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Metal-ion promotion of the oxidative dehydrogenation of coordinated amines and alcohols

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Contents

Abstract

The oxidative dehydrogenations of amines and alcohols are promoted by their coordination to transition metal centers, with ruthenium and osmium being particularly effective. The dehydrogenation reaction is well known in macrocyclic chemistry, and has been reported for

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a variety of monodentate and bidentate ligands as well. The initial step in the process is the one-electron oxidation of the metal center. However, the mechanism of the subsequent intramolecular redox reaction (in which the ligand is oxidized and the metal reduced) is ambiguous—it may take place either by one-electron steps through a ligand-radical intermediate, or involve higher oxidation states of the metal so that alternative two-electron pathways are possible. This review investigates studies of the mechanistic features of the reaction. The particular efficacy of ruthenium and osmium in promotion of ligand oxidation is related to their ability to attain an oxidation state two units greater than the final state, stabilized by deprotonation, and allowing a low-energy pathway for the even-electron processes required in the dehydrogenations of the amine and alcohol substrates.

Keywords: Coordinated alcohols; Coordinated amines; Metal-ion promotion; Oxidative dehydrogenation

1. Introduction

Oxidative dehydrogenation reactions of alcohols and amines are widespread in biochemistry (e.g. alcohol dehydrogenase, galactose oxidase, amine oxidase enzymes, and in systems which are suspected of degrading proteins thereby contributing to ageing), and are of potential importance with regard to the operation of fuel cells based on simple alcohols such as methanol.

The nature of the products obtained, and their rates of formation, may vary depending on the conditions of the reaction but are often profoundly influenced by the presence of metal ions. In the biochemical processes alluded to above, Zn(II) is present at the active site of alcohol dehydrogenase, Cu(II) in both galactose oxidase [1,2] and amine oxidase [1]. Fe(II) is present in MCO (metal-catalyzed oxidation) systems which contribute to enzyme damage by dehydrogenation [3]. The oxidation of amines may lead to a variety of products (including nitriles, nitro species and carbonyl compounds formed by cleavage reactions of highly reactive imine species formed in the oxidation): by contrast however, the oxidation of amines coordinated to metal centers leads quantitatively to the dehydrogenated product, as will be noted later in this review.

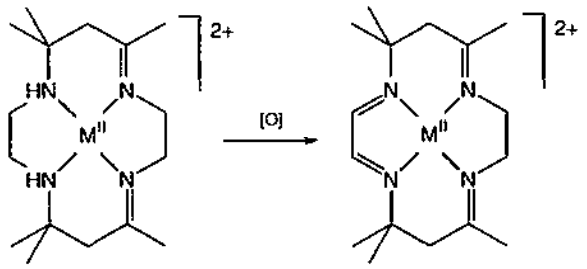
The promotion of oxidative dehydrogenations of amines and alcohols by their attachment to a metal center has been known for some time. This review probes the extent of the reaction, and the significant work in the last 10–20 years devoted to the elucidation of the mechanism of the process, and specifically to the role of the metal.

2. Historical background

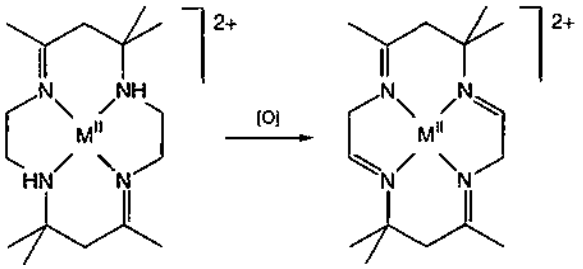
2.1. Macrocyclic ligands

The phenomenon of oxidative dehydrogenation of ligands attracted particular attention during the rapid development of macrocyclic chemistry which occurred

from the 1960s, because of the consistent observation of the conversion of secondary amine groups to azomethine linkages. Curtis [4–6] initially reported the oxidation of a number of nickel(II) macrocycles by nitric acid (Eqs. 1 and 2).

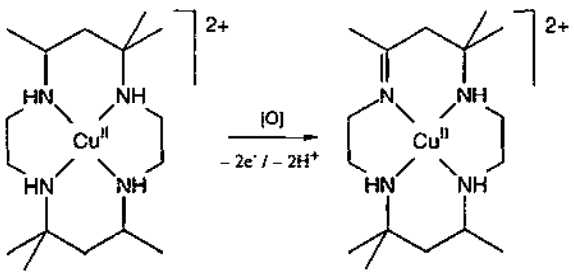


(1)



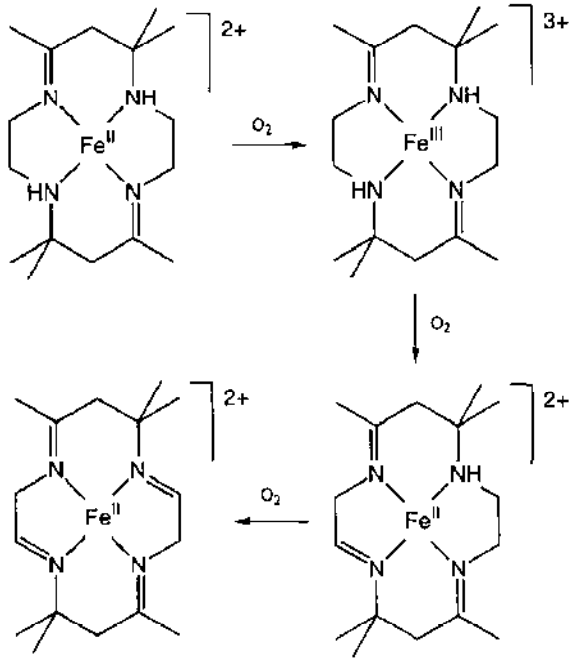
(2)

In these reactions it was suspected that higher oxidation states of the metal were involved in the oxidation process, in part because of the sensitivity of the reaction to the identity of the metal ion [7]. For example, iron(II) as the metal center promoted the reaction under mildly oxidizing conditions [8,9], while nickel(II) and copper(II) species required stronger oxidizing agents [5,10,11], and cobalt(III)—for which there are no easily accessible higher oxidation states of the metal—was inactive. Electrochemical studies were consistent with this hypothesis. For example, in the two-electron electrochemical oxidation of the copper(II) macrocycle shown in Eq. 3, polarographic and cyclic voltammetric data indicated the involvement of a Cu(III) species [12].



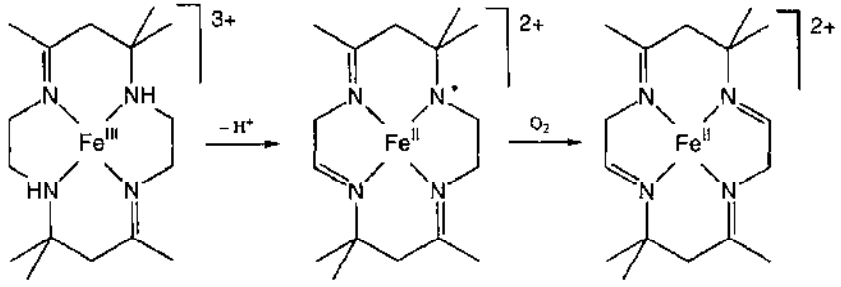
(3)

As in the case of the analogous nickel(II) complex, the monoimine was further oxidized to ultimately yield the tetraimine ligand.



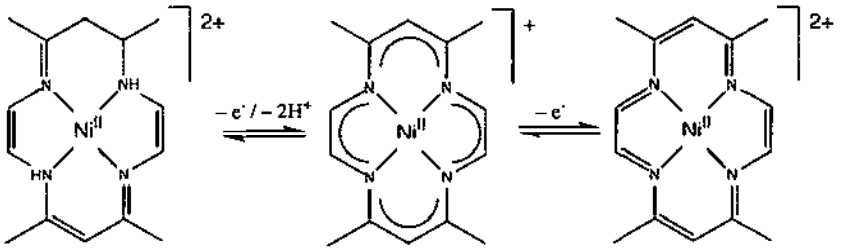
(4)

Goedken and Busch investigated the oxidative dehydrogenation of unsaturated tetra-aza macrocycles coordinated to iron(II) [9]. They isolated an Fe(III) intermediate in dry acetonitrile and on this basis suggested the reaction sequence shown above (Eq. 4). The intramolecular redox reaction was assumed to proceed via a free-radical mechanism (Eq. 5), although there was no evidence for such a proposal, or for the existence of the free-radical intermediate.



(5)

The three-membered oxidation series shown below (Eq. 6) was studied by Holm and coworkers, and the nature of the one-electron oxidation product probed by EPR techniques [13,14].



(6)

This intermediate species could be isolated as a stable monocation, and the EPR studies unequivocally showed it to be a ligand free-radical species of Ni(II)—although such an observation does not eliminate the possibility of a prior one-electron oxidation at the metal ion, with a subsequent electron transfer from ligand → metal giving the ligand free-radical species.

A number of pulse radiolysis studies were undertaken on the oxidation of a series of nickel macrocyclic complexes [15–20]. The data were interpreted to demonstrate the initial oxidation of the metal center to Ni(III) [15], with subsequent deprotonation of an amine nitrogen, followed by electron transfer from ligand to metal forming a ligand free-radical species which underwent further oxidation to produce the two-electron oxidation product [15–20] (see Fig. 1).

The facile oxidation of a number of macrocyclic complexes of ruthenium(II) has also been reported, although no mechanistic insights into the process were given [21].

2.2. Bidentate amine ligands

The oxidation of coordinated amines is not restricted to macrocyclic ligands. Studies of the oxidative dehydrogenation of simple amines were initiated by the

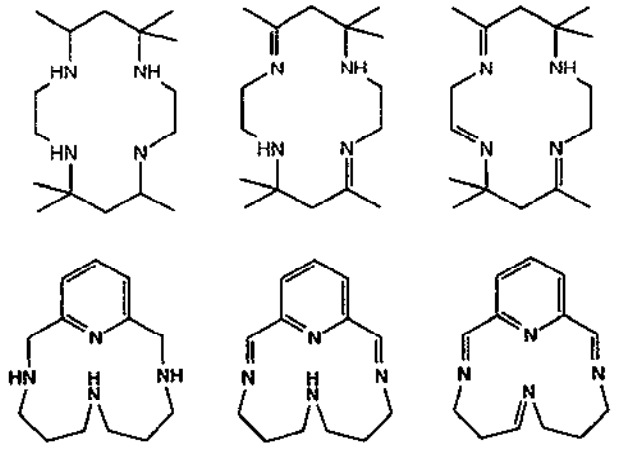
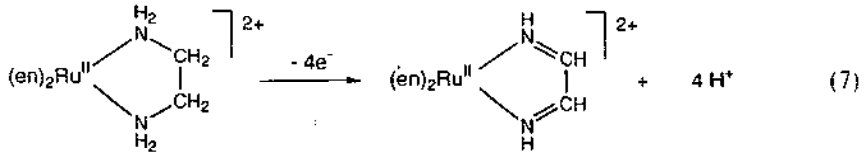


Fig. 1. Macrocyclic ligands used in pulse radiolysis studies of dehydrogenation studies of their nickel(II) complexes [15–20].

observation that tris(ethylenediamine)ruthenium(II), $[Ru(en)_3]^{2+}$, underwent a four-electron oxidation. The product was initially erroneously assigned as a Ru(VI) species [22], but subsequent work [23,24] showed that one ethylenediamine ligand had undergone oxidative dehydrogenation to give a ruthenium complex containing an α,α′-diimine ligand (Eq. 7).

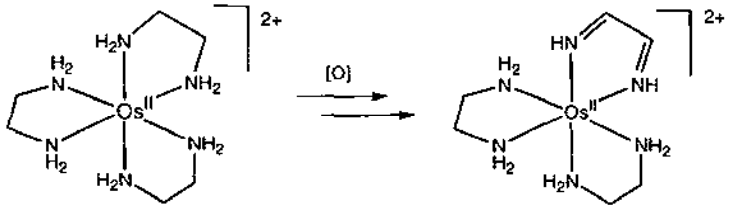


(7)

It was observed that the product of the oxidation of $[Ru^{III}(en)_3]^{3+}$ was the same as the oxidation product of $[Ru^{II}(en)_3]^{2+}$, consistent with the intermediary higher oxidation states of the metal ion—in the same manner as claimed in the oxidation of the macrocyclic ligands. The system has recently been re-visited in a detailed mechanistic study [25], as will be described subsequently.

The ethylenediamine ligand also has been shown to undergo dehydrogenation to the α,α′-diimine in the complexes $[Ru(hfac)_2(en)]$ and $[Ru(hfac)(en)_2]^+$ {hfac = hexafluoroacetylacetonate ion} [26].

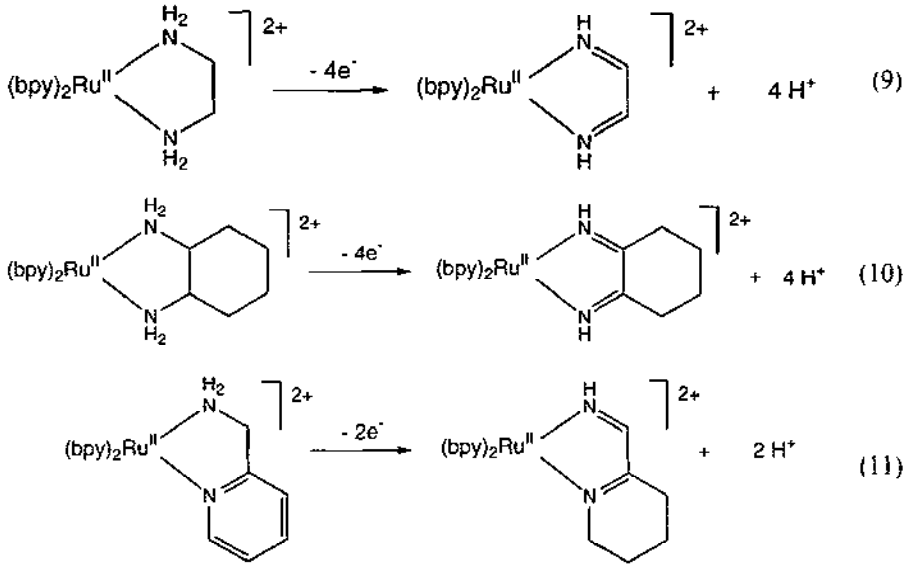
Osmium(II) also promotes the oxidation of coordinated ethylenediamine in $[Os(en)_3]^{2+}$ (Eq. 8) [27,28]. Early work by Dwyer and Hogarth [29,30] had claimed higher oxidation state complexes of ethylenediamine: two complexes formed by the reaction of $[OsBr_6]^{2-}$ with ethylenediamine were assigned as $[Os(en\text{-}H)_2(en)]^{2+}$ and $[Os(en\text{-}H)(en)_2]^{3+}$ primarily on the basis of measurements of magnetic moments, and both of which could be readily reduced to $[Os(en)_3]^{3+}$. However, after the erroneous assignment of similar structures to oxidized ruthenium complexes containing the same ligand (see above), the osmium chemistry was re-examined and the assignment of the 2+-charged product confirmed for the osmium case by X-ray crystallographic studies as $[Os(en\text{-}H)_2(en)]^{2+}$ [27]. The identity of the reduction product of $[Os(en\text{-}H)_2(en)]^{2+}$ was also established as $[Os(en)_3]^{3+}$ [31], as originally formulated. The species $[Os(en\text{-}H)_2(en)]^{2+}$ and $[Os(en\text{-}H)(en)_2]^{3+}$ spontaneously dehydrogenated to give imine complexes: the identification of possible intermediate species in the reaction provided a valuable insight into the mechanism of the oxidation, as described subsequently.



(8)

A similar four-electron oxidation of tetracyano(ethylenediamine)iron(II) has also been reported [32–35].

The chemical and electrochemical oxidation of a series of a range of bidentate amines to the corresponding α,α′-diimines has been studied by Meyer and coworkers (Eqs. 9–11; bpy = 2,2′-bipyridine) [36].



Ford et al. [37] have also observed the oxidation of the last ligand in this series (Eq. 11), 2-(aminomethyl)pyridine (ampy), in the complex $[(NH_3)_4Ru^{II}(ampy)]^{2+}$. In this case a stable Ru(III) complex was formed at low pH, but on raising the pH the oxidation of the amine to the imine occurred. This was a further demonstration of the intermediacy of high-valent intermediates in the oxidation of coordinated amines.

The system $[(bpy)_2Ru^{II}(ampy)]^{2+}$ (and complexes of related ligands) was used by Keene et al. [38,39] in a detailed study of the mechanism of these dehydrogenation reactions, as discussed below.

The oxidation of coordinated ethylenediamine and related ligands stops at the diimine stage and does not continue to the dinitrile. The α,α′-diimine entity –N=C–C=N– formed in the four-electron oxidation is particularly stable, due to both conjugation in the system and metal–ligand interaction where donation of charge through the dπ–pπ orbitals of appropriate symmetry enormously stabilizes the Ru(II)–diimine complexes [37,40]. There may well also be a steric factor as an M–N≡C linkage would be constrained to be linear.

A very limited number of studies have also dealt with stereochemical consequences of the dehydrogenation process. The work of Ridd and Keene [39] showed that in the oxidation of the diastereoisomeric forms of $[Ru(bpy)_2(Meampy)]^{2+}$ {Fig. 2A; Meampy = 2-(1-aminoethyl)pyridine}, the chirality of the metal center was retained during the reaction. Subsequently, Jandrasics et al. [41] confirmed the conclusion by observation of retention of the chirality of the metal center in the oxidation of the diastereoisomers of $[Ru(bpy)_2\{(R,R)\text{-dach}\}]^{2+}$ {Fig. 2B; dach =

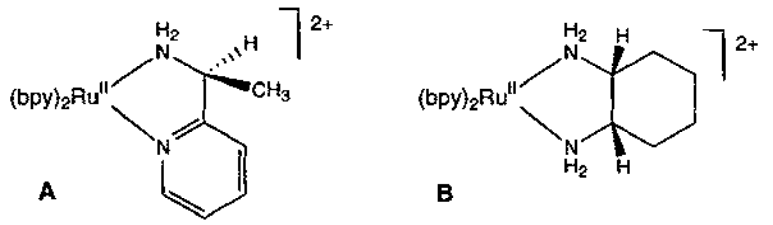
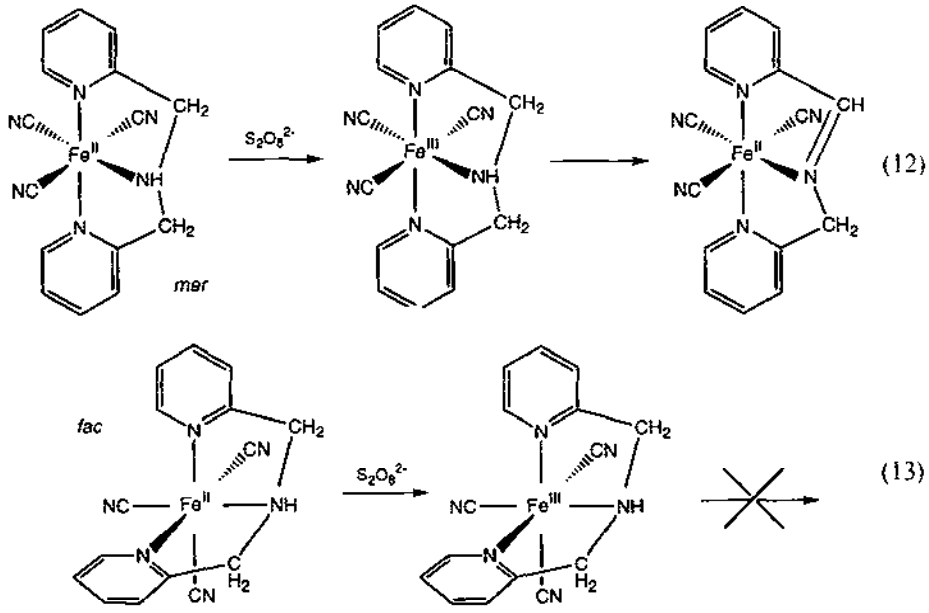


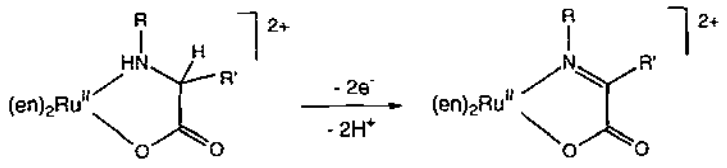
Fig. 2. $[Ru(bpy)_2(Meampy)]^{2+}$ (**A**) and $[Ru(bpy)_2\{(R,R)\text{-dach}\}]^{2+}$ (**B**), used in studies of the stereochemical course of dehydrogenation reactions [39,41].

1,2-diaminocyclohexane}. In studies of the oxidation of the tridentate ligand di(2-pyridylmethyl)amine (2-DPA) in the complex $[Fe(CN)_3(2\text{-DPA})]^-$ [42], it was also reported that the ligand in the *mer* configuration underwent dehydrogenation to give a monoimine species (Eq. 12), whereas the reaction of the complex with the *fac* orientation of the ligand stopped at the formation of the Fe^{III} species (Eq. 13).



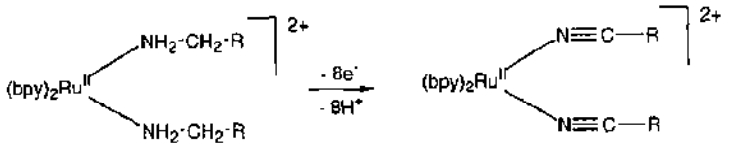
2.3. Bidentate amino-acid ligands

An analogous dehydrogenation has been reported for an α-aminoacid coordinated to the $[Ru^{II}(bpy)_2]$ moiety (Eq. 14) [43,44].



2.4. Monodentate amine ligands

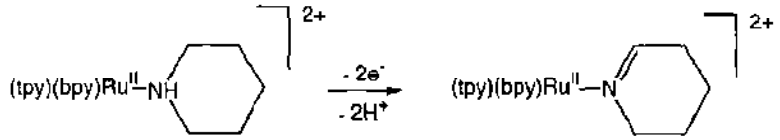
For monodentate primary amines, there are no steric constraints on the further oxidation of the imine to the nitrile. Thus, oxidation of a methylamine complex of Ru(II) resulted in the formation of the four-electron oxidation product, coordinated cyanide [45,46], and the oxidation of $[(NH_3)_5Ru(benzylamine)]^{2+}$ produced $[(NH_3)_5Ru(benzonitrile)]^{2+}$ [47,48]. In this latter study, it was also noted that the oxidation of the corresponding complex of cyclohexylamine led to the formation of $[(NH_3)_6Ru]^{3+}$ and free cyclohexanone, presumably as a consequence of the hydrolysis of the imine intermediate formed in the oxidative dehydrogenation of the cyclohexylamine ligand. Keene et al. [49] reported the oxidative dehydrogenation of a series of monodentate amines coordinated to the bis(2,2′-bipyridine)ruthenium(II) moiety (benzylamine → benzonitrile; *n*-butylamine → *n*-butyronitrile; allylamine → acrylonitrile), and in all cases the reactions were quantitative (Eq. 15).



(15)

R = -C6H5, -CH2CH2CH2CH3, -CH2-CH=CH2

Similarly, a study of the oxidation of secondary amines coordinated to ruthenium(II) was reported by Whebell and Keene in which the corresponding coordinated imines formed, which although unstable in the free state, were stabilized as a consequence of their attachment to the Ru(II) metal center (Eqs. 16–18) [50].



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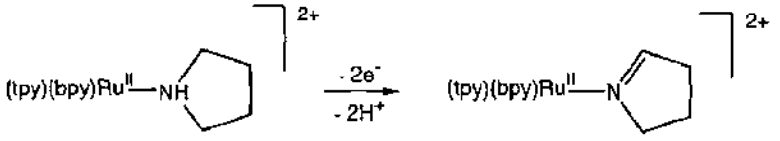

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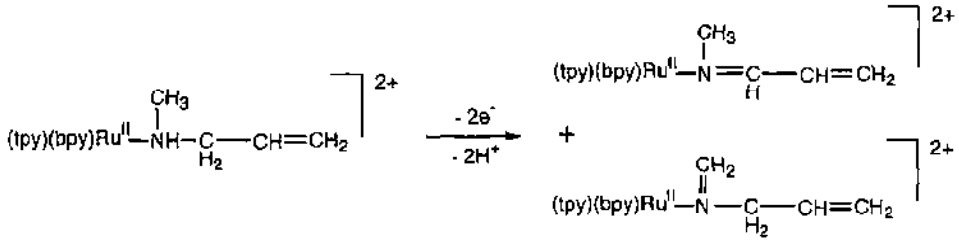
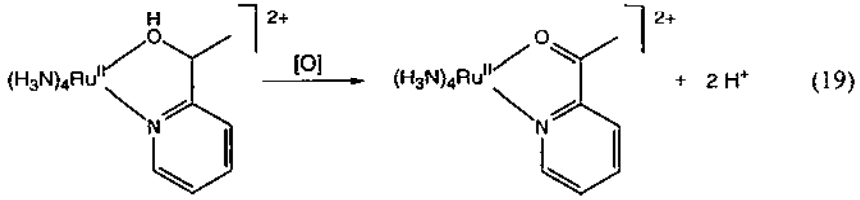


(18)

The last of these reactions (Eq. 18) was used as a means of stabilizing a 1-aza-1,4-butadiene moiety, which would normally rapidly polymerize, to allow it to undergo a Diels–Alder reaction with an appropriate dienophile [50].

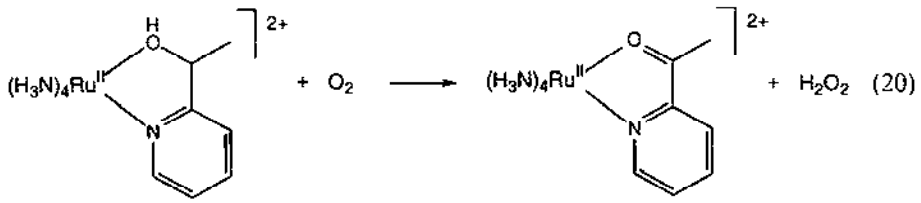
2.5. Alcohol ligands

The first example of the metal-promoted oxidation of a bidentate alcohol {2-(1-hydroxyethyl)pyridine; hetp} attached to Ru(II) was reported by Ford and coworkers (Eq. 19) [37].



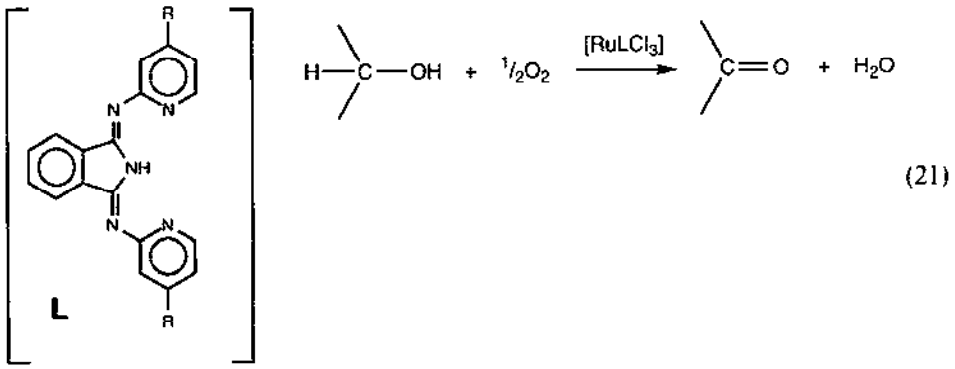
(19)

The same complex was used subsequently by Tovrog et al. [51] in a study in which the oxidation was achieved by oxygen, producing hydrogen peroxide (Eq. 20).



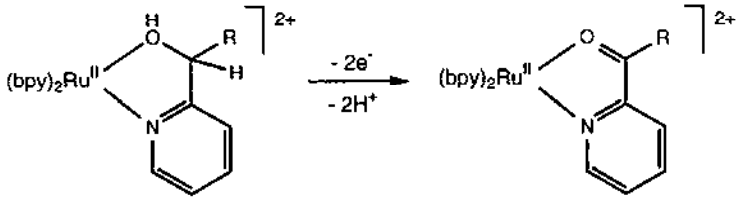
(20)

In the oxidation of coordinated monodentate alcohols, Reichgott and Rose have reported the photoassisted oxidation of methanol, catalyzed by a macrocyclic iron complex [52]. Gagné and Marks [53] also observed that the complex {1,3-bis(4-methyl-2-pyridylimino)isoindoline}trichlororuthenium(III) catalyzed the autoxidation of alcohols to aldehydes or ketones in basic alcoholic solution (Eq. 21). The involvement of species in which the substrate alcohol was attached to the metal center was invoked to promote the oxidation process.



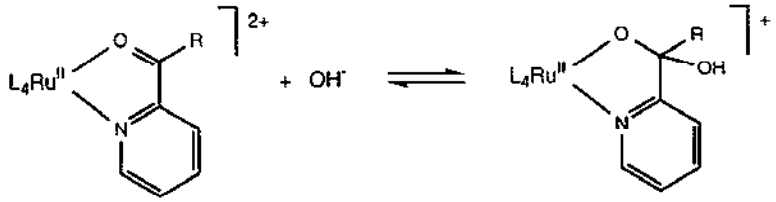
(21)

Ridd et al. [54] have subsequently undertaken a detailed mechanistic study of the oxidation of the alcohol ligand analogous to the bidentate amine system they had studied previously (Eq. 22) [38,39]. This investigation will be discussed subsequently.



(22)

It is interesting to note that the initial product of the alcohol oxidation is the corresponding aldehyde or ketone. These complexes undergo conversion to the hydrated form to an extent dependant on the nature of the metal center and the other 'innocent' ligands (Eq. 23) [37,54,55].



(23)

3. Mechanism of oxidative dehydrogenation

3.1. The general dichotomy

The metal-promoted ligand dehydrogenation reactions necessarily require the removal of (multiples of) two electrons and two protons from the substrate during the process. It is clear that the initial step is a one-electron oxidation of the metal center, so that two general classifications are possible for the subsequent intramolecular redox process in which the metal is reduced and the ligand oxidized.

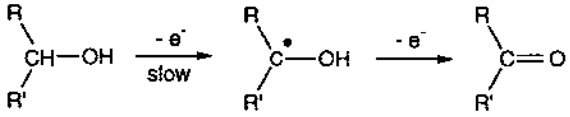
1. Schemes involving consecutive one-electron oxidations of the ligand, coupled with proton removal, which therefore must necessarily involve free-radical intermediates.
2. Schemes involving a two-electron transfer from ligand to metal, which may result from a hydride transfer (transferring both a proton and two electrons simultaneously), or via a proton abstraction with a subsequent two-electron transfer. In both cases, the question as to whether the two-electron transfer occurs by simultaneous transfer of two electrons, or by two one-electron transfers in rapid succession, may not be answered by kinetic studies.

Of course, the two alternatives may both exist and there may not be an exclusive mechanistic path for these reactions. This review looks at our current understanding of the intricacies of the reaction.

3.2. Early studies of oxidation of coordinated alcohols and amines

Mechanistic investigations of metal-catalyzed alcohol oxidations are more numerous and more detailed than is the case for the amine analogues, and information from kinetic studies indicates that in terms of their role in elementary processes the metal ions may act as either one- or two-electron oxidants [56].

For the one-electron oxidants {e.g. Co(III), Ce(IV), V(V), Mn(III), Fe(III), Cu(II)} [56] the oxidation involves an electron transfer between the substrate and the metal accompanied by the rate-determining breaking of an α-CH bond, producing a radical species. Subsequent rapid oxidation of the radical gives rise to the product (Eq. 24).



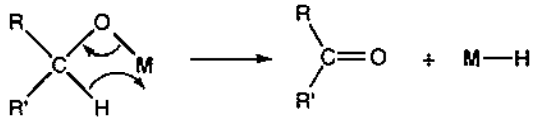
(24)

Frequently, complex formation between the metal ion and the alcohol (or the alkoxide ion derived from it) takes place prior to an intramolecular redox process {e.g. Ce(IV), V(V)} [56].

For two-electron oxidants {e.g. Tl(III), Pb(IV), Hg(II), Mn(VII), Cr(VI)} the mechanistic pathway may not always be unambiguous and there are cases that may be variously regarded as (i) two successive one-electron transfers via a radical species; (ii) a concerted two-electron transfer from substrate to metal, coupled with two deprotonations of the substrate; or (iii) a deprotonation of the substrate followed by hydride transfer from substrate to the metal. These three possibilities exist whether or not the alcohol is coordinated to the metal, but the mechanistic studies are simplified if it is known that the alcohol is coordinated to the metal ion during the reaction.

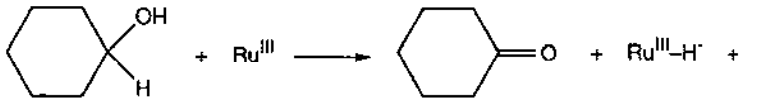
A number of oxidations of coordinated alcohols are thought to proceed via consecutive one-electron transfers from ligand to metal, thereby involving free radical intermediates {(i) above}. Examples include the oxidation of methanol by cobalt aromatic azo compounds where a free radical mechanism is proposed on the basis of product distribution [57], and the oxidation of alcohols by $[IrCl_6]^{4-}$ in which a free radical intermediate was detected by the acrylamide polymerization test [58].

There are many examples of metal-catalyzed alcohol oxidations which are thought to proceed via the hydride transfer mechanism {(iii) above} [59–66]. The reaction of alcohols with certain platinum metal ions in the presence of strong base has been used as a preparative method for hydride complexes [67], for these processes result in the oxidation of the alcohol by elimination of a hydride ion from the α-CH groups of the coordinated alkoxide ion (Eq. 25).



(25)

Metal-hydride intermediates have also been suggested for the catalytic oxidation of alcohols by Pd^{II}/NaOAc [60] and for the oxidation of both amines and alcohols by $RuCl_3 \cdot xH_2O$ [66]. The latter system was claimed to be the first catalytic oxidation of an amine group. A number of papers have appeared [62,65] detailing the oxidation of butanol or cyclohexanol by ferricyanide ions with Ru(III) as a catalyst. A hydride transfer to Ru(II) was proposed in the oxidation of cyclohexanol although the intermediate was not isolated (Eqs. 26 and 27) [62].



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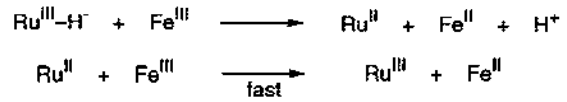
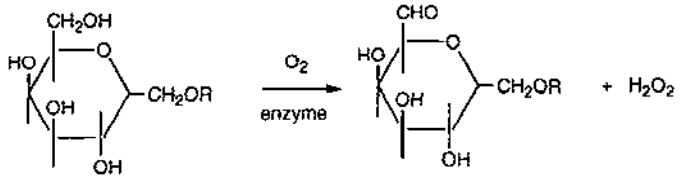


(27)

The mechanism of oxidation of organic substrates by ruthenyl (Ru^{IV}=O) and osmyl (Os^{IV}=O) species was originally studied using the oxidation of isopropanol by $[Ru(tpy)(bpy)O]^{2+}$ as an example (tpy = 2,2′:6′,2″-terpyridine) [68]. The oxidation was shown to occur via two pathways, one of which was postulated to involve a concerted two-electron oxidation of the alcohol by the Ru(IV) species. On the basis of deuterium isotope effect studies the reaction was thought to involve a hydride transfer from the alcohol to the metal, perhaps in a concerted manner with proton abstraction from the alcohol. Similar conclusions were reached in the study of the mechanism of the oxidation of aromatic hydrocarbons by the same complex [69].

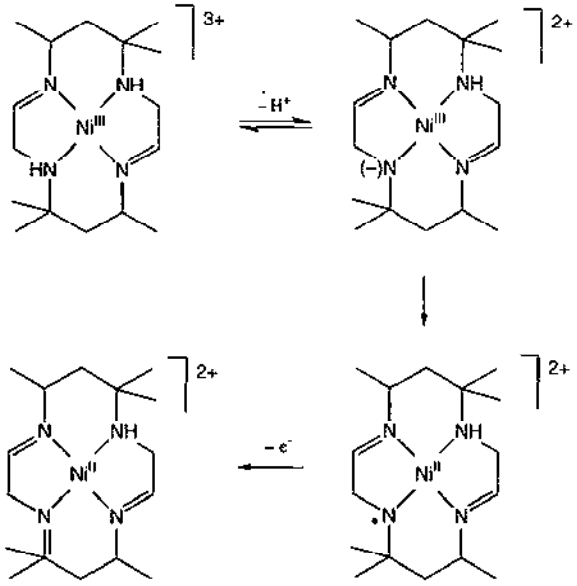
An example of a metal-catalyzed oxidation which was claimed to proceed via reaction scheme (ii) {two deprotonations coupled to a two-electron transfer} was the oxidation of a bidentate alcohol coordinated to Ru(II), shown above in Eq. 20 [51]. The authors proposed that the mechanism proceeded via a Ru(IV) species formed by the disproportionation of two Ru(III) centers, although there was minimal evidence provided. Such a disproportionation 2Ru(III) → Ru(II) + Ru(IV) had been reported previously for $[Ru(NH_3)_5py]^{3+}$ at high pH, by Rudd and Taube [70]. In this example, no oxidation was observed at low pH, which was interpreted to indicate that an oxidation by two one-electron processes was not possible.

Another system which proceeds via a two-electron transfer from the ligand to the metal is found in the enzyme galactose oxidase (Eq. 28) [2]. In this enzyme, high-valent Cu(III) performed a two-electron oxidation of a primary alcohol to the corresponding aldehyde, the metal center being converted to Cu(I) before its re-oxidation to Cu(III) by O_2.



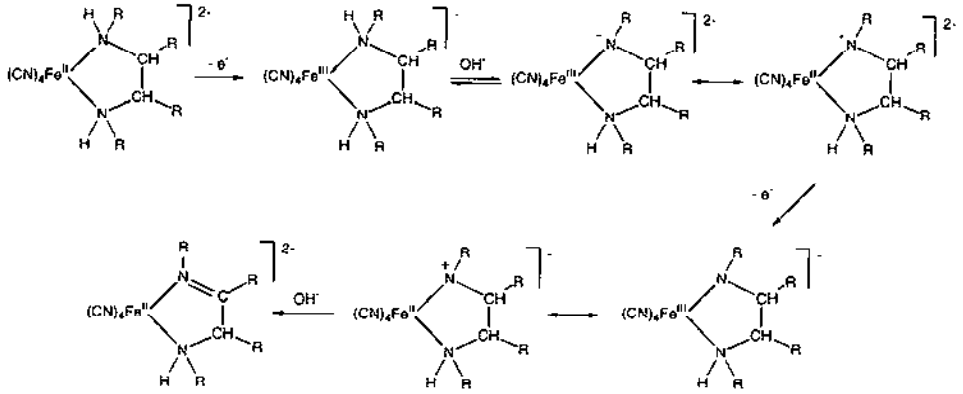
(28)

For coordinated amines, much of the initial understanding of the mechanism of the dehydrogenation reaction was obtained from studies of macrocyclic complexes, using predominantly the nickel complexes of a series of 14-membered tetra-aza-macrocyclic ligands (shown above). A series of pulse radiolysis studies was undertaken in which the oxidation of the metal center was initiated by $^{\bullet}OH$, Cl_2^-, Br_2^- and $(NCS)_2^-$ with the subsequent reactions being probed by spectral and chemical methods [15–20]. For the hydroxyl radical there may be some ambiguity concerning its site of attack (on a metal center or an alkene linkage), and the complication of protonic equilibria in aqueous solution. However, such ambiguities are not associated with the other radicals which are produced by the reaction of $^{\bullet}OH$ with X^- in solution. All these radicals reacted very rapidly with the Ni(II) center in a reaction producing a species which was spectrally consistent with the formulation of an Ni(III) species. The subsequent disappearance of the Ni(III) species was pH dependant, suggesting a deprotonation occurred which led to the formation of a ligand radical species, which was itself rapidly oxidized to the dehydrogenated product (Scheme 1). The rate of formation of the dehydrogenated product was also dependant on the identity of the radical ($^{\bullet}OH$ or X_2^-) used in the radiolytic oxidation (varying by three orders of magnitude), which was interpreted to indicate



Scheme 1.

that the anion X^- was involved in the transient oxidation product, presumably as an axial ligand or as a ligand involved in competitive substitutional equilibria for occupancy of such a site.



Scheme 2.

The ligand oxidations within a series of complexes of the type $[Fe^{III}(CN)_4(1,2\text{-diamine})]^+$ {1,2-diamine = ethylenediamine [32–35], (*R*)-1,2-diaminopropane, (*R,R*)-1,2-diaminocyclopentane, (*R,R*)-1,2-diaminocyclohexane, *N,N'*-dimethylethylenediamine} [35] and $[Fe^{III}(CN)_4\{2\text{-(aminomethyl)pyridine}\}]^-$ [35] have been studied, and the results interpreted in a similar manner to the macrocyclic complexes above. The Fe(II) species undergo oxidative dehydrogenation induced by a variety of oxidants, such as H_2O_2, ClO_2^-, O_2 and $[Fe(CN)_6]^{3-}$. The disproportionation of products into an intact diamine and a dehydrogenated diimine complex confirmed the intermediacy of the Fe(III) compounds, and the mechanism of the dehydrogenation was described in terms of two one-electron transfers [35]. Following oxidation of the metal to Fe(III), a base-assisted deprotonation occurs; deuterium isotope effect studies confirmed the site as the N-H rather than the α-CH bond. Intramolecular transfer from the deprotonated nitrogen atom to the Fe(III) center allowed the formation of a Fe(II)-radical species, which was subsequently oxidized to an Fe(III)-radical analogue. A further intramolecular electron transfer from the nitrogen radical to Fe(III) generated a putative Fe(II)-cation species; proton release may then occur to form the imine product (Scheme 2) [35].

3.3. Ruthenium and osmium—special cases for ligand oxidative dehydrogenations?

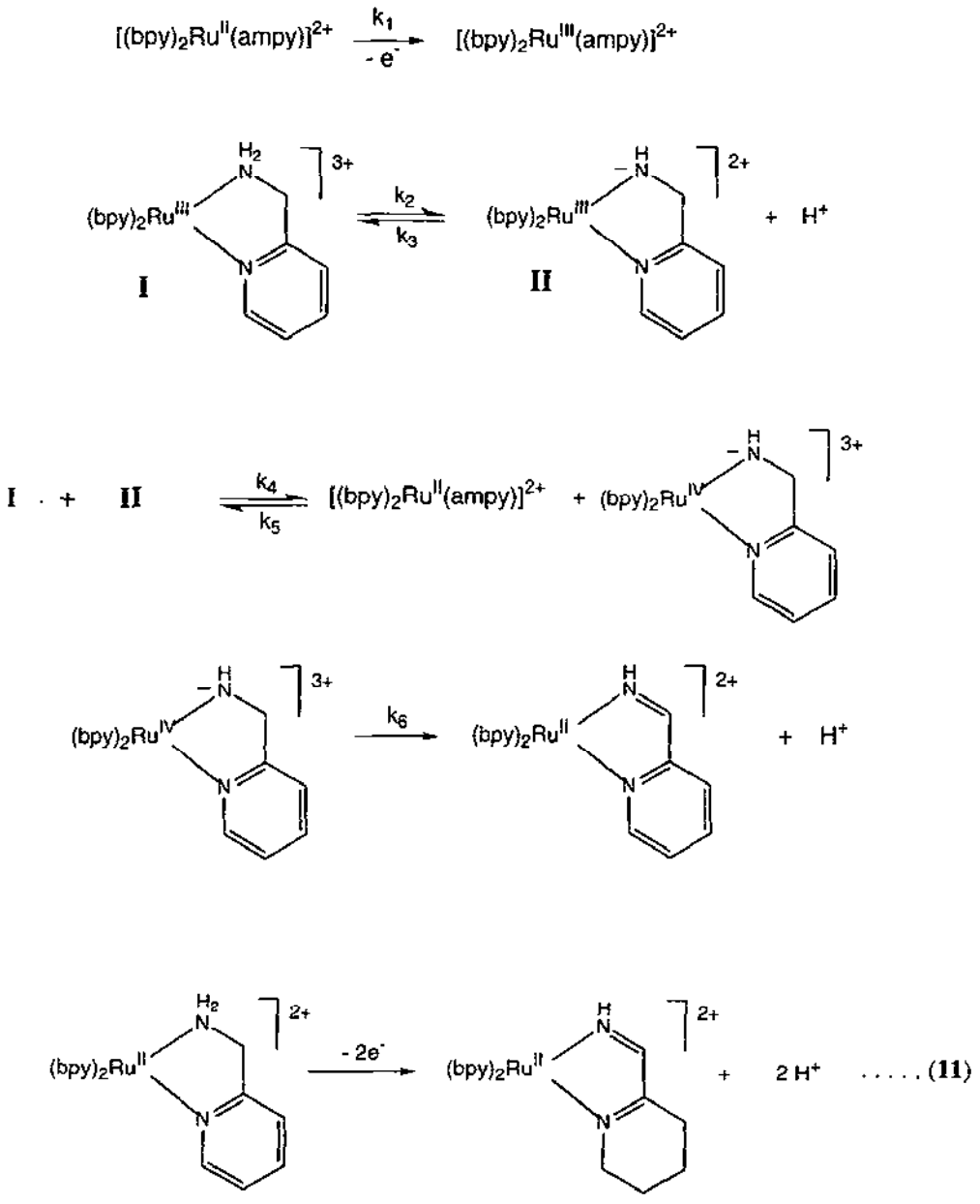
The systems involving iron as a metal center raise an interesting point of conjecture regarding the oxidative dehydrogenation processes. It has been well known for some time that ruthenium and osmium are particularly effective in the promotion of the oxidation of amine and alcohols coordinated to them. This phenomenon has been studied in great detail, and different mechanistic insights on

the problem have been provided, and in particular by Keene, Ridd [38,39,54,71–73], Sargeson, Bernhard [25,74–77], Lay [27,28,31] and their respective coworkers. Their collective work has allowed a deep insight into the process.

However, prior to these studies, two important factors had emerged that impinged upon the role of the ruthenium and osmium centers. It was clear from work by Rudd and Taube that a $2Ru(III) \rightarrow Ru(II) + Ru(IV)$ disproportionation did occur under basic conditions in ruthenium complexes containing dissociable protons—so that higher oxidation states were readily accessible [70]. Secondly, there were long-standing reports of higher oxidation state osmium amine species in which the amine ligands underwent deprotonation [29,30]. A mechanistic pathway involving initial oxidation of the metal center from Ru(II) to Ru(III), followed by base-assisted disproportionation to form a Ru(IV) species which then underwent a two-electron reduction with concomitant two-electron oxidation of the ligand, was first suggested (without kinetic studies) by Tovrog et al. [51] in their report on the autoxidation of 2-(1-hydroxyethyl)pyridine attached to ruthenium(II) (Eq. 20).

The first detailed mechanistic studies of such reactions were reported by Ridd and Keene [38], who investigated the oxidative dehydrogenation of 2-(aminomethyl)pyridine {ampy} in the system $[Ru(bpy)_2(ampy)]^{2+}$ to the corresponding imine (Eq. 11). The study was performed by using chemical, electrochemical and flash photolysis methods to promote the initial oxidation of the metal center from Ru(II) to Ru(III). The chemical oxidation studies, performed by stopped-flow techniques using Ce(IV) in aqueous 1 M H_2SO_4 solution, followed the intramolecular ligand oxidation process subsequent to the initial oxidation of the metal center. Attempts, using numerical methods, were made to fit the observed absorbance responses with a number of mechanistic schemes based on the intermediacy of either a Ru(II)-free radical species or a Ru(IV) species formed by disproportionation. An excellent correlation was found with the following mechanistic scheme (Scheme 3).

Much less satisfactory fits were obtained with schemes based on the free radical proposal. However, a limitation of these stopped-flow studies was the inability to vary the acid concentration due to the complicated behavior of Ce(IV) under varying conditions of pH. Accordingly flash photolysis experiments were also undertaken where the Ru(III) species was generated by rapid oxidative quenching using $[Fe(OH_2)_6]^{3+}$ of the MLCT excited state formed during the flash. The technique allowed variation in $[H^+]$ of the solution and in [Ru(III)] by variation of the flash intensity. The absorbances obtained following the flash were tested against the mechanistic schemes in the same manner as the chemical oxidation data, and gave entirely consistent results under the same conditions. The numerical solution required that the pK_a of the Ru(III)–amine species was 2.4, and that the equilibrium constant for the disproportionation process was 208 (which implies there is a difference of ca. 0.14 V between the two couples involved in the equilibrium). The rate constant for the final process was determined at $k_6 = 93\ s^{-1}$; however, the process clearly involves the transfer of two electrons from the ligand to the metal (in a concerted manner or by two one-electron steps), as well as a single deprotonation from the α-methylene carbon group. To satisfy the kinetic data, one of these


[(bpy)2Ru^II(ampy)]2+
k1
- e-
[(bpy)2Ru^III(ampy)]2+
(bpy)2Ru^III
I
k2
k3
II
+ H+
I + II
k4
k5
[(bpy)2Ru^II(ampy)]2+
+ (bpy)2Ru^IV
(bpy)2Ru^IV
k6
(bpy)2Ru^II
+ H+
(bpy)2Ru^II
- 2e-
(bpy)2Ru^II
+ 2 H+ ..... (11)

Scheme 3.

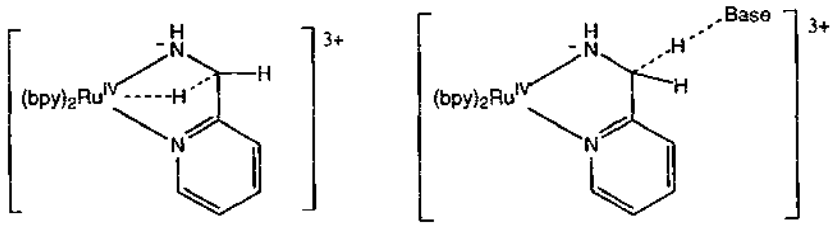


Fig. 3. Possible transition states for the deprotonation at the α-methylene group (k_6) in the dehydrogenation of $[Ru(bpy)_2(ampy)]^{2+}$ [39].

alternative electron transfer processes, or the deprotonation, or a concerted process, would be rate-determining.

In a subsequent study [39], these authors specifically addressed this final step of the dehydrogenation reaction by examining the oxidation of analogous complexes, in which the ampy ligand was firstly deuterated at the α-methylene group (d_2-ampy), and also where the α-methylene group bore one methyl substituent (Meampy). The values of k_6 for the non-deuterated and deuterated ampy complexes are 93 ± 3 and 52 ± 3 s^{-1}, respectively, so that the deuterium isotope effect $k_H/k_D = 1.78$. This indicates that the deprotonation at the α-methylene carbon is rate-determining, and the low magnitude implies the transition state is either linear but asymmetric, or nonlinear. Two possible arrangements are shown below in Fig. 3—one involving a bridging hydride between the metal center and the α-carbon atom and the other involving a linear but asymmetric association between the departing proton and an external base.

NMR studies performed in D_2O/D^+ as solvent also showed that no hydrogen exchange occurred at the α-methylene carbon atom during the oxidation of d_2-ampy. This implies that each act of deprotonation leads to ligand oxidation, so that either deprotonation and intramolecular electron transfer are concerted, or they are consecutive with electron transfer being more rapid than the re-protonation of the conjugate base. A concerted process had also been postulated at the same time for the dehydrogenation of en coordinated to Os [27].

The nature of the k_6 step was also probed by studying the relative rates of oxidation of the two diastereoisomeric pairs of $[Ru(bpy)_2(Meampy)]^{2+}$ {$\Delta R/\Lambda S$ and $\Delta S/\Lambda R$}. In one of these diastereoisomers, $\Lambda S/\Delta R$, the methine proton which is removed will have an axial orientation to the chelate ring whereas in the other it will be equatorial, so that any observed differences in the k_6 values would reflect the differences between the two geometries. In fact there is a significant difference between the two values for k_6 (103 ± 3 and 76 ± 2 s^{-1}, respectively). The axial orientation of the methine proton means that it has relatively unhindered access to the nearest face of the coordination octahedron, allowing ready formation of a hydride bridge between the metal center and the α-carbon atom. However, a hydride transfer mechanism involves a seven-coordinate intermediate and a possible configurational rearrangement. If the mechanism were a base-assisted proton abstraction, the configuration of the metal center would be expected to be retained. Since chirality is absolutely preserved during the reaction, the base-assisted removal

mechanism was preferred, although a study of the base dependence of the series of reactions was not possible in the low pH solutions in which they were performed.

An insight into the latter issue was provided subsequently by a detailed study of the oxidation of an analogous series of alcohols coordinated to Ru(II), shown earlier in Eq. 22 [54]. The kinetic studies (using chemical oxidation by $[Os(bpy)_3]^{3+}$), were consistent with the overall mechanism previously derived for the corresponding amine ligand, invoking in this case the intermediacy of a Ru(IV)–alkoxide species. It was observed that the presence of a vast excess of the radical scavenger acrylamide had no effect on the rate of the oxidation reaction and that no polymerization occurred, thereby effectively ruling out the involvement of a ligand radical intermediate. From studies of the reaction in the presence of a variety of bases, general base catalysis was established. A kinetic isotope effect $k_H/k_D = 9$ was observed for the reaction, clearly demonstrating that the α-CH bond was broken in the rate-determining step. Further, a study of the dependence of the rate of the reaction as a function of ionic strength showed a dependence which was interpreted to indicate that the charge on the metal complex involved in the base-catalyzed dehydrogenation reaction was +3, consistent with the proposed deprotonated Ru(IV) intermediate.

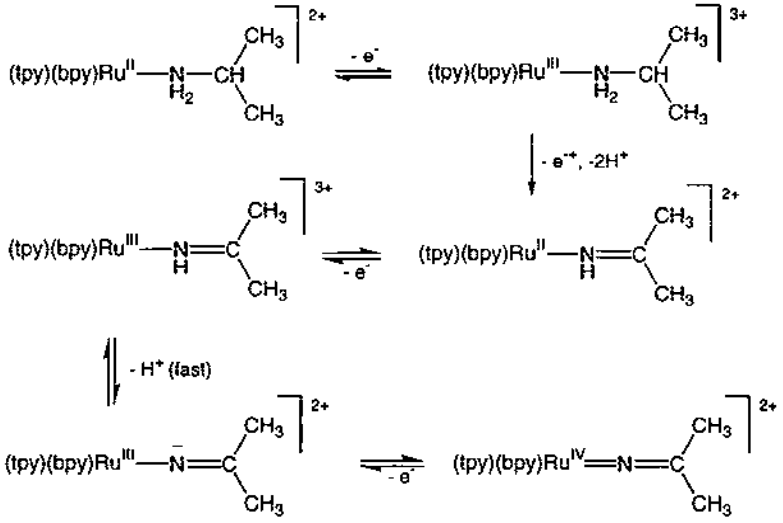
The comparative rate studies for the two diastereoisomeric complexes where $R = CH_3$ revealed a difference of a factor of ca. 10 between the two forms—interestingly in the opposite direction to the trend observed for the amine system. The variation between the two diastereoisomers could arise from a difference in the acidity of the methine proton in the two forms, or from stereochemical effects which obviously differ between the analogous amine and alcohol systems.

The conclusion of these two studies was that the particular effectiveness of the Ru center in the promotion of the oxidative dehydrogenation of amine and alcohol ligands was related to its ability to attain an oxidation state two units greater that the final state. This Ru(IV) center was formed by disproportionation and stabilized by deprotonation, allowing a low energy pathway for the even-electron process required in the dehydrogenation.

Although there was little evidence at the time of the above studies for the stabilization of the Ru(IV) state by the presence of a deprotonated amine or alcohol ligand, the phenomenon is now well substantiated. The particular acidity of Os(IV)–amine complexes compared with their Pt(IV) analogues had been pointed out by Taube and coworkers [78], and attributed to the high electron affinity of the d^4 t_{2g} orbitals which stabilized the bond with the anionic amido group. Such a stablization might also be expected for Ru(IV) species, although to a lesser extent because of the more limited extension of the metal orbitals. The extremely rich redox chemistry of the M(IV) 'oxo' {M = Ru, Os} chemistry elucidated by Meyer and coworkers, and subsequently Che and coworkers, is a testimony to this effect [79–90]. Without ligand deprotonation the difference between the redox potentials of the Ru(III/II) and Ru(IV/III) couples for a given complex might normally be expected to exceed 1 V: however, in the case of the $[Ru(tpy)(bpy)(OH_2)]^{n+}$ system, [82] the two couples (Eq. 29) differ in potential by ca. 0.1 V because of the accompanying stabilization of the oxidized product induced by deprotonation.

$$[Ru^{II}(tpy)(bpy)(OH_2)]^{2+} \overset{-e^-,\,-H^+}{\rightleftharpoons} [Ru^{III}(tpy)(bpy)(OH)]^{2+} \overset{-e^-,\,-H^+}{\rightleftharpoons} [Ru^{IV}(tpy)(bpy)(O)]^{2+} \quad (29)$$

An analogous chemistry has unfolded for nitrido, imido and amido complexes [90–92]. The extent of the stablization of the deprotonated Ru(IV) species was emphasized by the isolation of a Ru(IV) complex containing an N-bound isopropylideneamide ion, obtained from the four-electron oxidation of the species $[Ru(tpy)(bpy)(isopropylamine)]^{2+}$ (Eq. 30) [71,72]:



(30)

Significantly, the Ru(IV/III) redox potential of the isopropylidenamido complex is considerably cathodic of the Ru(III)/Ru(II) potentials for either the isopropylamine or isopropylideneamine analogues, demonstrating the stabilization of the Ru(IV)–isopropylideneamido species by substantial charge donation from the deprotonated-N to the metal center.

Studies by Lay et al. [27,31,93] on osmium complexes of 1,2-diamine ligands have provided fundamental information on the issue of the analogous higher-valent osmium species. The establishment of the structure of the Os(IV) complex $[Os(en\text{-}H)_2(en)]^{2+}$ by X-ray crystallography of the dibromide salt was particularly important [27], and revealed the deprotonated sites were *cis* to one another on separate chelate rings (Fig. 4). This structure was also established for the species in solution on the basis of NMR studies [28].

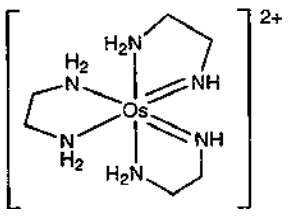


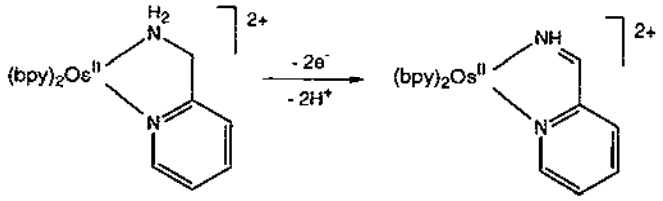
Fig. 4. Structure of $[Os(en\text{-}H)_2(en)]^{2+}$ cation [27].

The stabilization of the Os(IV) center in this case clearly results from π-donation of electron density from the deprotonated amine to the metal, as it leads to a shorter bond length (1.90–2.11 Å for the other planar ligands and 2.19Å for the axial ligands) and an expanded angle (110°) between the double bonds. A related complex involving the ligand 2,3-diamino-2,3-dimethylbutane (tmen) has also been shown to have an analogous formulation $[Os(tmen\text{-}H)_2(tmen)]^{2+}$ and structure [93].

With the characterization of the nature of the potential intermediate species in the process, the mechanism of the oxidative dehydrogenation of $[Os(en)_3]^{2+}$ to $[Os(en)_2(diim)]^{2+}$ has been described in some detail [27,28]. The Os(IV) complexes underwent spontaneous oxidative dehydrogenation to form the Os(II)–monoimine species $[Os(en)_2(monoim)]^{2+}$, with first-order kinetics. No deuterium exchange was observed at the α-CH protons when the reaction was performed in D_2O. The results clearly established the species involving the Os(IV) center as intermediates in the dehydrogenation reactions of $[Os(en)_3]^{2+}$. Further, because of the particular protonation equilibria involved, it is clear that such species may arise from the base-catalyzed disproportionation $2Os(III) \rightarrow Os(II) + Os(IV)$, with the stabilization of the deprotonated Os(IV) complexes arising from donation of charge from the amide group to the metal center. The two Os(IV) species $[Os(en)_2(en\text{-}H)]^{3+}$ and $[Os(en)(en\text{-}H)_2]^{2+}$ are related by a protonic equilibrium (pK_a ca. 5) and the 'protonated' form is a much stronger oxidant, which is not unexpected given that the respective Ru(IV/III) redox couples were determined at $E_{1/2} = +0.29$ V (vs. Ag/AgCl; reversible) and $E_{p,c} =$ ca. -1.2 V (irreversible) in acetone solution at an Au or Pt working electrode. The consequence of this property is that the rate of the oxidation is observed qualitatively to increase at lower pH values. The further protonation to $[Os(en)_3]^{4+}$ was not observed under any conditions.

$[Os(en)_3]^{3+}$ in basic solution produced the imine complex, but with evidence of the formation of $[Os(en\text{-}H)_2(en)]^{2+}$. The subsequent oxidation to the diimine takes place in the presence of an oxidant. A mechanism consistent with the kinetic, electrochemical and spectral observations was presented as given below (see also Scheme 4). Alternative proposals for the final two steps {via an intramolecular hydride transfer from a methylene group to an imide nitrogen on an adjacent chelate, or the transfer of a hydride ion to Os(IV)}, were considered less likely.

A subsequent study on the oxidative dehydrogenation of $[Os(bpy)_2(ampy)]^{2+}$ (Eq. 31) provided substantial corroboration for this mechanistic scheme, involving the intermediacy of an Os(IV) species of the deprotonated amine [73].

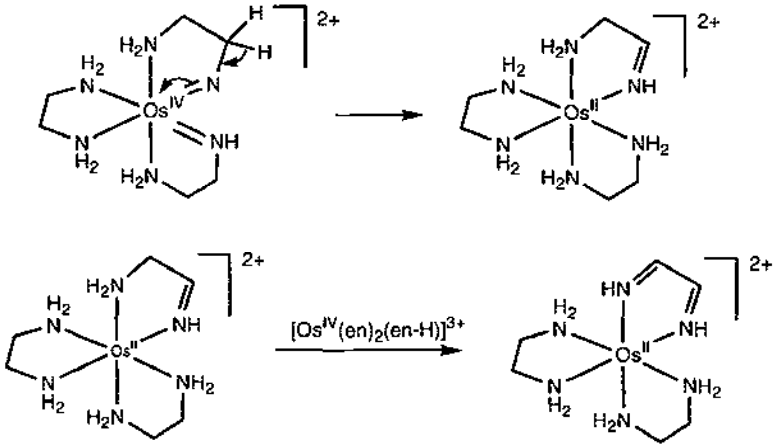


(31)

$$[Os(en)_3]^{3+} + OH^- \leftrightarrows [Os(en)_2(en\text{-}H)]^{2+} + H_2O$$

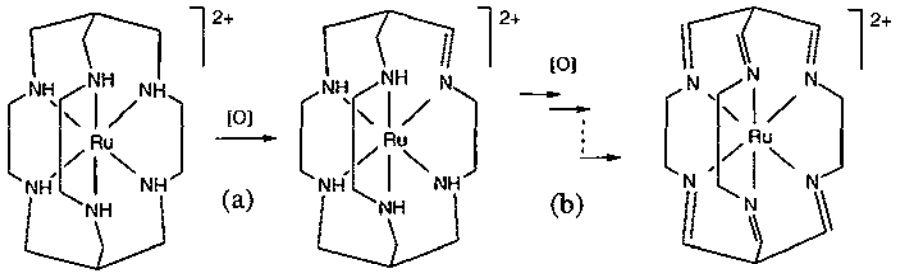
$$[Os(en)_3]^{3+} + [Os(en)_2(en\text{-}H)]^{2+} \leftrightarrows [Os(en)_3]^{2+} + [Os(en)_2(en\text{-}H)]^{3+}$$

$$[Os(en)_2(en\text{-}H)]^{3+} \leftrightarrows [Os(en)_2(en\text{-}2H)]^{2+} + H^+$$



Scheme 4.

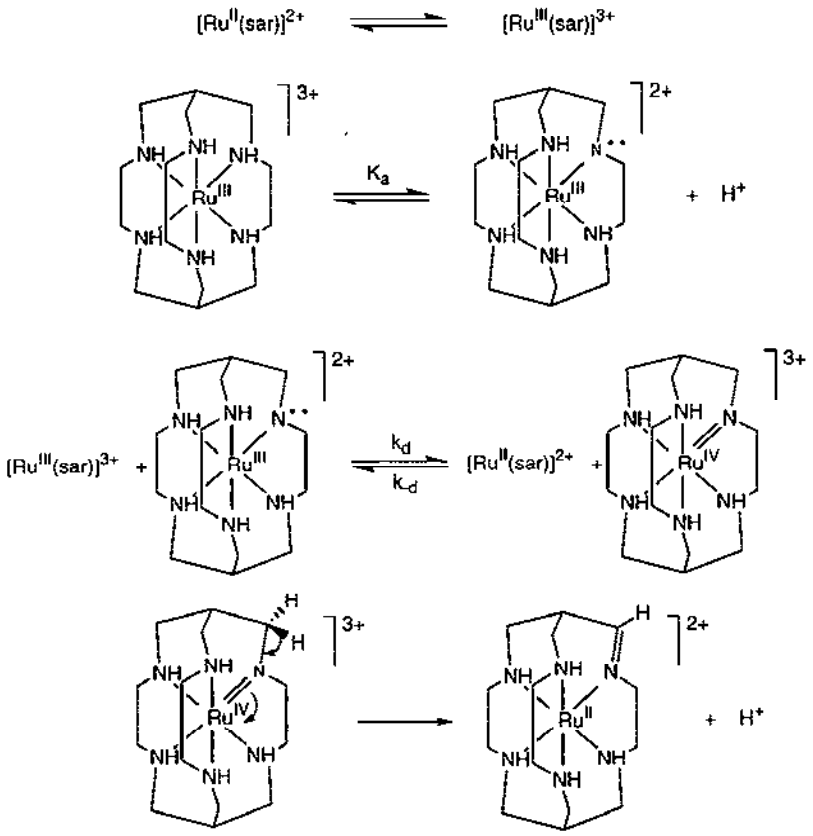
A number of outstanding questions on the mechanism of the dehydrogenation of amine complexes of ruthenium have been addressed by Bernhard, Sargeson and coworkers in their detailed studies of the oxidative dehydrogenation of the $[Ru(sar)]^{2+}$ system {sar = sarcophagine; 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane}, Eq. 32 [25,74–77].



(32)

The first study [76] of the mechanism of this dehydrogenation process proposed a scheme (Scheme 5) analogous to that given previously for the $[Ru(bpy)_2(ampy)]^{2+}$ system [38,39]. Importantly the study with the cage complex allowed the first direct observation of the Ru(IV) intermediate and its first-order decay to the monoimine species.

In addition, the ligand oxidation of $[Ru^{III}(sar)]^{3+}$ is unusual as the process was very rapid in acid solution, whereas in other Ru(III)–amine complexes the reaction was retarded or the Ru(III) species are stable. In this original mechanistic study [76], this unusual feature was rationalized in terms of the formation of a Ru(IV)–



Scheme 5.

hydride species at low pH. To elucidate these points, the Ru(III) complexes (Fig. 5) of the ligands 1,1,1-tris(aminomethyl)ethane (tame) and 1,2-diaminoethane (en) were subsequently investigated since they represented the two different fragments of the cage complex (the 'cap' and the 'body') [25].

In particular, by the study of the $[Ru(tame)_2]^{3+}$ complex, a more complete overall scheme was deduced (Scheme 6), involving a doubly-deprotonated Ru(IV) intermediate in addition to the singly-deprotonated species proposed previously.

In this study, the intermediate $[Ru^{III}(tame)_2\text{-}H^+]^{2+}$ was identified, and importantly the $[Ru^{IV}(tame)_2\text{-}2H^+]^{2+}$ was obtained directly from it by rapid oxidation under highly basic conditions. With the independent assessment of the rate of the intramolecular redox reaction to form the monoimine complex [Ru(tame)(imtame)]$^{2+}$ (k_{2im}) for the doubly-deprotonated intermediate ($1.1 \pm 0.3\ s^{-1}$), the corresponding value for the equivalent reaction of the singly-deprotonated intermediate $[Ru^{IV}(tame)_2\text{-}H^+]^{3+}$ (k_{1im}; $320 \pm 20\ s^{-1}$) and the value of pK_{IV} for the interconversion of the two intermediates (8.2 ± 0.1) could be calculated. The intramolecular ligand oxidation occurs more rapidly for the singly-deprotonated

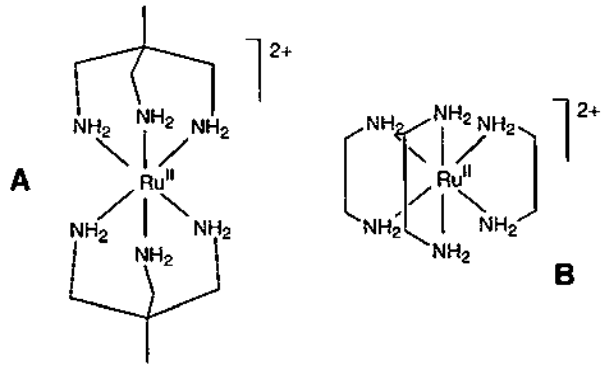


Fig. 5. The systems $[Ru(tame)_2]^{2+}$ (**A**) and $[Ru(en)_3]^{2+}$ (**B**).

form of the Ru(IV) complex than for the doubly-deprotonated form (i.e. $k_{1im} = k_{2im}$). This result is consistent with the fact that the reduction potential of the Ru(IV/III) couple is expected to be more positive for the singly deprotonated form, so that the metal would be a stronger oxidant in this case. The same conclusion had been established in the mechanism of oxidation of $[Os(en)_3]^{2+}$ [28], although the intramolecular oxidation would be expected to be many orders of magnitude faster for Ru centers than the Os analogues because of their relative oxidizing powers.

The rates of the two disproportionation reactions (k_{1d} and k_{2d}) were determined to be of the same order of magnitude (8300 and 3900 $M^{-1}s^{-1}$, respectively), following deprotonation ($pK_{III} = 10.3$).

The corresponding re-examination of the oxidative dehydrogenation of $[Ru(en)_3]^{2+}$ to $[Ru(imen)(en)_2]^{2+}$ revealed a totally analogous mechanistic path to the $[Ru(tame)_2]^{2+}$ system, with rate and equilibrium constants of similar values.

Overall

$$2\,[Ru^{III}(amine)]^{3+} \longrightarrow [Ru^{II}(amine)]^{2+} + [Ru^{II}(imine)]^{2+} + 2H^+$$

$$[Ru^{III}(amine)]^{3+} \overset{K_{III}}{\rightleftharpoons} [Ru^{III}(amine\text{-}H^+)]^{2+} + H^+$$

$$[Ru^{III}(amine)]^{3+} + [Ru^{III}(amine\text{-}H^+)]^{2+} \xrightarrow{k_{1d}} [Ru^{II}(amine)]^{2+} + [Ru^{IV}(amine\text{-}H^+)]^{3+}$$

$$2\,[Ru^{III}(amine\text{-}H^+)]^{2+} \xrightarrow{k_{2d}} [Ru^{II}(amine)]^{2+} + [Ru^{IV}(amine\text{-}2H^+)]^{2+}$$

$$[Ru^{IV}(amine\text{-}H^+)]^{3+} \overset{K_{IV}}{\rightleftharpoons} [Ru^{IV}(amine\text{-}2H^+)]^{2+} + H^+$$

$$[Ru^{IV}(amine\text{-}H^+)]^{3+} \xrightarrow{k_{1im}} [Ru^{II}(imine)]^{2+} + H^+$$

$$[Ru^{IV}(amine\text{-}2H^+)]^{2+} \xrightarrow{k_{2im}} [Ru^{II}(imine)]^{2+}$$

Scheme 6.

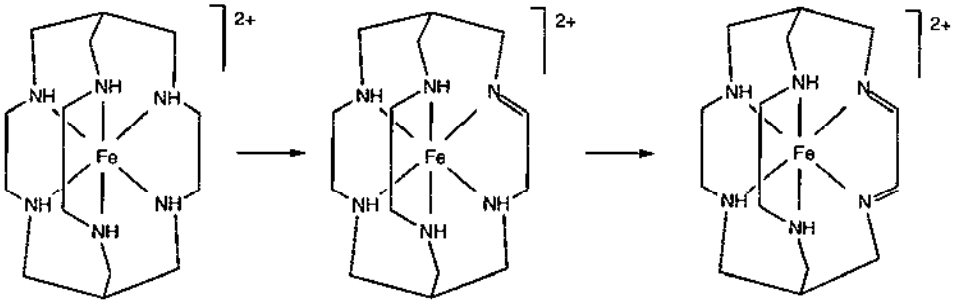
In the light of the elucidation of the mechanistic path for the oxidation of these two systems, the oxidation of $[Ru(sar)]^{2+}$ to $[Ru(imsar)]^{2+}$ (Eq. 32a) was re-evaluated. The kinetic studies are also consistent with Scheme 6, but there are significant differences in the rate parameters for the 'cage' complex and those of its 'cap' and 'body' components: in this case the rates of the disproportionation were much faster $\{k_{1d} = 4 \times 10^7\ M^{-1}s^{-1};\ k_{2d} = \geq 2 \times 10^7\ M^{-1}s^{-1}\}$ and those of the intramolecular redox process much slower $\{k_{1im} = 17\ s^{-1};\ k_{2im} = 5 \times 10^{-4}\ s^{-1}\}$ for the $[Ru(sar)]^{2+}$ system. The values of pK_{III} (6.3) and pK_{IV} (2.0) also indicated higher acidities for the $[Ru(sar)]^{2+}$ system.

Three factors were noted by the authors which determine the differences between the characteristics of the $[Ru(sar)]^{2+}$ system and those of the $[Ru(tame)_2]^{2+}$ and $[Ru(en)_3]^{2+}$ components. Firstly, the lower value of pK_{III} (attributed to relief of strain in the hexadentate system by deprotonation) implies that the deprotonated $[Ru^{III}(sar)\text{-}H^+]^{2+}$ species is more accessible (by a factor of ca. 10^4) than its analogues. Secondly, because the potential of the Ru(III/II) couple is far more accessible for $[Ru(sar)]^{n+}$ (0.29 V vs. NHE) than for $[Ru(tame)_2]^{n+}$ (0.03 V) or $[Ru(en)_3]^{n+}$ (0.15 V), and the favoring of the doubly deprotonated form in the sar system by over five orders of magnitude ($pK_{IV} = 2.0$ cf. 8.2 and 8.9 for the tame and en systems, respectively), the disproportionation reaction is favored kinetically and thermodynamically in the sar system. Thirdly, it is clear that there is greater flexibility in the tame and en systems than in the cage: this inherent strain may be relieved in the cage by forming the Ru^{IV}=N moiety but not necessarily by the formation of the imine product.

The reactions are clearly very complex and are controlled by a variety of factors—the acidities, ligand strain and disproportionation rates of the M(III) state, the inherent rate of oxidation of the M(IV) state and the strain and orientation factors which control the stability of the delocalized M(IV) state, whether or not the M(IV) state is singly or doubly deprotonated, and the stability of the M(II) imine product.

In forming the doubly-deprotonated intermediate, the two deprotonations appear likely to be localized on two separate adjacent ligands, rather than on a single ligand. It is worth briefly revisiting the $[Ru(bpy)_2(ampy)]^{2+}$ [38,39] and analogous alcohol systems [54] in the light of this more complete mechanistic proposal. In both cases, doubly-deprotonated Ru(IV) species cannot form so that the dehydrogenations would be expected to occur via the singly-deprotonated intermediate only, as originally proposed (Scheme 3).

In the paper which addressed the detailed analysis of the oxidation of the $[Ru(sar)]^{3+}$, $[Ru(tame)_2]^{3+}$ and $Ru(en)_3]^{3+}$ systems, it was noted that in the oxidation of the analogous $[Fe(sar)]^{3+}$ system, there was a different regioselectivity such that the imine formed in the five-membered chelate rings in the 'body' of the cage whereas they formed in the 'cap' of the cage in the ruthenium species (Eq. 33) [25,94]. Since the characteristics of the oxidation of the 'cap' and 'body' components are so similar for the ruthenium complexes, the reason for the stereoselectivity in the 'cage' complex is not obvious. Clearly, the interaction of the balance of the factors listed above is a delicate one.



(33)

3.4. The case of iron

There are fundamental similarities in the way in which ruthenium and osmium influence the oxidation of their ligands, in both cases via an intermediate in which there is stabilization of a deprotonated M(IV) center by donation of charge from the ligand to the metal. Such effects would be expected to increase in the order Fe ≪ Ru < Os, by virtue of the radial extension of the d orbitals [95]. Accordingly, the M(IV) oxidation state would be a stronger oxidant, and less accessible, for Fe compared with Ru and particularly osmium [27]. Such an intermediate may be very short-lived in the case of Fe, and probably not observable.

The question of the mechanism of oxidation of amines and alcohols coordinated to iron therefore remains ambiguous. While the earlier kinetic studies were interpreted in terms of the a pathway involving the formation of radical cation intermediates, there seems no reason why the mechanistic path should be fundamentally different from the ruthenium and osmium analogues and it should occur via a Fe(IV) intermediates—albeit the rate and equilibrium parameters would be expected to differ considerably from those observed for ruthenium and osmium systems. This is undoubtedly a question that would benefit from a re-evaluation: one such recent study on the oxidation of the $[Fe(sar)]^{3+}$ system does indeed indicate that an Fe(IV) intermediate species is involved [94,96].

4. Conclusions

The oxidative dehydrogenation of amines and alcohols is promoted by their coordination to metal centers. The initial step in the process is the one-electron oxidation of the metal center, and there is a subsequent intramolecular redox process in which the metal is reduced and the ligand oxidized. The latter process necessarily involves two (or multiples of two) electrons, so that the intramolecular process may take place either by one-electron steps involving ligand-radical species, or alternatively by a path involving higher oxidation states of the metal. Both pathways have been identified: the ligand-radical scheme in dehydrogenations of nickel macrocyclic complexes, and the non-radical scheme in dehydrogenation

reactions involving ruthenium and osmium as the metal center. These two metals are particularly effective in promoting the dehydrogenation of their ligands: this property arises from their ability to attain an oxidation state two units greater than the final state-stabilized by deprotonation and formed by disproportionation—which provides a low-energy pathway for the even-electron processes required in the ligand dehydrogenation processes.

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