}$ rapidly with $k_{203} = 1.7 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1} [47]. As with CO_2^-, this is in marked contrast to the unreactivity of H towards Ni^{2+}.

$$H + Ni(CN)_4^{2-} \rightarrow H\ Ni(CN)_4^{2-} \quad (203)$$

(iii) Formation of Ni^{III} complexes

There is no evidence for the oxidation of Ni^{2+} by OH [36], but reaction does occur with Ni^{II} complexes although only a few have been investigated (see Sect. K(i)). Reaction of OH with $Ni(CN)_4^{2-}$ produces an absorbing species with λ_{max} at 250 and 270 nm having $\epsilon_{1250} = 9.5 \cdot 10^3$ and $\epsilon_{270} = 1.25 \cdot 10^4$ mol dm^{-3} cm^{-1} [47]. The reaction is written as (204) and $k_{204} = 9.1 \cdot 10^9$ dm^3 mol^{-1} s^{-1}.

$$OH + Ni(CN)_4^{2-} \rightarrow Ni(CN)_4^- + OH^- \quad (204)$$

Oxidation of Ni^{II} complexed with NH_3, ethylene diamine and glycine has also been studied [245,246]. NH_2 was the oxidant for the NH_3 complex and OH was the oxidant of the others. In all cases the oxidation products have similar spectra with $\lambda_{max} \sim 295$ nm and $\epsilon_{max} \sim 1300$ dm^3 mol^{-1} cm^{-1}, and on this basis are attributed to Ni^{III} complexes [245,246]. They decay by a second-order process which is pH dependent.

K. METAL COMPLEXES

(i) Coordinated free radicals and intramolecular electron transfer reactions

Electron transfer reactions involving metal complexes may involve direct reduction of the metal centre, or electron attachment to a ligand followed by a slower, intramolecular electron transfer to the metal. Reactions of the latter type have been postulated in a number of conventional kinetic studies [247], particularly where one of the ligands contains a system of conjugated double

bonds. Where the reactant is a radiolytically generated radical such as e^-_{aq} or OH, coordinated free radicals are produced. A number of these have been characterised by pulse radiolysis.

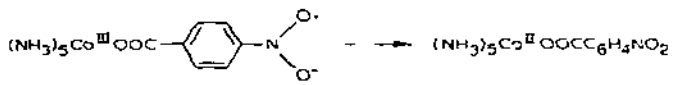
Reactions of e^-_{aq} and other reducing species. $Co(bipy)_3^{3+}$ is a low spin complex which on reaction with the hydrated electron yields as the final product high spin ($t_{2g}^5 e_g^2$) $Co(bipy)_3^{2+}$. An absorbing intermediate has been detected in this system, whose identity has been the subject of some difference of opinion. Waltz and Pearson [14] detected a weak absorber at $\lambda > 400$ nm, which reacted with such additives as O_2, Na_2SO_4, $MgSO_4$, $BaCl_2$ and the original complex, $Co(bipy)_3^{3+}$ itself. Since these additives are known quenchers of excited states, it was concluded [14] that the transient absorption was due to low spin ($t_{2g}^6 e_g$) $Co(bipy)_3^{2+}$. Baxendale and Fiti [16] reinvestigated this work, and, with the exception of the reaction of the intermediate with Na_2SO_4, $MgSO_4$ and $BaCl_2$ where only a slight salt effect was detected, were able to duplicate all of Waltz and Pearson's results, including seeing absorption at $\lambda > 400$ nm and reactivity with $Co(bipy)_3^{3+}$ for which $k = 8 \cdot 10^8$ dm^3 mol^{-1} s^{-1} was measured. Similar results were found with $Ru(bipy)_3^{2+}$ and $Cr(terpy)_2^{3+}$ [16]. They suggested [16], however, that the results were consistent with the intermediates being radical anions coordinated to the metal produced by electron attachment to one of the ligands. No explanation was given for the reaction of the intermediate with the starting material, but it was concluded that formation of the stable products (Co^{II} etc.) did not occur by simple internal electron transfer from ligand to metal.

Hoffman and Simic [17] also investigated this problem using $Co(bipy)_3^{3+}$ and $Cr(bipy)_3^{3+}$. With the Co^{III} complex they detected an intermediate with an intense absorption ($\lambda_{max} = 300$ nm, $\epsilon_{max} = 4.2 \cdot 10^4$ dm^3 mol^{-1} cm^{-1}) following reduction by e^-_{aq}, CO_2^- and $(CH_3)_2\dot{C}OH$. The intermediate decayed by first order kinetics which were independent of pH (0.5—10.5) and the concentration of the parent complex ($1—5 \cdot 10^{-5}$ mol dm^{-3}) and showed no reactivity with 1,4-benzoquinone. Very similar results were found with $Cr(bipy)_3^{3+}$. This behaviour is to be compared with that of the radical formed by electron attachment to the free bipyridyl ligand which absorbs with λ_{max} 365 nm, $\epsilon_{max} = 3.0 \cdot 10^4$ dm^3 mol^{-1} cm^{-1} at pH 9.5 (unprotonated form), reacts rapidly with 1,4-benzoquinone, and decays by pH dependent second order kinetics [17]. It was concluded [17] from these observations that the 300 nm absorption was completely unrelated to that detected by the earlier workers. The 300 nm absorption was attributed to the reduction of the complex by addition of an electron to a ligand orbital which, although similar to that formed by reduction of the free ligand (e.g. intense UV absorption), is perturbed by interaction with the metal centre causing a blue-shift in the spectrum and lack of reactivity with the quinone. The slow first order process was assigned to intramolecular electron transfer to the metal centre, whilst the earlier results of Waltz and Pearson [14], and Baxendale and Fiti [16] were thought [17] to be due to species formed in the reaction of e^-_{aq} with

impurities or the reaction of H atoms with the complexes.

The reaction of CO_2^- or $(CH_3)_2\dot{C}OH$ with *p*-nitrobenzoatopentaamminecobalt(III) provides a more direct demonstration of electron attachment to the ligand [248]. Pulse radiolysis of aqueous solutions of this complex containing formate ion or isopropanol yields a transient absorbing at λ_{max} = 330 nm, $\epsilon_{max} = 2.1 \cdot 10^4$ dm^3 mol^{-1} cm^{-1} [248]. Irradiation of the free *p*-nitrobenzoate ligand produces an almost identical absorption, and in this species the electron is predominantly associated with the nitro group. It is reasonable, therefore, to suppose that in the intermediate produced by electron reduction of the Co^{III} complex the electron is also associated with the nitro group (reaction (205)). This intermediate decays by a first-order reaction, due to intramolecular electron transfer reaction (206), giving ultimately Co^{2+} with G = 6.3 ± 0.3 in solutions containing formate ion [248].

(205)



(206)

A similar set of results has been obtained with the *ortho*- and *meta*-nitrobenzoate Co^{III} [249].

In very acidic solutions, where the radical anions are protonated (the acid dissociation constants of the radicals formed from the free ligands have values in the range 2—4 [250]), the decay is different from that in near neutral solutions. The *meta*- and *para*-nitro derivatives both decay by second-order processes [249], presumably involving electron transfer to give equimolecular amounts of the nitro and (after water elimination)nitroso benzoate complexes. The *ortho*-nitro substituted derivative, however, undergoes intramolecular electron transfer as in neutral solutions [249], the differences probably arising through steric effects.

When reduction is effected by e_{aq}^- rather than CO_2^- or $(CH_3)_2\dot{C}OH$ somewhat different behaviour results. With *p*-nitrobenzoate only some 70% of e_{aq}^- react with the ligand (reaction (207b)), the other 30% reducing the cobalt centre directly (reaction (207a)). This has been confirmed both by optical [251] and conductivity [252] measurements.

$$e_{aq}^- + Co^{III}(NH_3)_5O_2CC_6H_4NO_2 \rightarrow Co^{II}(NH_3)_5O_2CC_6H_4NO_2 \quad (207a)$$

$$e_{aq}^- + Co^{III}(NH_3)_5O_2CC_6H_4NO_2 \rightarrow Co^{III}(NH_3)_5O_2CC_6H_4NO_2^- \quad (207b)$$

No such coordinated radical intermediate has been detected following electron reduction of benzoatopentaamminecobalt(III). If electron attack at the

benzoate ligand does occur, this implies a very rapid ($k > 10^7\ s^{-1}$) intramolecular electron transfer to the cobalt. This, it is suggested [248], is because the electron enters a π orbital conjugated throughout the ligand, such that overlap with the metal orbitals at the carboxylate group provides a facile path for the electron transfer.

An attempt has been made to assess the significance of the carboxylate group in these reactions by studying the kinetics of electron transfer from the *p*-nitrobenzoate radical anion to a series of pentaamminecobalt(III) complexes, $[(NH_3)_5CoL^{3+}]$ [253]. By considering the reaction to occur in two steps, reactions (208) and (209), involving the formation of an outer sphere complex, Cohen and Meyerstein [253] concluded that the intermolecular electron transfer rate (reaction (209)) for the ligands studied was similar to that for the intramolecular reaction (206). Indeed for L = NH_3, $C_6H_5CO_2^-$ and *p*-NO_2-$C_6H_4CO_2^-$ k_{209} was greater than k_{206}, and it was suggested that this was due to the poor "electron permeability" of the carboxylate group [253].

$$Co^{III}(NH_3)_5L + {}^-O_2CC_6H_4\dot{N}O_2^- \rightleftharpoons [Co^{III}(NH_3)_5L \cdot {}^-O_2CC^6H_4\dot{N}O_2^-] \qquad (208)$$

$$[Co^{III}(NH_3)_5L \cdot {}^-O_2CC_6H_4\dot{N}O_2^-] \rightarrow Co^{2+} + 5\ NH_3 + L + p\text{-}NO_2C_6H_4CO_2^- \qquad (209)$$

The reaction of the hydrated electron with the nitroprusside ion produces an intermediate which has acid–base properties and absorbs with $\lambda_{max} = 425$ nm [19]. Originally this was thought to be associated with some Fe^{II} species, but as noted in Sect. A(iii) Hart and Anbar [7] attributed it to a long-lived excited state. It seems likely, particularly in view of the foregoing, that some of the electrons reduce the NO ligand rather than the metal centre, and that subsequently there is an intramolecular electron transfer. An intermediate in which the unpaired electron resides in a π^* orbital on the NO ligand has been detected in γ-irradiated solid sodium nitroprusside [254,255]. The one electron reduction of the $Ru(NH_3)_5NO^{3+}$ complex, on the other hand, produces an intermediate (λ_{max} = 280 and 360 nm) which does not exhibit acid–base properties [256]. There does seem to be some unpaired electron density associated with the NO ligand, however, since the reduced form of the complex reacts with the *t*-butanol radical ($k = 3.7 \cdot 10^9\ dm^3\ mol^{-1}\ s^{-1}$) [257]. The product is a stable ruthenium(II) alkylnitroso complex, $[Ru(NH_3)_5N(O)CH_2C(CH_3)_2OH]^{2+}$ [257].

Degradation of one of the ligands occurs in the reaction of e_{aq}^- with bis-(glycinato)copper(II) [258]. The mechanism of the reaction is unknown, and its elucidation must await pulse radiolysis studies, but on the basis of the yields of products [258] formed the stoichiometry of the reaction is

$$e_{aq}^- + Cu^{II}(NH_2CH_2CO_2^-)_2 + H_2O \rightarrow Cu^{II}(NH_3)(NH_2CH_2CO_2^-) + \dot{C}H_2CO_2^- + OH^- \qquad (210)$$

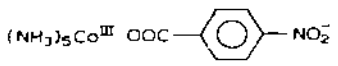
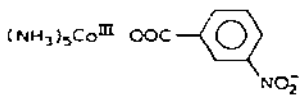
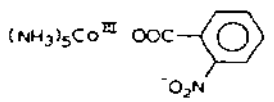
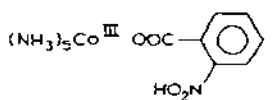
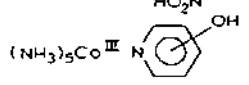
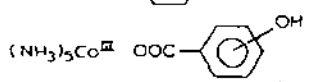
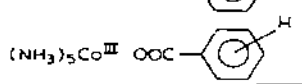
Deamination also occurs in the reaction of e_{aq}^- with the free ligand [258]. However, neither free ethylene diamine nor its Cu^{II} complex show any deam-

ination on reaction with e^-_{aq} [259]. Rate constants for some intramolecular electron transfer reactions are shown in Table 19.

Reactions of OH and H. Coordinated free radicals may also be produced by hydroxyl radicals and hydrogen atoms. A typical example, and one of the first of this type of species to be described, is the intermediate produced by OH addition to the aromatic ring of benzoatopentaamminecobalt(III) [260, 261]. This has been found to absorb with λ_{max} = 340 nm, ϵ_{max} = 3700 dm^3 mol^{-1} cm^{-1}, which is similar, but not identical, to the OH adduct of the benzoate ion [260,261]. The intermediate decayed by second-order kinetics, and it was suggested that the intramolecular electron transfer reaction did not occur under the conditions employed. In support of this view, it was found that at high dose rates only small amounts of Co^{2+} were formed as the stable product (probably arising from a small fraction of the hydrated electrons scavenged by the complex), together with some other material absorbing at ca. 290 nm [261]. Under low dose rate conditions however, $G(Co^{2+})$ = 1.6 was determined in N_2O saturated solutions, suggesting that intramolecular electron transfer may occur under favourable circumstances. Very similar re-

TABLE 19

Rate constants for intramolecular electron transfer reactions

Intermediate	k_{obs} (s^{-1})	Ref.
$Co^{III}(bipy)_2(bipy^-)$	3.5	17
$Cr^{III}(bipy)_2(bipy^-)$	3.5	17
	$2.6 \cdot 10^3$	248
	150	249
	$4.0 \cdot 10^5$	249
	$9.5 \cdot 10^3$	249
	6.0	27
	$<10^2$	261
	$<10^2$	261

sults were obtained with the hydrogen atom adduct. The intramolecular electron transfer reaction has been observed in the species formed by OH addition to pyridine pentaamminecobalt(III), and is slow (see Table 19) [27].

Ligands having abstractable hydrogens may also react with the hydroxyl radical etc. to give coordinated radicals. No such species have been characterised by pulse radiolysis, but their formation can be inferred from the yields of the products formed after steady state radiolysis. The γ- or X-irradiation of the EDTA complexes of Co^{III} [262, Cu^{II} [263] and Fe^{III} [264] gives the G(—complex) values shown in Table 20. These can be equated with the primary yields shown, * and clearly indicate that OH attack brings about reduction. Hydrogen abstraction (reaction (211)) followed by intramolecular electron transfer (reaction (212)) is the most obvious path by which this can occur. Another possibility, which seems unlikely for EDTA complexes, but may be important for more labile complexes, is that the radical ligand becomes detached from the metal (reaction (213)), and reduces another metal complex (reaction (214)). In aerated solutions reaction (212) is probably prevented by oxygen addition to give a peroxy radical (reaction (215)).

$$[MRCH_2R']^{n+} + OH \rightarrow [MR\dot{C}HR']^{n+} + H_2O \quad (211)$$

$$[MR\dot{C}HR']^{n+} \rightarrow [MRCR']^{(n-1)+} + H^+ \quad (212)$$

$$[MR\dot{C}HR']^{n+} \rightarrow M^{n+} + R\dot{C}HR' \quad (213)$$

$$[MRCH_2R']^{n+} + R\dot{C}HR' \rightarrow [MRCH_2R']^{(n-1)+} + RCR' + H^+ \quad (214)$$

$$[MR\dot{C}HR']^{n+} + O_2 \rightarrow [MRCH\dot{O}_2R']^{n+} \quad (215)$$

The intramolecular electron transfer apparently does not occur with Ni^{II}-EDTA, since in deaerated solutions of this complex G(—complex) is only $\frac{1}{2}G_{OH}$ (see Table 20). Bhattacharyya and Kundu [265] interpreted this as being due to reaction (211) followed by the disproportionation reaction (216). A mechanism not considered consists of reactions (211) and (212) (or production of a Ni^{I} complex by electron reduction) followed by the repair reaction (217). The reaction of the Ni^{+} aquo ion with radicals is well established [51] (see Sect. J(ii)).

$$[MR\dot{C}HR']^{n+} + [MR\dot{C}HR']^{n+} \rightarrow [MRCH_2R']^{n+} + [MRCR']^{n+} \quad (216)$$

$$[MR\dot{C}HR']^{n+} + [MRCH_2R']^{(n-1)+} \xrightarrow{H^+} 2[MRCH_2R']^{n+} \quad (217)$$

The reaction of OH with Ni^{II}EDTA has also been studied pulse radiolytically by Lati and Meyerstein [267], and they have found evidence for the formation of a relatively long-lived Ni^{III}EDTA complex as the product [267, 268]. They suggest that OH does not react with the ligand, but oxidises the

* The average energy of the X-rays in Bhattacharyya and Kundu's experiments was 27 KeV [263—266]. The primary yields under these conditions are approximately given by

$$3.8\ H_2O \rightsquigarrow 2.0\ e^-_{aq} + 2.00\ H + 0.6\ H + 0.9\ H_2O_2 + 0.6\ H_2 + 2.0\ H^+$$

TABLE 20

Destruction yields in the radiolysis of metal—EDTA solutions

Metal	pH	G(−complex)			Type of radiation	Ref.
		Deaerated solutions	Aerated solutions	N_2O saturated solutions		
Co^{III}	0.4	5.0 $G_{OH} + G_H$	2.5 G_{OH}	—	γ	262
Cu^{II}	6–7	2.0 G_{OH}	2.0 G_{OH}	4.6 $G_{OH} + G_{e^-_{aq}}$	X	263
Fe^{III}	1	5.85 $G_{OH} + G_H$	3.5 $G_{OH} + G_{H_2O_2}$	—	X	264
Ni^{II}	~7	1.2 $\frac{1}{2}G_{OH}$	2.1 G_{OH}	—	X	265
No metal	0.4	4.0 $\frac{1}{2}(G_{OH} + G_H)$	3.6 $\frac{1}{2}(G_{OH} + G_H)$	—	γ	262
No metal	6.1	1.7 $\sim\frac{1}{2}(G_{OH} + G_{H_2O_2})$	1.9 G_{OH}	—	X	266

metal centre directly to the trivalent state. The rate constant for the reaction of OH with the hexaquo Ni^{II} ion is $<5 \cdot 10^5$ dm^3 mol^{-1} s^{-1} [36]. It is perhaps noteworthy that all Lati and Meyerstein's [267,268] experiments were carried out in N_2O saturated solutions, and it seems possible that the pathway for Ni^{III} production involves a Ni^{I} species, formed either by reactions (211) and (212) or by electron reduction of the Ni^{II} complex, and which is oxidised in a two electron process by N_2O (218). Further experiments are required to distinguish between these suggested pathways.

$$Ni^{I}L + N_2O \xrightarrow{2H^+} Ni^{III}L + N_2 + H_2O \qquad (218)$$

The reaction of OH with the ethylene diamine complexes of Cu^{II}, Ni^{II}, Pb^{II} and Pt^{II} brings about deamination of the ligands [259]. It seems that the metal ions have little or no influence on the reaction since the free ligand is also deaminated following OH attack [259], and it is possible that the radical ligand dissociates from the complex before rearranging.

Coordinated radicals have also been detected following flash photolysis of trisoxalato cobalt(III) [269].

(ii) Metallo-proteins and related compounds

A number of studies have been made of the radiation chemistry of some metal containing compounds of biological importance. The mode of interaction of the primary radiolytic species with these compounds has many features in common with the simpler complexes described in the previous section, such as electron or radical attack at the ligand, followed by an intramolecular electron transfer to the metal centre. However the situation is more complex, in part because of the multiplicity of sites at which the radicals can attack, and also because these reactions may bring about conformational changes. In this section we describe briefly some of the more important observations.

Cu: superoxide dismutase and related systems. The Cu^{2+} aquo ion, copper(II) complexes with ligands such as formate, ammonia and amino acids, and the copper containing enzyme superoxide dismutase all catalyse the dismutation of O_2^-, as has been demonstrated by pulse radiolysis [217,270—272]. The rates of reaction of O_2^- with Cu^{II} species are summarised in Table 21. For the simple complexes increasing the number of ligands produces a progressive * decrease in rate constant, whilst for the amino acid complexes the rate constants for reaction with O_2^- are 2—3 orders of magnitude below those of the aquo ion

The reaction of O_2^- with bovine superoxide dismutase has been studied in detail by Klug-Roth et al. [273] and by Fielden et al. [274]. The enzyme contains two atoms each of copper and zinc, and the former are involved in

* The apparent anomalies observed when formate is the ligand disappear after correction of the rate constants to zero ionic strength.

TABLE 21

Rate constants for the reaction of O_2^- with copper complexes and enzymes

Cu species [a]	k ($dm^3\ mol^{-1}\ s^{-1}$) [b]	Conditions	Ref.
Cu^{2+}	$8 \cdot 10^9$	pH ~6	217
Cu^{2+}	$1.9 \cdot 10^9$	I = 2 mol dm^{-3}	271
Cu^{2+}	$2.7 \cdot 10^9$	pH 7.8	270
Cu^{2+} (+ HO_2)	$1 \cdot 10^8$	pH ~2	217
$Cu(HCO_2)^+$	$1.7 \cdot 10^9$	I = 2 mol dm^{-3}	271
$Cu(HCO_2)_2$	$3.0 \cdot 10^8$	I = 2 mol dm^{-3}	271
$Cu(HCO_2)_3$	$8.0 \cdot 10^8$	I = 2 mol dm^{-3}	271
$Cu(HCO_2)_4^{2-}$	$4.0 \cdot 10^8$	I = 2 mol dm^{-3}	271
$Cu(NH_3)^{2+}$	$2.2 \cdot 10^9$	pH 7.0—8.5	271
$Cu(NH_3)_2^{2+}$	$2.2 \cdot 10^9$	pH 7.0—8.5	271
$Cu(NH_3)_3^{2+}$	$1.0 \cdot 10^9$	pH 7.0—8.5	271
$Cu(NH_3)_4^{2+}$	ca. $2 \cdot 10^8$	pH 7.0—8.5	271
$CuEDTA^{2-}$	no reaction detected		
Cu^{II}(glycine)$_2$	$2.1 \cdot 10^6$	pH 7.9	271
Cu^{II}(glycyl glycine)$_2$	$2.0 \cdot 10^7$	pH 6.7	271
Cu^{II}(glycylhistidine)$_2$	$2.9 \cdot 10^8$	pH 7.8	270
Cu^{II}(glycyl histylleucine)$_2$	$2.1 \cdot 10^8$	pH 7.8	270
Cu^{II}(lysine)$_2$	$5.6 \cdot 10^8$	pH 7.8	270
Cu^{II}(hydroxy proline)$_2$	$1.0 \cdot 10^6$	pH 8.1	271
Cu^{II}(proline)$_2$	$5 \cdot 10^5$	pH 7.5	271
Erythrocuprein	$1.3 \cdot 10^9$	pH 7.8	270
Hemocyanine	$<10^6$	pH 8.0	271
Plastocyanine	$<10^6$	pH 8.0	271
Superoxide dismutase	$2.3 \cdot 10^9$	pH 4.8—9.5	272
Bovine superoxide dismutase	$1.2 \cdot 10^9$	in the presence of $9.1 \cdot 10^{-8}$ mol dm^{-3} of catalase	274
	$2.4 \cdot 10^9$	pH 9.0—9.5	274

[a] Reaction with O_2^- unless otherwise stated. [b] T = 23 ± 2° C in all cases.

the functioning of the enzyme. In its native form the enzyme contains two Cu^{2+} ions which can both be reduced to Cu^+ by H_2O_2 [275].

The mechanism by which the enzyme functions involves alternate reduc-

tion and oxidation of copper in reactions (219) and (220)

$$E{-}Cu^{2+} + O_2^- \rightarrow E{-}Cu^{+} + O_2 \qquad (219)$$

$$E{-}Cu^{+} + O_2^- \xrightarrow{2\,H^+} E{-}Cu^{2+} + H_2O_2 \qquad (220)$$

The rates of these processes are the same ($k = 2.4 \cdot 10^9$ dm^3 mol^{-1} s^{-1} [274]) as is the catalytic efficiency of the native and fully reduced forms of the enzyme [274]. Klug-Roth et al. [273] reported the fully reduced form to be less active than the native enzyme, but it is likely that the reduced form was partially inactivated under their experimental conditions [274].

Although the two Cu^{2+} ions in native superoxide dismutase are indistinguishable, ESR and pulse radiolysis studies reveal that only one copper is involved in the catalytic action. This is true both for the native enzyme (2 Cu^{2+}) and for the fully reduced enzyme (2 Cu^{+}). Fielden et al. [274] proposed that reduction of one Cu^{2+} or oxidation of one Cu^{+} renders the second copper ion transiently unreactive towards O_2^-. The mechanism of this inactivation is unknown, but Fielden et al. [274] favour conformational changes. These would have to be different for the native and fully reduced enzymes and very rapid [274] ($k > 10^6$ s^{-1}).

It is noteworthy that catalysis of the dismutation of O_2^- by free Cu^{2+} [247] is a factor of four faster than by superoxide dismutase. This is a unique situation in which a simple chemical model of the enzymic reaction is more efficient than the enzymic reaction itself. On the other hand, Cu^{2+} complexes such as those listed in Table 21 are much less efficient catalysts [271]. This may be connected with changes in the redox potential of the Cu^{II}, and the possibility that, in some cases, catalytic action involves reactions (221) and (222) cannot yet be ruled out [271].

$$O_2^- + Cu^{II} \xrightarrow{2\,H^+} H_2O_2 + Cu^{III} \qquad (221)$$

$$O_2^- + Cu^{III} \rightarrow O_2 + Cu^{II} \qquad (222)$$

Although these reactions are written as simple electron transfer processes, formation of copper—oxygen intermediates cannot be excluded (see Sect. I(iii)).

The radiation induced inactivation of superoxide dismutase has also been studied [276]. With Br_2^- radicals the effect is negligible at pH 7, but increases sharply above pH 10. This is thought [276] to be because at the lower pH's the copper protects essential histidine residues from damaging reactions with Br_2^-, and hence that strong copper—histidine interactions are necessary for enzymatic activity.

Cu—hemocyanine. The radiation-induced inactivation of hemocyanine has been studied by Schubert and Ke [277]. They found that the inactivation in neutral deoxygenated solutions which is brought about by the oxidation of the Cu^{I} centre to Cu^{II}, can be reversed by irradiating in the presence of an OH

scavenger such as formate, again in deoxygenated solutions. The regenerated metallo—enzyme appeared to be identical with the starting material. These observations are interesting in that they imply a high degree of specificity in the attack of OH, e^-_{aq} and CO_2^- on the protein.

Both hemocyanine and plastocyanine show no catalysis of O_2^- dismutation in pulse radiolysis experiments [271], indicating that k_{219} and $k_{220} < 10^6$ dm^3 mol^{-1} s^{-1}.

Fe—cytochrome c. A number of studies have been made of the radiation chemistry of ferricytochrome *c* ($Fe^{III}E$). Early γ-radiolysis studies showed that reduction occurs to give a species identical with the enzymatically reduced compound [278]. Some variation in the yield of the ferrocytochrome *c* ($Fe^{II}E$) formed is evident [279—281], but yields as high as ca. 6.0 have been reported in deaerated solutions buffered to pH 7 containing OH scavengers such as formate, ethanol etc. [280,281]. In the absence of an OH scavenger a value of $G(Fe^{II}E) = 5.2$ (pH = 6.5) has been reported [281], suggesting reduction not only by e^-_{aq} and H, but also following OH attack. Reduction also occurs in aerated solutions, but here OH damage is fixed by O_2, preventing electron transfer to the Fe^{III} centre.

Pulse radiolysis experiments show that quite complex changes occur following the reaction of ferricytochrome *c* with radiolytic transients. Unfortunately the agreement between the various studies is poor. Land and Swallow [282,283] reported the formation of a transient $Fe^{II}E$ species, following reduction of ferricytochrome *c* at alkaline pH's by e^-_{aq} or CO_2^-, which decays with $t_{1/2} \sim 0.1$ s at pH = 9.2. Further optical changes over a period of minutes were also evident before the full spectrum of ferrocytochrome *c* was obtained. At pH 6.84 reaction with e^-_{aq} was found to occur at practically the same rate as the formation of ferrocytochrome *c*, no intermediate being detected [282]. The reaction of hydroxyl radicals with ferricytochrome *c* gave a complex series of changes involving a fast initial reaction with $t_{1/2} \sim 3$ μs, followed by slower reactions following no simple kinetic order, but independent of enzyme concentration [282].

Pecht and Faraggi [284] also detected an intermediate following reduction by e^-_{aq} which was converted by a first order process to the ferro form with $k = 8.5$ s^{-1} at pH 6.7. A smaller reduction yield in alkaline than in neutral solutions was found, and this was thought to be associated with some pH linked conformational equilibrium of ferricytcochrome *c*. Both Land and Swallow [282,283] and Pecht and Faraggi [284] attribute the slow reactions observed following electron reduction to conformational changes, the intermediate representing an Fe^{II} ion in the conformational environment of Fe^{III}.

Lichtin et al. [286] also observed a first order reaction ($k = 1.2 \cdot 10^5$ s^{-1} at pH 6.8) under similar conditions. They also detected a further, slower first order process with $k = 1.3 \cdot 10^2$ s^{-1}, but found no evidence of the much slower process ($k = 8.5$ s^{-1}) reported by Pecht and Faraggi [284]. Lichtin et al.

[286] attributed both the processes which they observed to conformational relaxation of ferrocytochrome *c*. A recent study by Witting et al. [285] of the reduction by e^-_{aq} at pH ~ 7 has found evidence for a much shorter lived intermediate. The results can be interpreted according to the following scheme

$$e^-_{aq} + Fe^{III}E \rightarrow Fe^{III}E^- \qquad k = 4.5 \cdot 10^{10}\ dm^3\ mol^{-1}\ s^{-1} \tag{223}$$

$$Fe^{III}E^- \rightarrow (Fe^{II}E)' \qquad k = 5 \cdot 10^6\ s^{-1} \tag{224}$$

$$(Fe^{II}E)' \rightarrow Fe^{II}E \qquad k = 1.3 \cdot 10^5\ s^{-1} \tag{225}$$

where reaction (224) represents an intramolecular electron transfer to the Fe centre following attack by e^-_{aq} at some remote site (223), and (225) represents a conformational change.

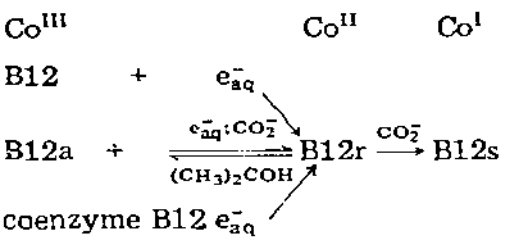
The reduction of ferricytochrome *c* by malate and other organic radicals, and by hydrogen atoms has been reported by Shafferman and Stein [287]. The former group all react at less than the diffusion controlled rate (ca. 10^8 $dm^3\ mol^{-1}\ s^{-1}$), and with ~100% efficiency. Hydrogen atoms on the other hand were found to react more rapidly, but with 50% efficiency and with only 15% of the reaction yielding ferrocytochrome *c* rapidly. The differences were suggested to be due to attack by malate etc. at some specific point on the enzyme surface, whilst H atoms reacted by H atom abstraction giving radicals only some of which were able to transfer an electron intramolecularly to the Fe^{III} centre.

Further experiments are required to characterise these reactions more fully, and to resolve the apparent conflicts between the results of the various workers.

Fe—haemoglobin and related compounds. Both haemoglobin and oxyhaemoglobin are oxidised when their aqueous solutions are irradiated, whilst methaemoglobin is reduced [288,289]. A pulse radiolysis study of the reduction of the latter by e^-_{aq} has been made [290]. The initial reaction is very rapid ($k = 5.8 \cdot 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ at pH 7.3), and remains unchanged when the β(93)SH groups are blocked with iodoacetamide. It is followed by two consecutive first order reactions which are independent of enzyme concentration. The more rapid reaction occurs with $t_{1/2} = 15 \pm 2\ \mu s$, and disappears upon addition of inositol hexaphosphate. The latter is known [291,292] to promote a change of the quaternary structure of methaemoglobin with H_2O as a ligand to the deoxy structure, and this is, therefore, taken to be the mechanism of the reaction. The slower process shows a sigmoidal dependence on pH with $pK \sim 8$, and is thought to be due to the release of heme bound water (low pH) or of OH^- (high pH) [290]. Metmyoglobin is also reduced by the hydrated electron, but here only the slower pH dependent reaction is observed.

Co. Blackburn et al. [293—295] made some studies on the radiation chemistry of the cobalt containing vitamin B12 system. Reduction of the Co^{III} and

Co^{II} forms of the vitamin occurs readily on reaction with e^-_{aq}, but less readily or not at all with reducing radicals such as CO_2^-. The reactions which have been characterised can be summarised as follows



Not all the products specified are formed in 100% yield [294—296]. The actual percentages are given in Table 22. Presumably this behaviour arises because the enzymes are attacked at many sites; some, such as the corrin ring or the benzimidazole moiety, giving rise to radicals which rapidly transfer an electron to the cobalt centre, whilst others such as amide functional groups act as electron "sinks". No intermediates have been detected in these reactions, and the reduced cobalt product forms at very nearly the same rate as the starting material is consumed. The intramolecular electron transfer reactions must therefore be very rapid. Also, since vitamins B12 (cyanocobalamin), B12a (aquo- and hydroxocobalamin) and co-enzyme B12 are all reduced to the same compound, vitamin B12r, some rapid rearrangement reactions must

TABLE 22

Percentage yields of products in the reactions of some radiolytic transients with vitamin B12 and related compounds

Reaction	% conversion to product shown	Ref.
e^-_{aq} + B12 → B12r	67	294
CO_2^- + B12 → B12r	~0 [a]	294
OH + B12 → B12r	0	294
e^-_{aq} + B12a → B12r	65 pH 6.1	296
CO_2^- + B12a → B12r	66 pH 9.2 95 pH 6.0	294
e^-_{aq} + coenzyme B12 → B12r	80	295
$CO_2^-/(CH_3)_2\dot{C}OH$ + coenzyme B12 → B12	≤15 [a]	295
CO_2^- + B12r → B12s	~100	294
$(CH_3)_2\dot{C}OH$ + B12r → B12a	~100 [b]	294
$\dot{C}H_2CHO$ + B12r → B12a	~100 [b]	294

[a] Reaction is slow if it occurs at all. [b] In acidic solutions.

occur. These involve the detachment of a cyanide ligand bound directly to the Co ion in the case of vitamin B12, and the loss of an adenosine moiety from coenzyme B12.

The reactions of $(CH_3)_2\dot{C}OH$, $\dot{C}H_2CHO$ etc. with vitamin B12r are of interest because they result in oxidation of the Co^{II} centre [294]. In alkaline media the radicals add to the metal giving a species which can formally be described as a Co^{III}—carbanion complex (reaction (226)). At acidic pH's the stable product of the reaction is vitamin B12a [294]. It seems probable that this forms via hydrolysis of the Co^{III} $E.R^-$ (227).

$$R + Co^{II}E \rightarrow Co^{III}E.R^- \quad (226)$$

$$Co^{III}E.R^- + H_2O \rightarrow Co^{III}E.OH^- + RH \quad (227)$$

Hydroxyl radicals react rapidly with these vitamins to give uncharacterised transient and permanent products [293—295]. The reactions do not result in reduction of the cobalt centre [293—295].

Mn. Pulse radiolysis has been employed to measure the rate of dismutation of O_2^- catalysed by *Escherichia coli* manganese superoxide dismutase [297]. The decay of the O_2^-, formed by the radiolytic reduction of O_2, was found to depend on the ratio of the initial $[O_2^-]$ and [enzyme]. With $[O_2^-]_0 \leqslant 0.1$ [enzyme]$_0$ a first order decay with $k_{obs} = k$[enzyme]$_0$ was found, k having a value of $(1.5 \pm 0.15) \cdot 10^9$ dm^3 mol^{-1} s^{-1}. When $[O_2]_0 \geqslant 15$[enzyme]$_0$ the decay consisted of two consecutive first order reactions. The results were found to be consistent with either of the following mechanisms (E = enzyme).

Mechanism A	Mechanism B	Rate constant (dm^3 mol^{-1} s^{-1})
$E + O_2^- \rightarrow E^- + O_2$	$E + O_2^- \xrightarrow{2H^+} E^+ + H_2O_2$	$1.3 \cdot 10^9$
$E^- + O_2^- \xrightarrow{2H^+} E + H_2O_2$	$E^+ + O_2^- \rightarrow E + O_2$	$1.6 \cdot 10^9$
$E^- + O_2^- \rightarrow E^{2-} + O_2$	$E + O_2^- \rightarrow E^- + O_2$	$\sim 2 \cdot 10^9$
$E^{2-} + O_2^- \xrightarrow{2H^+} E^- + H_2O_2$	$E^- + O_2^- \xrightarrow{2H^+} E + H_2O_2$	$\sim 1 \cdot 10^7$

The enzyme (E) is thought to contain manganese in valency state three, and so the intermediate forms may involve Mn^I, Mn^{II} or Mn^{IV}.

Zn. The reduction of the zinc hematophorphyrin complex has been studied [298] by pulse radiolysis, three intermediates being detected. The starting material (ZnP) is reduced by the $(CH_3)_2CO^-$ radical ($k = 1.0 \cdot 10^9$ dm^3 mol^{-1} s^{-1}), to give an intermediate, which has an absorption spectrum with at least three maxima in the visible region, thought to be the reduced form of the complex, ZnP^-, or its protonated equivalent, ZnPH. This decays by a second order process ($2k = 2.1 \cdot 10^8$ dm^3 mol^{-1} s^{-1}), which may be a disproportiona-

tion or dimerisation, and is followed by two further first order processes ($t_{1/2}$ = 40 ms and ≥5 s) [298] before formation of the stable products. In view of these subsequent reactions, the process obeying second-order kinetics is thought to be a dimerisation (if it were a disproportionation the conversion of the intermediates formed to the stable products would involve either loss or gain of protons, processes likely to be rapid) to give $(ZnPH)_2$. This is presumed to rearrange to give a dihydroporphyrin complex and the starting material.

Radiation chemical studies have also been made on the Zn containing enzymes yeast alcohol dehydrogenase [299] and bovine carbonic anhydrase [300]. Both are inactivated by oxidising radicals such as OH, Br_2^- etc., whereas with bovine carbonic anhydrase the metal ion exerts a protective effect in comparison with the metal free enzyme. Presumably this is because it acts as an electron "sink".

(iii) Kinetics of ligand—solvent exchange reactions

A novel application of the pulse radiolysis technique has been the measurement of ligand—solvent exchange kinetics following electron reduction of the metal centre of some complexes. With the $Co(NH_3)_6^{3+}$ complex, for instance, electron reduction produces $Co(NH_3)_6^{2+}$ (reaction (228)), and, since Co^{II} is labile, rapid exchange of the ammine ligands with the solvent occurs.

$$e_{aq}^- + Co(NH_3)_6^{3+} \rightarrow Co(NH_3)_6^{2+} \qquad (228)$$

The kinetics of the latter process can be monitored through changes in the conductivity brought about by reaction of the detached ammonia molecules with protons, and by this means Simic and Lilie [301] found that the exchange of the first three ammine ligands (reaction (229)) is too rapid to be detected with their apparatus, but that the subsequent reactions occur in three distinguishable steps as follows

$$Co(NH_3)_6^{2+} + 3\ H_2O \rightarrow Co(NH_3)_3(H_2O)_3^{2+} + 3\ NH_3 \qquad k > 10^6\ s^{-1} \qquad (229)$$

$$Co(NH_3)_3(H_2O)_3^{2+} + H_2O \rightarrow Co(NH_3)_2(H_2O)_4^{2+} + NH_3 \qquad k = 6 \cdot 10^4\ s^{-1} \qquad (230)$$

$$Co(NH_3)_2(H_2O)_4^{2+} + H_2O \rightarrow Co(NH_3)(H_2O)_5^{2+} + NH_3 \qquad k = 1 \cdot 10^4\ s^{-1} \qquad (231)$$

$$Co(NH_3)(H_2O)_5^{2+} + H_2O \rightarrow Co(H_2O)_6^{2+} + NH_3 \qquad k = 1.5 \cdot 10^3\ s^{-1} \qquad (232)$$

The rate constant for reaction (229) can be compared with $k = 5 \cdot 10^6\ s^{-1}$ for the exchange of one NH_3 by another [302], whilst the value for k_{232} compares favourably with that of $k_{232} = 1.1 \cdot 10^3\ s^{-1}$ (at 20°C) measured by the temperature jump method [303]. A similar situation was found to exist following reduction of $Co(NH_3)_5Cl^{2+}$ [301].

Lilie et al. [116] also studied the ligand—water exchange reactions of a number of Rh^{II} complexes generated by pulse radiolytic reduction of the corresponding Rh^{III} compounds. The first two ligands are very rapidly exchanged

($t_{1/2} \leq 1$ μs), so that irrespective of the starting material ($Rh(NH_3)_5X^{3+}$ or $Rh(NH_3)_4X_2^{3+}$), the first intermediate detected is $Rh(NH_3)_4^{2+}$ (see also Sect. D(v)). This exchanges two further NH_3's for water with rate constants of 350 s^{-1} and 40 s^{-1} [116].

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