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Ozonolysis in coordination chemistry and catalysis: recent advances

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Dedicated to Barry, a good friend since our undergraduate and postgraduate days at Imperial College; a great and original chemist

Contents

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Abstract

Ozone, as produced by conventional commercial silent discharge ozonisers with a dioxygen carrier atmosphere, can be used to prepare in a simple manner a number of coordination complexes of the transition metals, lanthanides and actinides in which the central metal has a high oxidation state. A number of the species thus produced have the potential to function as catalysts for useful and specific homogeneous organic oxidation reactions. Ozone can also be used as an environmentally acceptable co-oxidant for a number of homogeneous metal-catalysed oxidation reactions of organic substrates. Recent developments in all these areas are reviewed here.

Keywords: Ozone; Oxidation catalysis; High oxidation states; Transition metal complexes; Lanthanide and actinide complexes

1. Introduction

1.1. Aims

There is currently much interest in metal-catalysed homogeneous oxidation reactions for organic substrates, particularly those which are heterolytic and thus generally selective in their action. Environmental pressures are such that there is, rightly, an increasing emphasis on the use of environmentally acceptable oxidants such as hydrogen peroxide, which decomposes to water and dioxygen. Ozone is in this class: it has the great advantage that there are no side-products apart from dioxygen; conventional oxidants (e.g. persulfate, peroxomonosulfate, hypochlorite, periodate) will give potentially contaminating side-products (sulfate, chloride, iodate, etc.). In this respect it is rivalled only by dioxygen and hydrogen peroxide but is of course a much more powerful oxidant than these (see Section 1.2.3 below for oxidation potentials of ozone and other oxidants).

The aim of this review is to show how ozone has been used to prepare transition-metal, lanthanide and actinide complexes in which the central atom has a high oxidation state and which in some cases may have the potential for such organic oxidations, and to review systems in which ozone functions as a co-oxidant in the presence of transition-metal catalysts.

It is hoped that this might stimulate further research in an area which is at present rather unexploited and indeed relatively unexplored.

1.2. A brief introduction to ozone

1.2.1. Reviews

The best recent review is that published in Kirk–Othmer's Encyclopaedia, which contains much physical and chemical data [1a]; there is also a useful review by Oyama which appeared after this was submitted [1b]. The older compilation by Horváth et al. [2], while useful, omits references in some cases and does not always give references to original sources.

1.2.2. History and occurrence

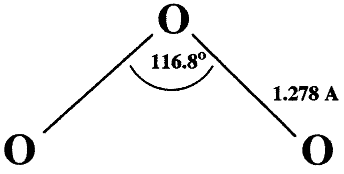
Ozone was discovered in 1840 by Christian Friedrich Schönbein (1799–1868), initially by anodic oxidation of acidified water and later by the passage of oxygen over white phosphorus [3]. It is related [4] that he noted a 'sulphurous smell' after thunderstorms in mountainous areas, and recalled that Homer had twice [5] in the Odyssey and also in the Iliad mentioned such an odour occurring after the gods had hurled thunderbolts. It thus seemed appropriate to Schönbein to give a Greek-based name to the gas; he named it ozone after the Greek οξειν (ozein, to smell; the related Greek word οξμε, osme, a smell, had earlier been used by Smithson Tennant in 1803 to name the metal osmium, since OsO_4 has a rather similar odour). Its correct constitution [6] was however suggested, not by Schönbein but by William Odling in 1861, and the formulation was confirmed by Brodie in 1872 [7].

Ozone is a natural component of the stratosphere (15–25 km high, where it exists at concentrations of 1–10 ppm), being produced there by the action of solar ultraviolet radiation (< 240 nm) on dioxygen. It has an essential function in Nature because it has itself a strong absorption in the ultraviolet at 255.3 nm and thereby protects us from extreme ultraviolet emissions by the sun. The depletion of the 'ozone layer' is of course a matter of great current concern [8,9].

1.2.3. Physical properties

Ozone (trioxygen, O_3, an allotrope of oxygen) is a colourless (or very pale blue) gas, forming a blue liquid (b.p. -111.9°C) and a violet–black solid (m.p. -192.5°C). The colour of the liquid arises from intense absorption bands at 557.4 and 601.9 nm [9]. The infrared spectrum shows three fundamentals, at 1134.9 ($V^s(O_3)$), 1089.2 ($V^{as}(O_3)$) and 716.0 cm^{-1} ($\delta(O_3)$); the corresponding values for $18O_3$ are 1070.0, 1026.5 and 674.8 cm^{-1} [10].

Microwave spectroscopy of the gas in the ground [11] and excited [12] states shows the molecule to be bent triatomic; the structure of the molecule in the ground state is shown below.



Ozone has a characteristic odour, detectable at 0.01 ppm and is very toxic (recent toxicity data have been reviewed [13]). It has strong oxidising properties: the redox potentials in acid, neutral and alkaline solutions are [14]:

$$O_3 + 2H^+ + 2e^- = O_2 + H_2O \quad E_0 = +2.075 \text{ V}$$

$$O_3 + 2H_2O + 2e^- = O_2 + 2OH^- \quad E_0 = +1.246 \text{ V}$$

In water it is unstable with respect to decomposition to oxygen [14]:

$$O_3 + H_2O + 2e^- = 2O_2 + 2H^+ + 2e^- \quad E_0 = -0.383 \text{ V}$$

It is worth noting that the oxidation potentials of other materials often used for production of high oxidation-state metal complexes or for general oxidations are + 2.08 V for persulfate, + 1.81 V for peroxomonosulfate, + 1.70 V for periodic acid, + 1.70 V for permanganate, + 1.7 V for cerium(IV), + 1.76 V for hydrogen peroxide in acid, and + 1.63 V for hypochlorite. The highest potential is + 2.87 V for fluorine [14].

Ozone has a very short lifetime in acid or neutral solutions, but in alkaline solutions there can be a half-life of several hours (presumably ozonide is formed under these circumstances). In alkali metal hydroxides the red ozonide (O_3^-) ion is formed; several of these have been isolated and the recently reported X-ray crystal structure of the NaO_3 has in the anion an O–O distance of 1.353(3) Å, significantly longer than that in ozone itself, as might be expected; however the O–O–O angle of 113.0° is little different [15].

Despite the toxicity of ozone it is widely used industrially, though because of its inherent instability and the hazards associated with it the production of the gas is almost always at, or close to, the point of reaction. This is normally done by the silent electric discharge method in which a current of dioxygen is passed between two closely-spaced electrodes at an applied potential of some 10 kV. It is widely used to purify drinking water, especially in Europe; for treatment of swimming pool water (avoiding the taste and smell associated with chlorine-treated water); treatment of industrial effluent, pulp bleaching, etc. It is also used for some industrial organic processes, e.g. in the perfume industry for production of piperonal; in the polymer industry for production of precursors for nylon [1]; for alkene cleavage and other specialised organic oxidations [1,16] and in general synthetic organic chemistry (see Section 3.1 below).

2. Ozone in the preparation of high-oxidation state coordination complexes

This review is limited to transition metal, lanthanide and actinide chemistry. In this and subsequent sections, 'ozonolysis' or 'ozone' means the use of an ozone-dioxygen mixture, normally provided by a commercial electric discharge ozoniser, rather than of course the action of pure ozone.

Most of the oxidations described in this section take place under ambient conditions and are normally carried out in aqueous solution. As such they do not present undue hazards, though obviously all reactions involving ozone in the laboratory should be carried out with great care in a dedicated, well-ventilated fume cupboard. Some of the reactions described were effected in alkali, and here of course a possible hazard can be the concomitant formation of explosive ozonides. Care should also be taken, if a vacuum line is being used, to avoid condensation in the trap of a purple liquid ozone and oxygen, a highly explosive mixture (the author is indebted to a referee for pointing this out). Standard safety texts should be consulted before attempting any oxidations or reactions involving ozone, and great care should be taken over the choice of organic solvents in particular.

2.1. Transition metals

2.1.1. Group 5 (V)

2.1.1.1. Vanadium. $[VO_4]^{3-}$ is formed when a solution of vanadyl(IV) sulfate in molar KOH is ozonised [17].

2.1.2. Group 7 (Mn)

2.1.2.1. Manganese. Manganese(III) acetates. As with the cobalt(III) acetates considered below there is some doubt as to the structural chemistry of some of the species reported. Manganese(III) acetates are used in organic chemistry as one-electron oxidants for the oxidative addition of acetic acid to alkenes to give γ-butyrolactones; for the oxidation of β-dicarbonyls with acetic acid to the corresponding radicals, and for the α′-acetoxylation of alkenes [18].

$Mn^{III}(OOCCH_3)_3{\cdot}2H_2O$: Manganese (III) acetate, often formulated as $[Mn_3O(OOCCH_3)_6(H_2O)_3](OOCCH_3)$, can conveniently be made by ozonolysis of a suspension of $Mn(OOCCH_3)_2{\cdot}4H_2O$ in glacial acetic acid [17]. On the basis of electronic spectral data it is said that it can also be made in solution by adding an equimolar amount of $Mn(OOCCH_3)_2{\cdot}4H_2O$ to a solution of manganese(II) acetate which has already been ozonised [19].

It is normally made by reaction of $Mn(OOCCH_3)_2{\cdot}4H_2O$ with $KMnO_4$ [20] and may have a μ^3-oxo bridged structure $\{[Mn^{III}O(OOCCH_3)_6]{\cdot}(OOCCH_3)(CH_3COOH)\}_n$. In this the acetato and acetic acid molecules bridge $[Mn^{III}O(OOCCH_3)_6]$ units by hydrogen bonding to give a polymeric structure [21].

$[Mn_3O(OOCCH_3)_6L_3]ClO_4$ (L = py, pic) were made as brown complexes by ozonolysis of $Mn(OOCCH_3)_2{\cdot}4H_2O$ followed by addition of L. Electronic spectra, XRD and magnetic susceptibility data were recorded [22].

$Mn^{III}(pic)_3{\cdot}0.5H_2O$ (pic = picolinic acid, 2-pyrdinecarboxylic acid) is made as a red crystalline material by ozonolysis of a solution of manganese(II) chloride in aqueous picolinic acid. Infrared, Raman, magnetic and mass spectroscopic data were measured [23].

A number of heteropolyoxo complexes containing manganese(IV) are known. Three may very simply be made by ozonolysis.

$K_6[Mn^{IV}Mo_9O_{32}]{\cdot}10H_2O$. The conventional preparation of this dark red complex as the hexahydrate involves heating a solution of $MnSO_4$, $Na_2[MoO_4]$ and 'Oxone', $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$ in an acetate buffer [24]. This time-consuming and tedious procedure can be avoided if an O_3–O_2 mixture is passed though a 12:1 $Na_2[MoO_4]$:$MnSO_4{\cdot}4H_2O$ aqueous solution buffered to pH 4.5 for half an hour at room temperature [17]. It has recently been shown to act as a catalyst, with H_2O_2 as co-oxidant, for the hydroxylation of phenol [25].

$(NH_4)_2[Mn^{IV}Mo_6H_6O_{24}]{\cdot}20H_2O$ is made [17] by ozonolysis of the species formulated as $(NH_4)_4[Mn^{II}Mo_6H_6O_{24}]{\cdot}5H_2O$ [26], though the structure of this material is not clear.

$K_8[Mn^{IV}W_6O_{24}]\cdot 6H_2O$ can be made by ozonolysis of a 12:1 $Na_2[WO_4]$:$MnSO_4\cdot 4H_2O$ mixture of solutions buffered to pH 4.5 with O_3–O_2 [17]. As $Na_2K_6[MnW_6O_{24}]\cdot 12H_2O$ the complex is normally prepared by the prolonged reaction of $Na_2[WO_4]$, $MnSO_4\cdot 4H_2O$ and hot aqueous $K_2S_2O_8$; the X-ray crystal structure was obtained [27a].

$[Mn^{IV}(DPPF_{20})Cl$ ($DPPF_{20}$ = chloro(5,10,15,20)-tetrakis (pentafluorophenyl)-2,3,7,8,12,13,17,18-octaphenyl porphyrinate) [27b]. Evidence from XANES and EXAFS suggest that ozone may coordinate to $Mn(DFFP_{20})$ complexes [27c].

2.1.3. Group 8 (Fe, Ru, Os)

2.1.3.1. Iron. Reaction of ozone with Fe^{2+} is said to give $Fe^{IV}O^{2+}$ as an intermediate (see Section 2.3.3.1 below).

$[Fe^{II}O(DCPP^-)^+$ is said to be formed by ozonolysis of Fe(DCPP)Cl (DCPP = dichloroporphyrinate). The attribution of the formal oxidation state of II in effect implies a reduction rather than the expected oxidation [28].

$[Fe^{III}(CN)_6]^{3-}$ is formed when an aqueous solution of $[Fe(CN)_6]^{4-}$ is ozonised [17].

Prussian Blues. Ozonolysis of forms of these have been studied; in each case the $[Fe^{II}(CN)_6]$ fragment is oxidised to $[Fe^{III}(CN)_6]$, but Mössbauer, infrared and XRD data suggest that the original Prussian Blue skeleton is retained. Thus, ozonolysis of soluble Prussian Blue, $\{KFe^{II}[Fe^{III}(CN)_6\}_n$ gives $\{Fe^{III}[Fe^{III}(CN)_6]\}_n$ [29]:

$$2[KFe^{II}[Fe^{III}(CN)_6]\}_n + nO_3 + nH_2O$$
$$= 2\{Fe^{III}[Fe^{III}(CN)_6]\}_n + 2nK^+ + 2nOH^- + nO_2$$

Ozonolysis of a cobalt-substituted Prussian Blue, $\{Co_3^{II}[Fe^{III}(CN)_6]_2\}_n$ yields the unstable $\{Co_2^{III}[Fe^{III}(CN)_6]\}_n$ while ozonolysis of $\{Co_2^{II}[Fe^{II}(CN)_6]\}_n$ gives a mixed-valence system containing iron(II), cobalt(II) and iron(III) with a Fe^{II}–CN–Co^{II}–NC–Fe^{III} linkage. These conclusions were based on a study of the Mössbauer and infrared spectra of the reactants and products [30].

2.1.3.2. Ruthenium. RuO_4 can very easily be made by ozonolysis of an aqueous solution of $RuCl_3\cdot nH_2O$ or a suspension of $RuO_2\cdot nH_2O$ [17]. There are two patent references on a similar production of RuO_4 from RuO_2 (presumably as the more reactive hydrate) or salts of ruthenium; the RuO_4 so generated was then used to oxidise thioethers and sulphoxides to sulphones [31]. Ozone can be used to treat ruthenium-containing wastes by production and subsequent extraction of RuO_4 [32].

$[RuV^{II}O_4]^-$, the deep green 'perruthenate' ion, can be made by ozonolysis of $RuCl_3\cdot nH_2O$ in a borax buffer at pH 10 [17].

Trans-$[Ru^{VI}(OH)_2O_3]^{2-}$, the bright orange ruthenate ion, is obtained by ozonolysis of $RuCl_3\cdot nH_2O$ or a suspension of $RuO_2\cdot nH_2O$ in M KOH [17].

Cis-$[Ru^{II}(bpy)_2(NCC_6H_5)_2](PF_6)\cdot 2.3H_2O$. An unusual example of ligand rather than metal oxidation by ozone is illustrated here; ozonolysis of the bis-benzylamine complex *cis*-$[Ru^{II}(bpy)_2(NCC_6H_5)_2](PF_6)_2$ yields the above bis-benzonitrile complex [17].

$(PPh_4)_2[Ru_2^{IV}O(\mu\text{-}OCOC_2H_5)_2Cl_6]$. This unusual species was the unexpected product of the ozonolysis of a solution of $RuCl_3 \cdot 3H_2O$ with $(PPh_4)Cl$ in excess propionic acid; the known $(PPh_4)[Ru^{VI}O_2(OCOC_2H_5)_2Cl_2]$ was the anticipated product. The ruthenium(IV) dimer has a modified 'lantern' structure with two bridging propionato ligands and a μ-oxo ligand, as revealed by a single-crystal X-ray structure [17].

2.1.3.3. Osmium. OsO_4 can very easily be made by ozonolysis of an aqueous solution of *trans*-$K_2[Os^{VI}O_2(OH)_4]$ [17].

Cis-$[Os^{VIII}(OH)_2O_4]^{2-}$. This orange material is formed on ozonolysis of a suspension of *trans*-$K_2[Os^{VI}O_2(OH)_4]$ in a molar KOH solution [17].

2.1.4. Group 9 (Co, Ir)

2.1.4.1. Cobalt. $LiM[Co^{IIII}O_6]$ ($M = K, Rb, Cs$) are olive-green compounds, isolated by slow addition of $[Co(H_2O)_6]^{2+}$ under ozone to a dilute alkaline solution at 80°C containing lithium ion and the appropriate alkali metal periodate $M(IO_4)$. Reflectance electronic, infrared, Raman and EXAFS spectra were measured [33].

$K_5[Co^{III}W_{12}O_{40}] \cdot 20H_2O$ is easily prepared by ozonolysis of an aqueous solution of $[Co^{II}W_{12}O_{40}]^{6-}$ [23]. It is normally prepared by reaction of sodium tungstate, cobalt acetate at pH 7 (which gives $[Co^{II}W_{12}O_{40}]^{6-}$) and $K_2S_2O_8$ [34]; the X-ray crystal structure has very recently been re-determined [35].

2.1.4.2. Cobalt(III) acetates. A number of methods, including ozonolysis, have been used to make complexes believed to contain cobalt(III) acetate. The reaction is complicated with a number of products being formed from relatively minimal changes in reaction conditions. A useful review of earlier work in this area has been given [36].

Cobalt(III) acetates are useful in organic synthesis as one-electron oxidants for the oxidation of hydrocarbons to the corresponding acetates or, in the presence of halides, as halogenating reagents. Alkenes and dienes are oxidised to the 1,2-diol monoacetates. Benzylic alcohols are oxidised to aldehydes and secondary aromatic alcohols to ketones [37].

$[Co_2^{III}(\mu\text{-}(OH)_2))(OOCCH_3)_4] \cdot (CH_3COOH)]$ has been made by ozonolysis of a dispersion of cobalt(II) acetate in glacial acetic acid. Infrared and electronic spectra were reported as well as the magnetic susceptibility in the solid state and in solutions, and a dinuclear structure was proposed with four bidentate acetate groups, two per cobalt atom, these two metal atoms being linked by two bridging hydroxo ligands [38].

$[Co^{II}Co_2^{III}O(OOCCH_3)_6(CH_3COOH)_3]$ is thought to be the structure of the dark-green species made by ozonolysis of a solution of cobalt(II) acetate in glacial acetic acid. Polarographic studies showed the Co(III) to Co(II) ratio to be 2:1, and electronic and infrared spectra of the product were recorded, as were magnetic susceptibility data. A structure in which three cobalt atoms, bridged by six acetato ligands, surround a μ^3-oxo ligand, with the three remaining coordination positions on each octahedrally coordinated cobalt centre being occupied by acetic acid ligands. A qualitative molecular-orbital diagram was proposed [39].

$[Co_3^{III}O(OOCCH_3)_6(L)_3]$ (L = py, pic) were made as dark green materials by ozonolysis of cobalt(II) acetate in acetic acid followed by addition of pyridine and sodium perchlorate. A μ^3-oxo centred structure with three cobalt atoms bridged by three acetato groups was suggested, with each metal atom bridging a bidentate acetato ligand and a pyridine ligand. The complexes are diamagnetic; electronic spectra and XRD data were recorded [22].

$[Co_3^{III,III,II}(OOCCH_3)_6](CH_3COOH)$ may be one of the species formed by reaction of the product of the reaction between $Co^{II}(OOCCH_3)_2{\cdot}4H_2O$ in glacial acetic acid with ozone; EXAFS data were recorded [36].

$[Co_8O_4(OOCCH_3)_6(OCH_3)]Cl_4(OH_n)_4{\cdot}6H_2O$ ($n = 1$ or 2). This mixed-valence oligomer was made by recrystallisation from methanol-dichloromethane-diethyl ether of the product of the reaction between $Co^{II}(OOCCH_3)_2{\cdot}4H_2O$ and ozone in acetic acid (as made by the method of Wilkinson et al. [22]). The X-ray crystal structure was obtained, and the corresponding bromo analogue was also prepared [40].

2.1.4.3. Iridium. $(^nBu_4N)_2[Ir^{IV}Cl_6]$ has been made by ozonolysis of $IrCl_3$ in dilute HCl (pH 2) [17].

2.1.5. Group 10 (Ni, Pd, Pt)

2.1.5.1. Nickel. Reaction of KIO_4 and KOH with ozone, with subsequent addition of $Ni(NO_3)_2$, is said to give the red '$[Ni^{IV}(OH)_2(HIO_6)_2]^{4-}$'. This formula would imply the presence of nickel(VI) which is very unlikely; $[Ni^{IV}(OH)_2(HIO_6)_2]^{6-}$ would be the correct formulation Electronic spectra were measured; kinetics of the spontaneous reduction of the complex were measured [41].

2.1.5.2. Palladium. $(^nBu_4N)_2[Pd^{IV}Cl_6]$ is easily isolated by passage of ozone through $PdCl_2$ in dilute HCl (pH 2) [17].

2.1.5.3. Platinum. $K_2[Pt^{IV}Cl_6]$ was made, in perhaps the earliest instance of a high oxidation state complex being made by ozonolysis, by Chugaev and Chlopin in 1926, by ozonolysis of $K_2[Pt^{II}Cl_4]$ [42]. The *n*-tetrabutylammonium salt $(^nBu_4N)_2[Pt^{IV}Cl_6]$ was made by ozonolysis of $K_2[Pt^{II}Cl_4]$ in dilute HCl at pH 2 with $(^nBu_4N)Cl$ [17].

$K_2[Pt^{IV}Cl_6]$, $[Pt^{IV}(en)_2Cl_2]Cl_2$ and $[Pt^{IV}(NH_3)_4Cl_2]Cl_2$ have been made by ozonolysis of $K_2[PtCl_4]$, *cis*-$[Pt(en)_2]Cl_2$ and $[Pt(NH_3)_4]Cl_2$ in HCl, while $[Pt^{IV}(NH_3)_4Cl_2]Cl_2$ was made by ozonolysis of *cis*-$[Pt(NH_3)_2Cl_2]$ in NH_4OH and $(NH_4)_2CO_3$ [42].

Unspecified and ill-defined platinum(IV) superoxo complexes have been claimed from ozonolysis of $[Pt(OH)_6]^{2-}$. In highly basic solutions ($[OH^-] > 5$ M) pink species are formed and may be binuclear complexes containing bridging, superoxo ligands. At lower pH intensely blue species are formed. For these complexes electronic and ESR spectra together with cyclic voltammetric data were reported [43].

2.1.6. Group 11 (Cu, Ag, Au)

2.1.6.1. Copper. Alkaline solutions containing copper(II) hydroxide are said to give CuO on ozonolysis although this is not an obvious oxidation; other copper(II) species are not affected by ozone (chloride, sulfate, nitrate, carbonate) [44]. The effect of ozonolysis on unspecified copper(II) chelate complexes EDTA, NTA (nitriloacetic acid) and glycine has been reported for pH 4–10. Attack on coordinate EDTA occurs by electrophilic attack of ozone on the lone pairs of the donor nitrogen atoms, and NTA and glycine are amongst the decomposition products [45].

$Ba_3K[Cu^{III}(HIO_6)_2]\cdot 0.5KOH(OH)_2\cdot 8H_2O$ and $Ba_4K[Cu^{III}(H_2TeO_6)_2](OH)_4\cdot-6H_2O$ have been made by ozonolysis of a solution of KIO_4 or H_6TeO_6 in KOH to which was added a solution of copper(II) nitrate. Infrared, XRD and diffuse electronic spectra were measured [46].

2.1.6.2. Silver. Ozone has sometimes been used to prepare silver(II) complexes from their silver(I) precursors, though classically persulfate has been used for this purpose. The formation of silver (II) and silver(III) complexes has been reviewed [47]. Early work showed that a black 'silver(II) nitrate' was formed in solution when a solution of $AgNO_3$ in concentrated nitric acid was ozonised, though total oxidation of Ag(I) to Ag(II) was not effected [48].

$[Ag(bpy)(NO_3)_2]$ has been made by ozonolysis of $[Ag(bpy)_2](NO_3)$ in 5 M HNO_3; the X-ray crystal structure of the complex was reported, and showed a distorted octahedral structure with a bidentate bipyridyl group coordinated to each silver atom, a monodentate and a bridging nitrato ligand [49].

$[Ag(bpy)_2]X_2$ ($X = NO_3$, ClO_4, ClO_3) is made by ozonolysis of $[Ag(bpy)_2]X$ in nitric acid followed by addition of excess NaX [50].

$[Ag(phen)_2]X_2$ ($X = NO_3$, ClO_4) can be been made by ozonolysis of $[Ag(phen)_2]X$ in neutral solution [51].

$Ag(pic)_2$, $Ag(nic)_2$, $Ag(isonic)_2\cdot H_2O$, $Ag(cincH)_2\cdot H_2O$; $Ag(isocincH)_2$, $Ag(quinH)_2\cdot 2H_2O$, $Ag(dipic)(dipicH_2)\cdot 2H_2O$, $Ag(dinicH)_2$, $Ag(lutH)_2\cdot 3H_2O$.

All these silver(II) complexes of pyridinecarboxylic acids (pic = picolinic (pyridine-2-carboxylic) acid; nic = nicotinic (pyridine-3-carboxylic) acid; isonic = isonicotinic (pyridine-4-carboxylic) acid; cinc = cinchomeronic (pyridine-3,4-dicarboxylic) acid; isocinc = isocincomeronic (pyridine2,5-dicarboxylic) acid; quin = quinolinic (pyridine-2,3-dicarboxylic) acid; dipic = pyridine-2,6-dicarboxylic) acid; dinic = dinicotinic (pyridine-3,5-dicarboxylic) acid; lut = lutidinic (2,6-dimethylpyridine-3-carboxylic) acid. These were all made by ozonolysis of a solution of silver(I) nitrate in an aqueous solution of the appropriate acid. The colours vary from red to cream; infrared and mass spectra were measured as well as magnetic susceptibilities [23].

Some of these complexes have also been made by Banerjee and Ray using persulfate as the oxidant [52]. The single crystal X-ray structure of $Ag^{II}(dipic)(dipicH_2)$, made in that instance by persulfate oxidation, shows a distorted octahedral configuration with coordination from the tridentate picolinate ligands, one neutral and one dianionic. The two N atoms are *trans* to each other [53]. The complex $Ag(quin)_2{\cdot}2H_2O$ has a tetragonally distorted octahedral structure if the two weakly bound axial aqua molecules are taken into account [54].

AgO can be made (mixed with Ag_2O) by the action of ozone on silver metal, or by ozone on Ag_2O. In neither case is Ag_3O_4 produced. The reference contains useful thermochemical data on ozone [55].

2.1.6.3. Gold. $(Me_4N)[Au^{III}Cl_4]$ has been prepared by ozonolysis of $(Me_4N)[Au^{I}Cl_2]$ in aqueous HCl at pH 2 [17].

2.1.7. Lanthanides (Ce, Pr, Tb)

2.1.7.1. Cerium. Oxidation of $Ce(NO_3)_3$ in acetonitrile in the presence of Ph_3PO gave initially intense purple species, thought to contain mixed cerium(III)/(IV) species; eventually pale yellow cerium(IV) complexes were formed. Electrochemical and electronic spectral measurements were made [56].

$Na_8[Ce^{IV}W_{10}O_{36}]{\cdot}8H_2O$ is formed by ozonolysis of an aqueous solution of $Na_9[Ce^{III}W_{10}O_{36}]{\cdot}6H_2O$ in HCl at pH 2 [17].

2.1.7.2. Praseodymium. Oxidation of $Pr(NO_3)_3$ in acetonitrile in the presence of Ph_3AsO gave a golden-yellow Pr(IV) species after four hours; with Ph_3PO no such oxidation was observed. Electrochemical data and electronic spectra were reported [56]. Oxidation of Pr(III) in alkali with $Na_4P_4O_{12}$ is said to give the yellow–brown Pr(IV): addition of cerium(III) accelerates the oxidation. Kinetics of the decay of Pr(IV) back to Pr(III) were also studied [57].

2.1.7.3. Terbium. Terbium(IV) can be produced by ozonolysis of $Tb(NO_3)_3$ with $Na_4P_4O_{10}$ in aqueous solution buffered to pH 11–12.7. The red-brown solution is stable for some 2 weeks. The species was not identified; the kinetics of its reduction was studied [58,59].

An unidentified orange-brown complex has been reported, made by ozonolysis of $TbCl_3$ in 1–5 M K_2CO_3 and 0.1–0.6 M KOH solutions. Raman and infrared spectra were measured as were cyclic voltammograms, and it was thought that a polymeric carbonato-hydroxy polymer of terbium(IV) or a mixed terbium(IV)/(III) species was formed [60]. It was also suggested that the product of this reaction is $TbO_2{\cdot}xH_2O$ [61].

Oxidation of $Tb(NO_3)_3$ in acetonitrile in the presence of Ph_3AsO gave a yellow terbium(IV) species [56]. A terbium(IV) species has also been made by ozonolysis of a terbium(III) orthotellurate complex, and the kinetics of its reduction back to terbium(III) were measured using electronic spectroscopy [62].

2.2. Actinides (U, Np, Pu, Am, Bk)

There has been a considerable amount of work on ozonolysis of some of the actinides, particularly by Russian workers in the 1950–1990 period, principally for the separation of some of these for radiochemical purposes. Much work (Section 2.5) has been carried out on the kinetics of such reactions.

2.2.1. Uranium

$UO_3 \cdot 0.8H_2O$ is made by ozonolysis at 90°C of an aqueous suspension of $U(OH)_4$ (or, more slowly, U_3O_8). It is yellow [63].

2.2.2. Neptunium

$Np^{VI}O_3 \cdot 2H_2O$ (chocolate-brown) and $Np^{VI}O_3 \cdot H_2O$ (red–brown) have been made by ozonolysis of a suspension of $Np(OH)_5$ in water at 18° and 90°C respectively [63]. However it appears that $Np^{VI}O_3 \cdot 2H_2O$ made in this way is contaminated with some Np(VII) if made from $Np(OH)_3$ suspended in water at 90°C from pH 8–10.6 after ozonolysis. At pH 14 some 80–100% of heptavalent neptunium is formed in this way [64].

$M[Np^{VII}O_4]$ ($M = Rb$, Cs) were made by ozonolysis of $Np^V(OH)_5$ in 1–3 M MOH; the effect of ultrasound on the reaction was studied. Infrared spectra and XRD data were given, as were the infrared spectra of the lithium and potassium salts [65].

$M_3[Np^{VII}(OH)_2O_4] \cdot xH_2O$ were isolated as dark-green materials by ozonolysis of $Np(OH)_5$ in solutions containing > 3 M RbOH or CsOH. Their infrared spectra were measured [65].

A mixed Np(VII)–Np(VI) species, formulated as $NpO_2(OH)NpO_4 \cdot 4H_2O$, can apparently also be obtained by ozonolysis of moist $Np(OH)_5$ [66]. Unspecified Np(VII) complexes are obtained when $Np^{IV}(OH)_4$ is suspended in 0.5–8 M NaOH and ozone passed; such reactions may be carried out at even higher hydroxide concentrations, e.g. 14 M NaOH. The product was detected spectrophotometrically [67]. In buffers of pH 4–8 Np(VII) is found after ozonolysis of aqueous solutions of $NpO_2(ClO_4)_2$ unspecified cobalt or silver materials did not catalyse the oxidations [68].

2.2.3. Plutonium

$PuO_3 \cdot 0.8H_2O$ is formed as a reddish-gold material by ozonolysis of $Pu(OH)_4$ in water at 90°C. [63].

$Na[Pu^{VI}O_2(OOCCH_3)_3]$ can be made by ozonolysis of plutonium(IV) nitrate in nitric acid followed by addition of sodium acetate. It was suggested that the two ‘plutonyl’ oxo ligands are derived from ozone [69].

$M[PuO_4]$ ($M = Rb$, Cs) are formed, albeit in much lower yields than the corresponding neptunium complexes, by ozonolysis of $Pu(OH)_5$ in 1.5–3 M RbOH or CsOH solutions [65]. An unspecified Pu(VII) species is formed when a suspension of $Pu(OH)_4$ is suspended in 0.5–8 M NaOH and ozone passed; the product was detected spectrophotometrically [67].

2.2.4. Americium

Formation of americium(VI) carbonato complexes has been observed on ozonolysis of Am(III) or Am(V) solutions in carbonate-bicarbonate solution; electronic and infrared spectra were recorded [70]. Oxidation of Am(V) to Am(VI) by ozone has been studied at room temperature in molar HNO_3, and the rate of oxidation is accelerated by ultrasound at room temperatures. It was suggested that the reactions

$$\mathrm{Am(V)} + \mathrm{O_3} + \mathrm{H^+} = \mathrm{Am(VI)} + \mathrm{HO_3}^{\bullet}$$

$$\mathrm{HO_3} = \mathrm{O_2} + \mathrm{OH}^{\bullet}$$

occurred. Attempts to oxidise Am(III) by ozonolysis with ultrasound in 0.01–0.1 M $HClO_4$, HNO_3, H_2SO_4 or H_3PO_4 were unsuccessful [71].

Oxidation of Am(III) to Am(IV), Am(V) and Am(VI) can be effected by ozonolysis in an aqueous solution of sodium paratungstate (formulated as $Na_5H[W_6O_{21}]$); formation of the unspecified species was shown spectrophotometrically [72].

2.2.5. Berkelium

Ozonolysis of Bk(III) in 0.05–10 M HNO_3 to Bk(IV) has been studied; OH radicals are likely to be involved [73].

2.3. Kinetics of ozone-induced oxidations catalysed by coordination complexes

There is a brief review on this topic [74] and there is also a useful though rather out-of-date bibliography of kinetic aspects of the reactions of inorganic species in aqueous solution with ozone from 1913–1981 [75]. The kinetics of the deactivation by ozone of a variety of complexes of cobalt(II), nickel(II), Cu(II), Cr(III), Mn(III), Fe(III), Co(III), Pd(II) and Pt(II) with dithiocarbamate, dithiophosphate and acetylacetonate ligands have been studied, though the products were not identified [76].

In most of the papers referred to in this section metal species, which are mostly in aqueous media albeit at a variety of pH values, are referred to as M^{n+}; presumably in at least some of these cases the aqua complex $[M(H_2O)_x]^{n+}$ is involved. Rather than use this ionic form with its attendant uncertainties, in this section Roman numerals are used, e.g. Bk^{3+} is referred to as Bk(III), unless overall equations are presented, in which case for simplicity the ionic forms are used.

2.3.1. Group 6 (Cr)

2.3.1.1. Chromium. Kinetics of the oxidation of $Cr(OH)_3$ in H_2SO_4 to give chromium(VI) have been measured; the rate of oxidation is much increased by addition of manganese(II) sulfate [77]. The function of the manganese(II) catalyst has been investigated; it is thought that, in its oxidation to manganese(III), OH radicals are produced which effect the oxidation of the chromium. Both Cr(IV) and Cr(V) are thought also to be involved [78].

2.3.2. *Group 7 (Mn, Re)*

2.3.2.1. Manganese. Kinetics of the oxidation of Mn(II) and Mn(III) in 11.5 M H_2SO_4 were studied spectrophotometrically [79]. The overall stoichiometry is thought to be

$$2Mn^{2+} + O_3 + 2H^+ = 2Mn^{3+} + O_2 + H_2O$$

and

$$2Mn^{3+} + O_3 + 2H^+ = 2Mn^{4+} + O_2 + H_2O$$

Kinetics of the oxidation of $[Mn(H_2O)_6]^{2+}$ by ozone in $HClO_4$ and H_2SO_4 were followed using spectrophotometric, pulse radiolysis and stopped-flow procedures. It was shown that an oxygen atom transfer to give the 'manganyl' ion $Mn^{IV}O^{2+}$ is likely, without formation of OH radicals:

$$Mn^{2+} + O_3 = MnO^{2+} + O_2$$

and this is followed by a fast reaction of the manganyl ion with Mn(II) to give the product, Mn(III):

$$MnO^{2+} + Mn^{2+} + 2H^+ = 2Mn^{3+} + H_2O$$

Eventually the Mn(III) disproportionates to Mn(II) and MnO_2. At $pH > 3.0$ MnO_2 is formed and, with excess ozone, $[MnO_4]^-$ [80].

There is a brief mention of the kinetics of the ozonolysis of manganese(II) acetate in acetic acid to Mn(III) and Mn(IV) [19].

2.3.2.2. Rhenium. The oxidation of *trans*-$[Re^VO_2(en)_2]^+$ by ozone to $[Re^{VII}O_4]^-$ has been studied. Tracer studies with $H_2^{18}O$ show that two oxygen atoms are transferred to $[ReO_4]^-$, 1.62 atoms are from the water solvent, so that ca. 0.4 oxygen atoms from ozone are involved. No mechanism could be adduced for this observation [81].

2.3.3. *Group 8 (Fe, Ru)*

2.3.3.1. Iron. There has been much interest in this area. In particular there has been much work on the reaction of ozone with iron(II) and there is a large literature on the topic; only recent references are given here.

Stopped-flow work on the reaction of Fe(II) (presumably as $[Fe(H_2O)_6]^{2+}$) from pH 0–2 gives the 'ferryl' ion $Fe^{IV}O^{2+}$ as a transient intermediate, detectable by its electronic spectrum. The basic reaction is thought to be

$$Fe^{2+} + O_3 = FeO^{2+} + O_2$$

followed in the presence of excess Fe^{2+}, by oxygen atom transfer from O_3 to Fe^{2+}:

$$2FeO^{2+} + H_2O = 2Fe^{3+} + OH^- + OOH^-$$

With excess ozone a more complex sequence of reactions occurs, again leading to Fe^{3+}. A composite mechanism was proposed, accounting for all the observed kinetic data [82].

The kinetics of oxidation of the reaction of ozone with aqueous $FeSO_4$ in neutral [83] and acid [83,84] media were studied by measurement of ozone uptake. The overall reaction is

$$2Fe^{2+} + O_3 + 2H^+ = 2Fe^{3+} + H_2O + O_2$$

The intermediate formation of an iron-ozone or iron-ozonide complex was proposed, with decomposition to OH radicals which effects the oxidation of Fe(II) to Fe(III) [83].

Kinetics of the oxidation of Fe(II) by ozone in $HClO_4$ at pH 0–3 from 5–40°C [84] and from 10–25°C [85] have been studied by stopped-flow methods; the formation and decay of $Fe^{IV}O^{2+}$ were indicated [84]. Reaction of Fe^{2+} and FeO^{2+} gives the dimer $[Fe^{III}(OH)_2Fe^{III}]^{4+}$ and Fe^{3+} [84].

Kinetics of the oxidation of $[Fe(trpy)_3]^{2+}$ to $[Fe(trpy)_3]^{3+}$ by ozone in perchloric acid were studied by stopped-flow methods. The reaction is thought to involve electron transfer as the first step with production of an ozonide radical

$$[Fe^{II}(trpy)_3]^{2+} + O_3 = [Fe^{III}(trpy)_3]^{3+} + O^{3-}$$

This then produces the OH radical which effects the oxidation of Fe(II) to Fe(III). Addition of NaCl accelerates the reaction; it was suggested that Cl^- scavenges the OH radical to give Cl^{2-} radicals which further oxidises $[Fe(trpy)_3]^{2+}$ [86].

2.3.3.2. Ruthenium. The kinetics of oxidation of Ru(III), Ru(IV) and Ru(II)(NO) complexes in nitric acid by ozone have been measured; in all cases the final product is the tetroxide $Ru^{VIII}O_4$; the $[RuO_2(O_3)]^{2+}$ species was proposed as an intermediate [87]. Kinetics of the oxidation of Ru(IV) in nitric acid have been measured spectrophotometrically; the formation of a $Ru^{IV}O \cdots O_3^{2+}$ intermediate was proposed as the rate-determining step. The $Ru^{VI}O_2^{2+}$ species, postulated as the product of ozonolysis of Ru(IV) in molar nitric acid was not detected, although there was some evidence for its existence in 15 M nitric acid [88].

2.3.4. Group 9 (Co, Ir)

2.3.4.1. Cobalt. Kinetics of the formation of cobalt(III) acetate by ozonolysis of $Co^{II}(OOCCH_3)_2$ in glacial acetic acid have been studied spectrophotometrically. The possible intermediacy of cobalt(IV) was discussed [19].

2.3.4.2. Iridium. Kinetics of the oxidation of the reaction

$$2[IrCl_6]^{3-} + O_3 + 2H^+ = 2[IrCl_6]^{2-} + O_2 + H_2O$$

have been measured spectrophotometrically. The initial step seems to be an outer-sphere electron-transfer from $[IrCl_6]^{3-}$ to ozone, followed by rapid protonation of O_3^- (ozonide), and oxidation of a second molecule of $[IrCl_6]^{3-}$ by HO_3 or OH [89].

2.3.5. Group 10 (Pd)

2.3.5.1. Palladium. Kinetics of the oxidation of chloro complexes of palladium(II) to palladium(IV) have been studied. The reactivity decreases in the sequence $[PdCl_4]^{2-} > [PdCl_3]^- > PdCl_2 > [PdCl]^+ > Pd^{2+}$ [90].

2.3.6. Group 11 (Ag)

2.3.6.1. Silver. Kinetics of the oxidation of silver(I) to silver(II) in M $HClO_4$ has been investigated spectrophotometrically and rate constants evaluated [91]. For the oxidation of Ag^+ in nitric acid a free-radical mechanism involving OH radicals was proposed [92]; there are early data on the kinetics of oxidation of silver(I) to solver(II) nitrate in 1–21 M HNO_3 solution [93].

2.4. Lanthanides (Ce)

2.4.1. Cerium

Kinetics of the oxidation of cerium(III) to cerium(IV) in 0.1–10 M H_2SO_4 [94] and in 4 M HNO_3 [95] have been measured using spectrophotometric and reductimetric methods. Two parallel reactions are thought to be involved [95]:

$$2Ce^{3+} + 2H^+ + O_3 = 2Ce^{4+} + H_2O + O_2$$

and

$$4Ce^{3+} + 4H^+ + O_3 = 4Ce^{4+} + 2H_2O + 0.5O_2$$

Similarly kinetics of the oxidation of cerium(III) to cerium(IV) in nitric and sulfuric acids, and also in K_2CO_3 solutions, were studied spectrophotometrically as a model for oxidation of berkelium(III) to berkelium(IV) by ozone [96]. The effect of cerium(IV) in 3 M HNO_3 on the decomposition of ozone has been briefly considered [92].

2.5. Actinides (U, Pu, Bk)

2.5.1. Uranium

Early work [97] on the slow oxidation of aqueous U(IV) in 0.02–0.4 M $HClO_4$ suggests that in acid solution the overall reaction is slow, with the overall stoichiometry

$$U^{4+} + O_3 + H_2O = UO_2^{2+} + O_2 + 2H^+$$

It was subsequently suggested that an inner-sphere mechanism might operate, with a one-electron oxidative addition of ozone to U(IV) to give a monodentate ozonide intermediate [89a].

2.5.2. Neptunium

Kinetic data on the oxidation of neptunium(IV) to $\mathrm{Np^{VI}O_2^{2+}}$ by ozone have recently been given. The mechanism is thought to be similar to that for plutonium(IV) oxidation (see 2.5.3 below) [89b].

2.5.3. Plutonium

In the oxidation of Pu(III) to $\mathrm{Pu^{VI}O_2^{2+}}$ in aqueous solution in 0.25 M $HClO_4$ in ^{18}O-enriched water it appears that the ratio of oxygen atoms derived from water and from the ozone is ca. 1:1 [98]. Kinetics were measured of the rates of oxidation of Pu(IV) to Pu(VI) by ozone in 0.2 M HNO_3 using a spectrophotometric procedure. A rate law was determined, rate constants and activation energies; the reaction is thought to proceed via Pu(V) which is further oxidised to Pu(VI) [89b,99].

The oxidation of $\mathrm{[Pu^{IV}(OH)_3]^+}$ to Pu(VI) in HNO_3 was studied spectrophotometrically and the role of hydrolysis investigated [100].

2.5.4. Berkelium

Kinetics of the oxidation of Bk(III) to Bk(IV) in M, 9–10 M HMO_3 and in 0.05 M K_2CO_3 solutions were studied spectrophotometrically, with precipitation of ^{249}Bk and ^{144}Ce with zirconium phosphate in 9 M $HMNO_3$ using the Ce(III)/Ce(IV) couple (which has a similar potential) as a carrier [96]. The stability of Bk(IV) made by ozonolysis of Bk(III) in 9 M HNO_3 has been studied and rate constants were determined [101].

3. Ozone as a co-oxidant in metal-catalysed reactions

3.1. Ozone in organic chemistry

Ozone has been used for specific organic reactions for a long time. Schönbein was the first to show that alkenes were cleaved by it. Although now rather old, the two volumes by Bailey are still the best review of this aspect of ozone chemistry [102]; there is also a book by Razumovskii and Zaikov [103] and useful recent reviews by Berglund [16] and by Oyama [1b]. The latter concentrates on heterogeneous catalysed ozonolysis [1b]. Its principal application is as a stoichiometric oxidant for the cleavage of alkenes to carbonyl compounds or alcohols, depending on the workup procedures; the celebrated ‘Criegee mechanism’ is involved in this [104]. Ozonation of alkynes gives carboxylic acids or, if reductive procedures are used, α-carbonyl compounds. It has also been used for the oxidation of alcohols (in particular secondary alcohols), ozonation of aromatic compounds and of heteroatoms [16].

In this section we consider only the fledgling area of ozonolysis catalysed by transition metal complexes.

3.1.1. Alkane oxidations

Oxidation of *o*-xylene to *o*-toluic and *o*-phthalic acids, *m*-xylene to *m*-toluic acid and isophthalic acid, *p*-methoxytoluene to *p*-anisic acid and phthalide to phthalic anhydride is effected by ozone in the presence of cobalt(II) acetate. The involvement of cobalt(III) acetate was shown [105]. Cobalt(II) acetate also catalyses the oxidation of *p*-nitrotoluene to *p*-nitrobenzoic acid; acetates of manganese(II), chromium(III) and palladium(II) are partially effective also, but cobalt(II) acetate is the most efficient. A mechanism involving cobalt(III) was presented and kinetic data collected; the presence of bromide accelerates the reaction [106].

The hydroxylation of ethylbenzene to sec-phenylethyl alcohol by ozone in the presence of Fe(TMP)Cl (TMP = tetramesityl porphyrin) and substituted TMP porphyrin analogues was studied and the nature of the axial ligands varied in Fe(TMP)X (X = F, Cl, AcO, CF_3CO, ClO_4, MeOH); the methanol complex completely inhibits catalysis of this reaction. Catalysis was also studied using $Fe(Br_8{-}TMP)Cl(Br_8{-}TMP$ = 2,3,7,8,12,12,17,18 - octabromo - 5,10,15,20 - dichlorophenyl)porphyrinate) and Fe(TDCPP)Cl (TDCPP = 5,10,15,20-tetra-(2,6-dichlorophenyl)porphyrinate) [107]. The axial ligands affect both the reactivity of the catalyst and its stability towards ozone; in particular methanol has an inhibitory effect as an axial ligand on the reactivity of the catalyst. Halogenation of the phenyl rings in these porphyrin catalysts improves both the ozonolytic reactivity and stability of the catalyst more than does halogenation of the pyrrole hydrogen atoms.

Iron(III) porphyrin complexes with halogen substituents at the β-pyrrole positions are poorer catalysts than porphyrins not so substituted for catalysis of ethylbenzene hydrolysis. Of such substituted species the most effective is Fe(TDCPP)Cl [108].

Manganese-substituted polyoxometalates such as $Li_{12}[Mn_2^{II}ZnW\{ZnW_9O_{34}\}_2]$ are effective catalysts for the oxidation of alkanes to ketones in aqueous media; alkanes so studied were ethylbenzene, diphenylmethane, tetrahydronaphthalene, cumene, cyclohexane, cyclo-octane, *cis*-decalin and *n*-decane. Other polyoxometalates used were $K_5[PMn^{II}W_{11}O_{39}]$, $K_6[SiMn^{II}W_{11}O_{39}]$, $K_6H_6[SiMn_2^{II}W_{10}O_{40}]$ and $K_{10}[Mn_4^{II}\{PW_9O_{34}\}_2]$ were of similar efficiency, while $K_x[M_2ZnW\{ZnW_9O_{34}\}_2]$ and $K_y[SiMW_{11}O_{39}]$ (M = Co^{II}, Cu^{II}, Zn^{II}, Cr^{III}, Fe^{III}, Ru^{III}) showed no catalytic effect. For the yellow $[Mn_2^{II}ZnW\{ZnW_9O_{34}\}_2]^{12-}$ it appears that the pink $[Mn_2^{III}ZnW\{ZnW_9O_{34}\}_2]^{9-}$ is first formed which is then converted to a brown manganese(IV) oxo complex [109].

3.1.2. Oxidation of carboxylic acids

Studies on the ozonolytic oxidation of carboxylic acids catalysed by manganese(II) have been carried out, particularly by Andreozzi et al. in connection with water purification.

The oxidation of glyoxalic acid to methanoic acid from pH 2–4 has been studied in the presence of $MnSO_4$, and the pathway is different in the presence of manganese catalysts, which give oxalic acid as an intermediate with CO_2 as the final product. It is likely that Mn(IV) is first produced and that this reacts with more Mn(II) to give Mn(III) [110].

Catalysis of the oxidation of formic acid to CO_2 by Mn(II) sulfate with ozone has been studied and rate constants were measured; it was suggested that manganese(IV) formato complexes were involved. The rates of oxidation are lower than those achieved by cobalt(II) acetate under comparable conditions [111]. Oxidation of acetic acid to CO_2 by ozone catalysed by cobalt(II) acetate has been studied [19,112]. Catalysis of the oxidation of oxalic acid to CO_2 by Mn(II) sulfate with ozone in $HClO_4$ at pH 0 and 4.7 has been investigated. At pH 4.7 there is likely to be involvement of manganese(III) oxalato complexes which then decompose and act as radical chain initiators. At pH 0 such radicals are less likely to be involved, but the rate-determining step is probably oxidation of Mn(II) to Mn(III) via Mn(IV) [113]. Kinetics of the ozonolytic oxidation of malonic acid, ultimately to CO_2, catalysed by $MnSO_4{\cdot}H_2O$ in molar $HClO_4$ were studied, and involvement of a chain-radical mechanism was proposed [114]:

$$\mathrm{Mn(II)} + O_3 + 2H^+ = \mathrm{Mn(IV)} + O_2 + H_2O \ \text{(slow)}$$

followed by

$$\mathrm{Mn(IV)} + \mathrm{Mn(II)} = 2\mathrm{Mn(III)} \ \text{(fast)}$$

3.1.3. Alkene epoxidation

Epoxidation of cyclic- and straight chain alkenes by ozone is catalysed by $Mn^{III}(Br^8{-}TMP)Cl$ ($Br^8{-}TMP$ = dianion of 5,10,15,20-tetramesityl-β-bromoporphyrin) in CH_2Cl_2 in the presence of pyridine or 4-*tert*-butylpyridine, which probably function as axial N-donor ligands to the otherwise square-based pyramidal manganese complex. Yields of epoxide were 5–40% over 15–40 min periods at room temperatures with catalytic turnovers of 5 to 59. Similar though less effective results were obtained with $Fe^{III}(Br^8{-}TMP)(OAc)$. It was suggested that metal-oxo intermediates were involved [115].

Later work aimed at using less exotic porphyrin complexes as catalysts for epoxidation reactions were studied, and it was found that $Fe^{III}(TMP)Cl$ (TMP = tetramesityl porphyrin) would also epoxidise a variety of terminal and cyclic alkenes in CH_2Cl_2 under ambient conditions; other catalysts which also effected this reaction but less effectively include ($Mn^{III}(TMP)Cl$, $Ru^{III}(TMP)Cl$, and the phthalocyaninato complex Fe(phth)Cl); the ruthenium analogue $Ru^{III}(TMP)Cl$ was slightly more effective than $Fe^{III}(TMP)Cl$. It is thought that the initial step (Fig. 1)

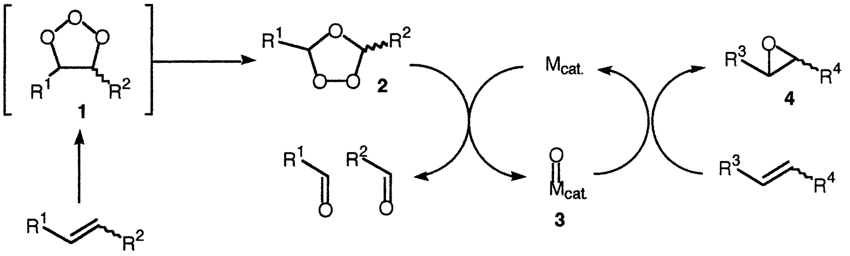


Fig. 1. Proposed reaction scheme for oxidation of alkenes catalysed by Fe(TMP)Cl [116]. The complex $Mn(DPPF_{20})Cl$ (see Section 2.1.2.1 above) will, in the presence of excess pyridine, catalyse the epoxidation of alkenes by ozone [27c].

is reaction of O_3 with the alkene to give a primary ozonide (1) which rearranges by the Criegee mechanism [108] to a secondary ozonide (2) which is in effect a peroxo complex, and it is this rather than ozone which effects the epoxidation of the alkene catalysed by Fe(TMP)Cl. The active intermediate is thought to be the green radical oxo tetramesitylporphyrinate cation $[Fe^{IV}O(TMP^{\bullet +})]^+$ which was detected by its electronic spectrum [116].

3.1.4. Oxidation of sugars and alcohols

Cleavage of the 2,3C–C bond in carbohydrates by ozone is increased in the presence of $RuCld_3 \cdot {}^nH_2O$; RuO_4 is produced, but unfortunately the rate of oxidation of Ru(III) to Ru(VIII) by ozone is too slow to allow a true catalytic process to occur [117].

The oxidation of cyclohexanol to adipic acid by ozone has been studied in the presence of $Co^{III}(acac)_3$, and the latter was shown to exert a small catalytic effect [118]. Oxidation of menthol to menthone in ethyl acetate or a Freon catalysed by $Co(OOCCH_3)_2 \cdot 4H_2O$ has been claimed, though ozone will effect such oxidations without a catalyst [119].

4. Conclusions

This review has attempted to show that ozone, used in dioxygen and produced by silent electric discharge (the procedure used in the vast majority of the experiments mentioned above) is, under safe, ambient conditions, a useful and environmentally acceptable oxidant for the production of transition metal, lanthanide and actinide complexes in which the central metal atom nears a high oxidation state. It is useful because there are no contaminating side-products after its use.

Although few high-oxidation state complexes produced by ozonolysis species have been used as oxidants or oxidation catalysts (particularly with ozone as a co-oxidant) the potential for doing so is considerable, and this would seem to be a research area of considerable promise.

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