Russian Chemical Reviews **62** (3) 279 – 290 (1993)
© 1993 Russian Academy of Sciences and Turpion Ltd

UDC 541.128 + 541.49 + 547.97

The catalase, peroxidase, and oxidase properties of the coordination compounds of manganese

A Ya Sychev, V G Isac

Contents

I.	Introduction	279
II.	Catalase properties. The mechanisms of the catalytic decompositon of H_2O_2	279
III.	Peroxidase properties. Oxidation of organic substrates	282
IV.	Oxidase properties	284
V.	Manganese compounds as catalysts of processes in the environment	286
VI.	Conclusion	287

Abstract. The experimental data on the oxidation – reduction catalysis by coordination compounds of manganese(II) of reactions involving the decomposition of H_2O_2 and the oxidation of organic substances by hydrogen peroxide and molecular oxygen are surveyed and modern ideas on these topics are described. The bibliography includes 170 references.

I. Introduction

Coordination compounds of transition metals are known to promote the occurrence of many industrially important technological processes under milder conditions than traditional heterogeneous catalysts, sometimes with a much greater activity and selectivity. The role of the active centre also in enzyme-like (analogue) systems designed to effect particular catalytic processes in homogeneous media has been attributed to the coordination compounds of transition metals. The study of the oxidation – reduction catalysis by transition metal compounds has made a definite contribution to the development of the theory of homogeneous catalysis. Homogeneous catalysis by coordination compounds in the liquid phase is a rapidly developing field of physical chemistry.

The interest in the study of the catalase, peroxidase, and oxidase properties of coordination compounds of manganese has been aroused by the presence of the latter in the active centres of manganese-containing catalases[1,2] and also by the discovery of the role of manganese in the oxidation of H_2O_2 to O_2 (in the photosystem II in photosynthesis),[1-5] in the dismutation of the superoxide radical in the living cell,[6,7] and in the catalytic oxidation – reduction reactions of organic substances in the tricarboxylic acid cycle (the Krebs cycle),[8] as well as the unique ability of the manganese ion to undergo relatively readily the change in the oxidation state from +2 to +7.

The coordination compounds of manganese with ligands containing nitrogen, oxygen, and both nitrogen and oxygen are effective catalysts of the decomposition of hydrogen peroxide, the liquid-phase oxidation of various organic compounds by molecular oxygen (synthetic molecular oxygen transferring agents have been obtained on the basis of manganese complexes), and also the oxidation of substrates by periodate and other oxidants, in contrast to the aquo-ions. There are numerous data on the reactivity of manganese complexes in such reactions and on the mechanisms of their catalytic action.[9,10]

All the studies devoted to the catalytic decomposition of hydrogen peroxide and the oxidation of substrates in the presence of manganese compounds can be divided into two large groups: studies of a phenomenological character[11-26] and studies in which the detailed kinetic characteristics of processes under the influence of catalysts were obtained and the mechanism of the corresponding process was established.[9,10,27-60]

From the practical point of view, studies in which the high peroxidase and oxidase activities of manganese complexes were established are of special interest.[10] Such complexes can be used to develop new highly sensitive and selective kinetic methods for the determination of microamounts of Mn^{2+} and also for the synthesis of new compounds. Since manganese complexes are effective catalysts of the oxidation by hydrogen peroxide (and its decomposition) and by oxygen of organic compounds, the investigation of the possibility of using such systems for the purification of waste water (especially from dye industries) is of special interest.

II. Catalase properties. The mechanisms of the catalytic decomposition of H_2O_2

Many transition metal compounds, including a series of coordination compounds of manganese, exhibit catalase activity.[11-60] In some studies, only the presence of catalase activity in particular manganese complexes was stated,[11-26] in others a comparative analysis of their activities was carried out, whilst in a third group attempts were made to elucidate the mechanism of the decomposition of hydrogen peroxide by manganese(II) complexes. At the same time, during the last 20 years a series of novel investigations have been carried out[10,31-60] † in which the

A Ya Sychev, V G Isac Department of Physical Chemistry, Moldavian State University, ul. Mateevicha 60, 277009 Kishinev, Moldova, Fax (7-042-2) 24 06 65

Received 11th November 1992
Uspekhi Khimii **62** (3) 303 – 315 (1993); translated by A K Grzybowski

† The results of the study of the catalytic properties of manganese aquo-ions permit an unambiguous conclusion: Mn^{2+} aquo-ions have no catalase, peroxidase, and oxidase activity.[10] On the other hand, they exhibit a definite catalytic activity in reactions involving the oxidation of certain substrates by periodate.[50] The Mn^{3+} aquo-ions catalyse the H_2O_2 decomposition reactions[61,62] and reactions involving the oxidation of organic substrates by molecular oxygen,[63-67] but the mechanisms proposed for these processes[61-67] cannot be regarded as being even qualitatively well-founded.

kinetics of the process and the composition and stability of the catalytically active complex were established and the mechanisms of the catalytic decomposition of hydrogen peroxide were justified on the basis of systematic investigations. It has now been established that the coordination compounds of manganese(II) with triethylenetetramine (Trien),[11,26,38] diethylenetriamine (Dien),[39,42] tetraethylenepentamine,[13] α,α′-bipyridyl (Bipy),[11] *o*-phenanthroline (Phen),[1,48,51] 2,2′,2″-terpyridyl,[11] 2- and 3-aminopyridines,[11] 2,9-dimethyl- and 4,7-diphenyl-1,10-phenanthrolines,[11] diethanolamine,[11,36,40] *N,N′,N″*-trimethyldiethylenetriamines,[11] acetylacetone (Acac),[31,32] the hydrogen carbonate ion,[29,33] histidine (His),[28,52] glycine (Gly),[43-45] sorbitol,[10] sucrose,[10] 8-hydroxyquinoline,[23,55] a series of α-aminoacids (Am),[46,47] and certain other substances[58-60] possess catalase activity.

The above compounds can be regarded as functional models of catalase (because, like the enzyme catalase itself, they catalyse the decomposition of H_2O_2 to O_2 and H_2O). It has come to be assumed that they possess catalase activity.

The catalase activity in the Mn(II)–Phen–H_2O_2 system is known to be determined[48,49] by the complex $Mn(Phen)_2^{2+}$, while in the Mn(II)–HCO_3^-–H_2O_2 system it is determined by the complex[10] $Mn(HCO_3)_2$. The decomposition of H_2O_2 is catalysed by the complex $MnEn_2^{2+}$ (En = ethylenediamine) in the Mn(II)–En–H_2O_2 system,[36,40] by the complex $Mn(Bipy)_2^{2+}$ in the Mn(II)–Bipy–H_2O_2 system, and by the complexes $MnTrien^{2+}$ and $MnTEA_2^{2+}$ (TEA = triethanolamine) in the Mn(II)–Trien–H_2O_2[27,38] and Mn(II)–TEA–H_2O_2[54] systems respectively. The complexes $Mn(Am)_2$ and $Mn(Am)_3$, incorporating bidentate and tridentate aminoacids and H_2O_2 in the corresponding systems,[46,47] $MnDien_2^{2+}$,[35,42] and the dinuclear complexes Mn_2His_3 [52] and $MnAcac_2$ [31,32] have the same properties.

Complexes having this composition manifest as a rule a high peroxidase activity. This has been confirmed by the results of studies on the oxidation reactions of various organic compounds in the Mn(II)–ligand–H_2O_2–S (S is the substrate) systems. The hydrogen carbonate ion,[68-70] triethylenetetramine,[71-74] ethylenediamine,[72] diethylenetriamine,[75,76] acetylacetone,[77,78] *o*-phenanthroline,[79-81] α,α′-bipyridyl,[50,78-81] and glycine[82] have been used as the ligands. The substrates are indigomonosulfonate, indigocarmine, indigotetrasulfonate, murexide, and carmine, which do not form complexes (or form only weak complexes) with Mn^{2+}, and also chelating ligands lumomagneson, lumogallion, alizarin C, tiron, and catechol.

A number of manganese complexes exhibit also oxidase activity. The catalytic oxidation of organic substances by molecular oxygen is carried out as a rule in non-aqueous media. The catalysts of such processes are manganese stearate and a series of manganese complexes:[83-86] porphyrin,[87-90] phthalocyanine,[91,92] caprylate,[93] carboxylate,[93] naphthenate,[94] tripropyl phosphate,[94] and other complexes.[95-97] The oxidation in the presence of manganese stearate $MnSt_2$ has been studied in greatest detail.

On the basis of literature data, manganese(II) complexes can be arranged in the following sequence in terms of their catalase activity:

$$Mn(HCO_3)_2 > MnTrien_2 > MnHis_2^{2+} > MnDien_2^{2+} >$$
$$> MnAcac_2^{2+} > MnEn_2^{2+} > MnBipy_2^{2+} > MnPhen_2^{2+} >$$
$$> MnAla_3 > MnVal_3 > MnGly_3 \simeq MnTre_2 >$$
$$> Mn(\beta\text{-Phen-}\alpha\text{-Ala})_3 > MnSer_2 > MnAsp_2 \simeq Mn(Aspa)_2$$

(Ala = alanine, Val = valine, Tre = threonine, Ser = serine, Asp = asparagine, and Aspa = aspartic acid).

The manganese(II) hydrogen carbonate complexes exhibit the highest catalase activity. In terms of their activity in the hydrogen peroxide decomposition reactions, they are inferior only by an order of magnitude to the iron(III) complex of triethylenetetramine — the most effective catalyst of the decomposition of hydrogen peroxide among low-molecular-mass compounds.‡

‡ The complex Fe^{3+}Trien has been called 'inorganic catalase' in the literature.[98]

Manganese complexes with ligands containing nitrogen and oxygen and both nitrogen and oxygen are catalytically active in the reactions involving the decomposition of hydrogen peroxide and the oxidation of substrates. Coordinatively unsaturated complexes catalyse the above processes as a rule, but coordinatively saturated complexes as well as a series of dinuclear compounds exhibit a catalytic activity in certain cases. The following oxidation–reduction reactions can occur in the course of the process:

$$L_nMn(II) \underset{+2e}{\overset{-2e}{\rightleftharpoons}} L_nMn(IV)\,,$$

$$L_nMn(III) \underset{+e}{\overset{-e}{\rightleftharpoons}} L_nMn(IV)\,,$$

$$L_nMn(III) \xrightarrow{e} L_nMn(II)\,.$$

Depending on which oxidation–reduction reactions occur in the decomposition of hydrogen peroxide by specific coordination compounds of manganese(II), the process proceeds via a radical-ion (radical-chain or cyclic) or ion-molecule mechanisms.

The radical-ion (radical-chain) mechanism of the decomposition of hydrogen peroxide operates in the following systems: Mn(II)–HCO_3^-–H_2O_2, Mn(II)–Triene–H_2O_2, Mn(II)–His–H_2O_2–H_3BO_3, Mn(II)–Phen–H_2O_2, and Mn(II)–Bipy–H_2O_2.[28,31,33,37,38,50,51] The kinetics and mechanisms of the decomposition of hydrogen peroxide by manganese(II) complexes of HCO_3^- and triethylenetetramine have been examined.[33,37,38,52] The catalase activity of these systems is due respectively to the complexes $Mn(HCO_3)_2$ and $MnTrien_2$.

The radical mechanism of the process has been confirmed by data on the inhibiting effect of the specific $\dot{O}H$ and $\dot{O}_2$ radical acceptors on the catalase process[27,30,37,38] and the fact that the rate of chain propagation (the rate of gas evolution) W_{O_2} exceeds appreciably the rate of initiation W_i [the ratio of these rates is $\sim 10^3$ for the Mn(II)–HCO_3^-–H_2O_2 system[30]]. This has been established[37,38] by introducing into the reaction medium before the start of the process a $\dot{O}H$ indicator (*N,N*-dimethyl-*p*-nitrosoaniline) and a $O_2^{\cdot-}$ acceptor (tetranitromethane). In both systems, $O_2^{\cdot-}$ radical-ions are generated on initiation of the process, and the radicals ·OH are formed in the subsequent stages. Data obtained by the spectrophotometric detection of the manganese(III) complexes indicate the generation in the system also of manganese(IV) complexes.[10,37,38,99] These results served as a basis for the formulation of the radical-chain mechanism of the decomposition of hydrogen peroxide by the complexes $Mn(HCO_3)_2$ and $MnTrien^{2+}$ in the following form:[10]

initiation:

$$Mn(II)L + H_2O_2 \longrightarrow Mn(IV)L + 2\,OH^-\,,$$
$$Mn(IV)L + HO_2^- \longrightarrow Mn(III)L + O_2^{\cdot-} + H^+\,;$$

chain propagation:

$$Mn(IV)L + O_2^{\cdot-} \longrightarrow Mn(III)L + O_2\,,$$
$$Mn(III)L + H_2O_2 \longrightarrow Mn(IV)L + \dot{O}H + OH^-\,,$$
$$\dot{O}H + H_2O_2 \longrightarrow O_2^{\cdot-} + H^+ + H_2O\,;$$

chain termination:

$$Mn(III)L + O_2^{\cdot-} \longrightarrow Mn(II)L + O_2$$

(L = 2 HCO_3^- or Trien).

Comparison of the rate constants and the corresponding concentrations in solution showed that[33,37] the following stage also occurs in the Mn(II)–HCO_3^-–H_2O_2 system:

$$\dot{O}H + HCO_3^- \longrightarrow CO_3^{\dot{-}} + H_2O ,$$

$$CO_3^{\dot{-}} + H_2O_2 \longrightarrow HCO_3^- + O_2^{\dot{-}} + H^+ .$$

The above reactions ensure the additional generation of the $O_2^{\dot{-}}$ radical-ions in the chain propagation process. This promotes the effective decomposition of hydrogen peroxide in the presence of the $Mn(HCO_3)_2$ complex. The decomposition of hydrogen peroxide in the Mn(II)–HCO_3^-–H_2O_2 system via this mechanism has also been confirmed by the results of other investigations.[100,101]

A similar mechanism operates in the decomposition of hydrogen peroxide in the Mn(II)–His–H_2O_2 system in borate buffer solutions.[31,102]

A somewhat different mechanism is observed in the Mn(II)–Phen(Bipy)–H_2O_2 systems. As noted above, the catalysts are the complexes $MnPhen_2^{2+}$ and $MnBipy_2^{2+}$.[48–51] The catalase process in the above systems is influenced by inhibitors such as specific $\dot{O}H$ radical acceptors (in particular, *N,N*-dimethyl-*p*-nitroso-aniline).[50] On the other hand, the gas evolution process is effectively inhibited by ascorbic acid, hydroquinone, *p*-benzoquinone, and tetranitromethane.[50,51] The radical-chain nature of the mechanism is indicated by the finding that in this case $W_{O_2}/W_i \simeq 10^3$.[50] Since $\dot{O}H$ radicals are not generated in these systems, one can justify the occurrence of a two-electron transfer stage:[50,51]

$$Mn(II)L_2 + H_2O_2 \longrightarrow Mn(IV)L_2 + 2\,OH^-$$

(L = Phen, Bipy).

The interaction of manganese(IV) compounds with hydrogen peroxide includes consecutive one-electron transfer steps with the generation of $O_2^{\dot{-}}$ in the reaction medium (this has been demonstrated by the method of inhibitors[50]). The complete process mechanism in the Mn(II)–Phen(Bipy)–H_2O_2 system under stationary conditions is as follows:[50]

initiation:

$$L_2Mn(III) + HO_2^- \longrightarrow L_2Mn(II) + HO_2^{\dot{}} ;$$

chain propagation:

$$L_2Mn(II) + H_2O_2 \longrightarrow L_2Mn(IV) + H_2O,$$

$$L_2Mn(IV) + H_2O_2 \longrightarrow L_2Mn(III) + HO_2^{\dot{}} + H^+ ,$$

$$HO_2^{\dot{}} \longrightarrow O_2^{\dot{-}} + H^+ ,$$

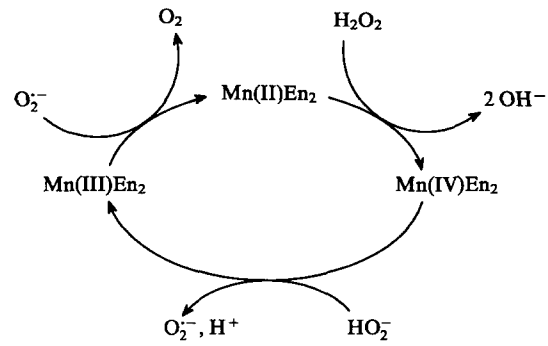
$$L_2Mn(III) + O_2^{\dot{-}} \longrightarrow L_2Mn(II) + O_2 ;$$

chain termination:

$$L_2Mn(II) + HO_2^{\dot{}} \longrightarrow L_2Mn(III) + HO_2^- .$$

Thus the characteristic features of the radical-chain mechanism of the decomposition of hydrogen peroxide by manganese complexes are as follows: the generation of the $O_2^{\dot{-}}$ and $\dot{O}H$ radical species (or of $O_2^{\dot{-}}$ alone) in the reaction volume; the formation of manganese(IV) and manganese(III) compounds owing to the catalase process; a significantly greater rate of chain propagation compared with the rate of initiation.

The formation of the $O_2^{\dot{-}}$ radical-ions has been observed also in the Mn(II)–En–H_2O_2 and Mn(II)–His–H_2O_2 systems, but in this case a distinctive feature of the process is the equality of the rates of gas evolution and initiation. This provided a basis for the classification of the given mechanism as of the radical-ion cyclic type. In relation to catalysis by the $MnEn_2^{2+}$ complex, this mechanism assumes the form shown below.[36,52,53,72] The radical-ion cyclic mechanism also operates in the Mn(II)–ethylenediaminetetramethyl phosphate–H_2O_2 system.[58] In the Mn(II)–His–H_2O_2 system, the reaction proceeds via a radical-ion mechanism with participation of dinuclear complexes of the type His–Mn(II)–His–Mn(II)–His (the formation of the latter has been demonstrated by EPR.[10,52,60]



The ion-molecule mechanism differs from that examined above primarily by the fact that free radicals are not formed in the reaction system. The absence of the inhibition of the catalase process by specific acceptors of the $\dot{O}H$ and $O_2^{\dot{-}}$ radical species (at concentrations such that they compete with the other reactants for free radicals) suggests that an ion-molecule mechanism of the decomposition of hydrogen peroxide operates in the system. In such cases, the reaction can proceed with formation of mono- or di-peroxo-compounds and may be accompanied by oxidation–reduction processes within the complex catalyst.[9] If such compounds are not formed, the mechanism includes stages involving the transfer of two electrons from the complex catalyst to hydrogen peroxide and conversely. This is clearly illustrated by the following general scheme:

$$Mn(II)L_n + H_2O_2 \longrightarrow Mn(IV)L_n + 2\,OH^- ,$$

$$Mn(IV)L_n + HO_2^- \longrightarrow Mn(II)L_n + H^+ + O_2 .$$

The decomposition of hydrogen peroxide proceeds via this mechanism in the Mn(II)–Dien–H_2O_2,[39,42] Mn(II)–sorbitol–H_2O_2,[10] Mn(II)–sucrose–H_2O_2,[10] Mn(II)–Gly–H_2O_2,[43–45] Mn(II)–Ala–H_2O_2,[46] and Mn(II)–Val (ser, Tre, Asp)–H_2O_2[46,47] systems. If the second stage is rate-limiting in the above mechanism, then one can write the following expression for the Mn(II)–Dien–H_2O_2 system:

$$W = \frac{k_2 K_{H_2O_2}[MnDien_2][H_2O_2]}{[H^+]} .$$

This expression agrees with the experimental equation, which confirms the reality of the proposed mechanism. The ion-molecule mechanism of the catalysis by manganese(II) complexes of sorbitol, sucrose, and a number of aminoacids has been demonstrated similarly.[10,43–47] In fact, the same mechanism operates also in the Mn(II)–Acac–H_2O_2 system.[31,32] The decomposition of hydrogen peroxide by trivalent manganese compounds in the Mn(III)–5,10,15,20-tetrakis-(2,6-dimethyl-3-sulfonatophenyl) porphyrinate–H_2O_2 system also proceeds via an ion-molecule mechanism.[59]

Thus one may conclude that hydrogen peroxide is capable of oxidising manganese(II) compounds to monomeric manganese(IV) compounds in neutral (and in a number of cases also weakly alkaline) media. One cannot rule out the possibility that such a process consists of two consecutive one-electron transfers without the emergence of the $\dot{O}H$ radicals from the inner sphere into the reaction volume,[50] but there is no rigorous evidence in support of the mechanism (with participation of manganese complexes).

At the same time, the unique ability of hydrogen peroxide to oxidise manganese(II) compounds to the permanganate ion is manifested in alkaline media. This has been demonstrated in relation to the catalytic decomposition of H_2O_2 by the manganese(II) complexes of triethanolamine.[10] The hypothetical

mechanism of this process, in which free radicals are not formed in the reaction volume (this has been demonstrated by the method of inhibitors), is as follows:[10]

$$Mn(II) + H_2O_2 \longrightarrow Mn(IV) + 2\,OH^-,$$

$$Mn(IV) + H_2O_2 \longrightarrow Mn(VI) + 2\,OH^-,$$

$$2\,Mn(VI) \longrightarrow Mn(V) + Mn(VII),$$

$$Mn(V) + Mn(II) \longrightarrow Mn(III) + Mn(IV),$$

$$Mn(III) + H_2O_2 \longrightarrow Mn(V) + 2\,OH^-,$$

$$Mn(V) + H_2O_2 \longrightarrow Mn(VII) + 2\,OH^-$$

[Mn(II)–Mn(V) are understood as the corresponding complexes, while Mn(VI) and Mn(VII) form the MnO_4^{2-} and MnO_4^- ions in alkaline media].

Thus in the systems of the type Mn(II)–ligand–H_2O_2 considered, manganese(III) manganese(IV) species (compounds) as well as $\dot{O}H$ and $O_2^{\cdot-}$ are generated and it is to be expected that they should ensure the effective oxidation of organic compounds.

III. Peroxidase properties. Oxidation of organic substrates

The high reactivity of many coordination compounds of manganese in catalytic hydrogen peroxide decomposition reactions has stimulated studies of the use of the Mn(II)–ligand–H_2O_2 systems for the oxidation of substrates and also of the application of manganese complexes as catalysts of the oxidation of organic compounds by molecular oxygen and periodate. The aim of such studies has been the search for new catalysts of the peroxidase oxidation of substrates, the establishment of the mechanism of the catalytic effect of the coordination compounds of manganese and of the role of the ligand environment of the central metal ion in this process, of the nature of the substrate being oxidised, of the experimental conditions (aerobic, anaerobic), and of the relation between the catalase and peroxidase properties of the manganese complexes, and the development on this basis of a new procedure for the synthesis of organic substances of practical importance and of new catalymetric analytical methods, and also the discovery of the general features of the catalytic oxidation of organic substrates.

The kinetics and mechanisms of the peroxidase activity of the coordination compounds of manganese with various ligands, including oxygen-containing (the monodentate hydrogen carbonate ion,[68-70] the bidentate acetylacetone,[77,78] and the tridentate triethanolamine[10]), nitrogen-containing (the bidentate ethylenediamine,[72] phenanthroline,[50] and bipyridyl,[50] the tridentate diethylenetriamine,[75,76] and the tetradentate triethylenetetramine[71,72,74]), as well as both nitrogen- and oxygen-containing (the tridentate histidine), have been investigated in detail hitherto in the oxidation reactions of organic substrates — both substrates with a weak capacity for the formation of complexes with Mn^{2+} (indigomonosulfonate, indigocarmine, indigotetrasulfonate, murexide, carmine, Procion Blue, Direct Bordeaux 150, Disperse Violet K) as well as ligands forming fairly stable complexes with Mn^{2+} (lumomagneson, lumogallion, alizarin, alizarin C, tiron, catechol). Alcohols are oxidised similarly under aerobic conditions (monohydric — methanol, ethanol, and isopropyl alcohol; dihydric — ethylene glycol; polyhydric — glycerol). In systems of the type Mn(II)–ligand–H_2O_2–substrate, the coordination compounds of manganese catalyse the oxidation of substrates and one can therefore regard them as functional models of peroxidase.¶

Among the reactions where molecular oxygen is used as the oxidant, the oxidation reactions of 8-pentadecanone and hexadecanone catalysed by manganese stearate have been investigated in greatest detail.[83-86] Systems incorporating porphyrin complexes, sodium tetrahydroborate, olefins, or other organic compounds[87-92] as well as the oxidation reactions of α-aminoacids, α-ketoacids, and other compounds, catalysed by the coordination complexes of manganese(II) with Schiff bases[94-97] have also been studied in detail.

The above analysis of the mechanisms operating in the Mn(II)–ligand–H_2O_2 systems shows that, in the course of the decomposition of hydrogen peroxide by manganese complexes, intermediate species (compounds $\dot{O}H$, $O_2^{\cdot-}$, $L_nMn(IV)$, and $L_nMn(III)$, with a high oxidising capacity, are generated in the reaction medium. The oxidation–reduction potentials of the corresponding pairs are as follows:

Pair	φ/V	Ref.
Mn^{4+}/Mn^{3+}	1.63	103
Mn^{3+}/Mn^{2+}	1.51	9
Mn^{4+}/Mn^{2+}	1.57	103
$\dot{O}H/H_2O$	2.83	104
$O_2^{\cdot-}/O_2$	−0.16	104

Subsequently, when the substrate S is introduced additionally into such systems, it can be oxidised by precisely these species. The mechanism of the oxidation reaction can include the following stages:

$$\dot{O}H + S \longrightarrow P_1,$$

$$O_2^{\cdot-} + S \longrightarrow P_2,$$

$$L_nMn(III)[L_nMn(IV)] + S \longrightarrow P_3 + L_nMn(II)[L_nMn(III)],$$

$$L_nMn(III)S[L_nMn(IV)S] \longrightarrow P_4 + L_nMn(II)[L_nMn(III)],$$

$$L_nMn(IV)S[L_nM(IV)\,S] \longrightarrow P_5 + L_nMn(II).$$

The substrate may be oxidised by active species (compounds) in the reaction volume (outside the first sphere of the complex catalyst). In this case, the mechanism is classified as of the outer-sphere type.[10,37,68,70,105] If the substrate S is oxidised by manganese ions in high oxidation states within the coordination sphere of the complex catalyst, an inner-sphere mechanism operates.[10,37,68,70,106]

The outer-sphere mechanism. In the systems where the radical-chain decomposition of hydrogen peroxide with generation of $\dot{O}H$ radicals takes place, various organic dyes are oxidised effectively.[37,68,71,72,74,82,105] The results of the study of the kinetics of the oxidation of the substrates having a weak complex-forming capacity (organic dyes, alcohols) shows that the same coordination compounds of manganese which determine the catalase activity of the given systems catalyse the above process. One can postulate that in the Mn(II)–HCO_3^-–H_2O_2,[33] Mn(II)–Trien–H_2O_2,[38,72] and Mn(II)–His–H_2O_2–H_3BO_3[31] systems the substrates are oxidised by the $\dot{O}H$ and $O_2^{\cdot-}$ radical species as well as the Mn^{4+} and Mn^{3+} ions forming part of the composition of the corresponding complexes. The above species (compounds) compete with one another for the substrate molecule. In terms of their 'oxidising strength', they can be arranged in the following sequence:[10]

$$\dot{O}H > L_nMn(IV) > L_nMn(III) > O_2^{\cdot-}.$$

The experimental results[10,37,53,105,107] indicate the dominant role of the $\dot{O}H$ radicals in the oxidation of the above substrates, in particular, potassium indigotetrasulfonate, murexide, and carmine.

The same type of kinetics of the catalase and peroxidase processes in the Mn(II)–ligand–H_2O_2 and Mn(II)–ligand–H_2O_2–S systems (where HCO_3^-, Trien, and His are used as the ligands, while the substrates are organic compounds with a weak complex-forming capacity), the equality of the rates of conversion

¶ The enzyme peroxidase is an effective catalyst of the decomposition of H_2O_2 and the oxidation of substrates by the intermediate compounds formed on decomposition of the peroxide. It has therefore come to be assumed that the above manganese compounds possess peroxidase activity.

of the substrate under aerobic and anaerobic conditions, and also the fact that the interaction of the selected substrates S with ȮH results in the formation of inactive substrate radicals permitted the conclusion that the reaction

$$\dot{O}H + S \longrightarrow S \text{ oxidation products}$$

can be included in the mechanism of the catalase decomposition of hydrogen peroxide as the chain termination stage.[10, 37, 53, 68, 105]

Thus substrates with weak complex-forming capacity in relation to Mn^{2+} do not affect the fundamental process mechanism. The radical-chain mechanism of the decomposition of hydrogen peroxide, established for the catalase process, is retained under these conditions.

In the systems considered, the mechanism of the oxidation of substrates by ȮH radicals is of the outer-sphere type. The above data permit the conclusion that the outer-sphere mechanism of the oxidation of substrates with a weak complex-forming capacity in relation to Mn^{2+} {$pK_s < 3$ for $K_s[S]/K_s[L] < 1$, where K_s is the stability constant} can operate in all catalytic systems of the metal–ligand–H_2O_2 type in which hydrogen peroxide undergoes a radical-chain decomposition with generation of ȮH radicals and a relatively inactive substrate radical is formed. In such systems, the mechanisms of the catalase and peroxidase activities of the complex catalyst should be to a certain extent similar. The mechanism becomes complicated when, as a result of the interaction with ȮH radicals, the oxidation of substrates involves the formation of reactive substrate radicals, which, possessing reducing properties, can react with manganese(III) and manganese(IV) compounds and, under aerobic conditions, also with molecular oxygen. The oxidation of alcohols (methanol, ethanol, isopropyl alcohol, ethylene glycol, and glycerol) in the Mn(II)–HCO_3^-–H_2O_2 systems under aerobic conditions can serve as an example.[108, 109]

Analysis of the results of a number of studies[108–110] shows that at certain concentrations of the test substances in the Mn(II)–HCO_3^-–H_2O_2–ROH systems the role of hydrogen peroxide reduces to the preparation of the alcohol (by converting it into the alkoxy-radical R_α) for interaction with oxygen. Consequently molecular oxygen participates in the oxidation of alcohols as a consequence of the formation of the reactive substrate radical R_α, which leads to an increase in the complexity of the process mechanism, namely to the appearance of a series of new stages:[10, 37, 53, 110]

$$R_\alpha + O_2 \longrightarrow RO_2^\cdot ,$$

$$RO_2^\cdot \longrightarrow ROHO + HO^\cdot ,$$

$$RO_2^\cdot + ROH \longrightarrow R_\alpha + RCHO + H_2O_2 .$$

These do not occur in the absence of substrates or in their presence if the substrate radical formed is inactive. Since alcohols are oxidised in the reaction volume (outside the coordination sphere of the catalyst), such a mechanism may be also referred to as of the outer-sphere type. The results of studies on the Mn(II)–HCO_3^-–H_2O_2–ROH systems under aerobic conditions permit the conclusion that alcohols and other organic compounds are oxidised effectively by hydrogen peroxide under aerobic conditions provided that the catalyst is a complex with a distinct catalase activity and that H_2O_2 decomposes via a radical-chain mechanism with generation of ȮH radicals. The following conditions must be maintained if this is to be achieved:

$$\frac{k_{S+\dot{O}H}[S]}{k_{\dot{O}H+H_2O_2}[H_2O_2]} \gg 1 \quad \text{and} \quad \frac{k_{S+\dot{O}H}[S]}{k_{P+\dot{O}H}[P]} \gg 1,$$

where $k_{S+\dot{O}H}$, $k_{\dot{O}H+H_2O_2}$, and $k_{P+\dot{O}H}$ are the corresponding rate constants for the interaction of ȮH with the alcohol (or the organic substrate S), hydrogen peroxide, and other system components (P). The above relations may serve as criteria for the selection of catalysts for the liquid-phase oxidation of alcohols (and other organic compounds) under mild conditions.

It is noteworthy that the active principle in the oxidation of organic substrates with a weak complex-forming capacity in relation to Mn^{2+} in the Mn(II)–HCO_3^-–H_2O_2, Mn(II)–Trien–H_2O_2, and Mn(II)–His–H_2O_2–H_3BO_3 system is the ȮH radical. However, such radicals are not generated in the disproportionation of hydrogen peroxide by manganese(II) complexes of *o*-phenanthroline, α,α′-bipyridyl, histidine (in the absence of borate buffer), ethylenediamine, diethylenetriamine, acetylacetone, and other compounds. At the same time, indigocarmine, potassium indigomonosulfonate and indigotetrasulfonate, murexide, and carmine are effectively oxidised in the above systems.[37, 68, 70, 72, 111] The results of the study of the kinetics and mechanisms of the decomposition of hydrogen peroxide and of the oxidation of substrates have shown that manganese(IV) compounds are the oxidant in the given instance. The general process mechanism can be represented as follows:

$$L_nMn(II) + H_2O_2 \longrightarrow L_nMn(IV) + 2\,OH^- ,$$

$$L_nMn(IV) + S \longrightarrow L_nMn(II) + P \text{ (S oxidation products)}.$$

The oxidation of substrates by manganese(IV) compounds has been demonstrated in cases where the catalysts are manganese(II) complexes of phenanthroline and bipyridyl,[50] as well as the acetylacetonate and histidine complexes.[10, 53, 78, 111]

Thus one may conclude that, in the oxidation–reduction decomposition of hydrogen peroxide by manganese(II) coordination compounds without the formation of hydroxyl radicals in the reaction medium, substrates having a weak complex-forming capacity in relation to Mn^{2+} are oxidised by manganese(IV) via an outer-sphere mechanism. The process takes place as a result of two-electron transfer. One cannot rule out the possibility that, when substrates incapable of being oxidised via a two-electron mechanism are used, consecutive one-electron transfer steps take place involving also manganese(III) compounds in the oxidation process.

The inner-sphere mechanism. The nature of the substrate oxidised affects the mechanism of the catalytic decomposition of hydrogen peroxide, particularly if the substrate has a chelating capacity and is able to form fairly stable complexes with Mn^{2+} ($pK_s > 3$). Such substrates are lumomagneson, lumogallion, alizarin, and alizarin C, the kinetics and mechanisms of the oxidation of which in the Mn(II)–ligand–H_2O_2 systems have been thoroughly investigated.[10, 37, 53, 69, 106] The above substrates, which play simultaneously the role of a ligand (S_L), are effectively oxidised [especially in a system such as Mn(II)–HCO_3^-–H_2O_2]. A distinctive feature of these processes is the fact that free hydroxyl and superoxide radicals are not generated in the reaction volume, but the substrates are oxidised within the coordination sphere of the metal complex catalyst (the inner-sphere mechanism).

A similar fundamental mechanism operates in the oxidation of lumomagneson in the Mn(II)–Triene–H_2O_2 and Mn(II)–En–H_2O_2 systems[106, 112] and in the oxidation of tiron and catechol in the Mn(II)–Phen(Bipy)–H_2O_2 systems.[50] The characteristic difference between the process in the above systems and that occurring in the latter without a substrate (the radical-chain mechanism) consists in the absence of the inhibiting effect and a diminishing role of radical acceptors in the course of the reaction. These data indicate unambiguously that hydrogen peroxide is decomposed and the substrate oxidised via a fundamentally new mechanism, differing from the mechanism of the catalase process. The substrate is oxidised in these systems via an inner-sphere mechanism[50, 106, 112] [as in the Mn(II)–HCO_3^-–H_2O_2–S_L systems]. The general process mechanism[106, 112] can be represented by the following set of stages:

$$Mn(II) + S_L \rightleftarrows Mn(II)S_L ,$$

$$Mn(II)S_L + H_2O_2 \longrightarrow Mn(IV)S_L + 2\,OH^- ,$$

$$Mn(IV)S_L \longrightarrow Mn(II) + P \text{ (S_L oxidation products)};$$

[Mn(II)–Mn(IV) are understood as the corresponding complexes $MnEn_2$ and MnTrien]. One cannot rule out the possibility that a peroxo-complex of the type $Mn(II)S_LH_2O_2$ is formed in the reaction of the complex catalyst with hydrogen peroxide, as has been suggested[69] for the catalysis by the manganese hydrogen carbonate complex, but this has not been confirmed experimentally. A somewhat different sequence of stages (within the framework of the same fundamental mechanism) occurs in the oxidation of tiron and catechol in the Mn(II)–Phen(Bipy)–H_2O_2 system:[50]

$$L_2Mn(II) + H_2O_2 \longrightarrow L_2Mn(II)HO_2^+ + H^+,$$

$$L_2Mn(II)HO_2^+ \longrightarrow L_2Mn(IV) + H_2O,$$

$$L_2Mn(IV) + S_L \rightleftarrows L_2Mn(IV)S_L,$$

$$L_2Mn(IV)S_L \longrightarrow L_2Mn(II) + P$$

(L = Phen, Bipy).

The mechanism of the oxidation of substrates of the type S_L in the Mn(II)–Acac–H_2O_2 system is much more complex,[77,78] since in this case a dinuclear complex participates in the reactions with hydrogen peroxide.

The coordination compounds of manganese [systems of the type Mn(II)–ligand–H_2O_2] and in the first place the hydrogen carbonate complexes exhibit a high peroxidase activity, so that they could be used in the development of new catalymetric methods for the determination of microamounts of Mn^{2+}, for preparative purposes, as polymerisation initiators, and for the removal of organic impurities from waste waters.

Catalymetric analytical methods. The effective catalytic activity of manganese compounds in reactions involving oxidation by hydrogen peroxide of various indicator substances made it possible to use them for the development[113–116] of catalytic methods for the determination of microamounts of manganese. Such indicator substances are alizarin C in the presence of HCO_3^- (the lower limit of the detection of Mn^{2+} ions is 0.4 ng ml^{-1}),[117] Catechol Violet in the presence of ethylenediamine (0.5 ng ml^{-1}),[118] lumomagneson (0.1 ng ml^{-1}),[119] sodium carminate in the presence of ethylenediamine and lead (0.1 ng ml^{-1}),[120] H-acids in the presence of ethylenediamine (0.1 ng ml^{-1}),[121] and Pyrogallol Red in the presence of bipyridyl (0.01 ng ml^{-1}).[122]

Catalymetric methods for the determination of Mn^{2+}, based on the oxidation with hydrogen peroxide of indigosulfonic acids,[117,123] *o*-dianisidine, Variamine Blue, gallion, and other indicator substances,[113–116] have been proposed. A series of kinetic methods have been developed in which use is made of the catalytic oxidation of dyes by molecular oxygen, for example, in the Mn(II)–morin–O_2 system,[124] or by periodate.[10,114–116,125]

The method based on catalytic oxidation with hydrogen peroxide in the presence of the manganese hydrogen carbonate complex of alizarin, alizarin C, and other organic dyes, is especially selective.[117,125] This method is highly sensitive: the lower limit of the detection of Mn^{2+} ions in the oxidation reaction is 0.4 ng ml^{-1}.

Catalymetric methods for the determination of microamounts of manganese in specially pure substances have found the widest application.[114]

A general deficiency of the kinetic methods developed for the determination of microamounts of Mn^{2+} is the large error of the determination caused by the occurrence of a rapid background reaction. Therefore one of the important tasks is the search for such new systems in which the rate of the background reaction is low or the development of methods of inhibiting the background reaction in known systems.

IV. Oxidase properties

Many coordination compounds of the 3*d* transition metals in low oxidation states are capable of binding reversibly molecular oxygen, as a consequence of which they are classified as synthetic O_2 transferring agents.[126–128] The coordinated oxygen is in an activated state in many compounds, which permits its use to effect various oxidation–reduction processes, in particular for the oxidation of organic substrates, in which transition metal complexes behave as catalysts. The coordination of molecular oxygen to transition metal complexes is one of the most effective methods of activating this commonest and cheapest oxidant.

A number of coordination compounds of manganese also have notable properties, although very little information is available about such compounds (O_2 transferring agents) and also about the reactivity of coordinated O_2 in manganese complexes. The reversible binding of molecular oxygen by manganese complexes takes place as a rule in non-aqueous media. The formation of oxygenated manganese complexes with porphyrin,[129] *para*-substituted *meso*-tetraphenylporphyrins,[130] dibutylcatechol, semiquinone,[131] picoline,[132] pyridine,[133] *N*,*N*-bis(salicylidene)ethylenediamine,[134] tetraphenylporphyrin,[135] threonyl- and phenyl-dialkylphosphines,[136] tripropylphosphine,[138] and others[137–140] has now been demonstrated. Certain coordination compounds of manganese(II) are oxygenated irreversibly. As a consequence of the activation of O_2, the central ion in the coordination sphere of the complex is oxidised with formation of manganese(*III*) and manganese(*IV*) complexes. It has been established that such oxygenation occurs in a series of porphyrin complexes,[141] in manganese complexes of phthalocyanine,[132] Schiff bases,[142,143] and triethanolamine,[144] and also in the gluconate[145] and sorbitol[146] complexes.

Studies on the activation by manganese complexes of molecular oxygen in the oxidation of organic substrates by the latter are of special interest. Such complexes may be regarded (subject to certain assumptions) as functional models of oxidases. As mentioned above, manganese stearate and a series of porphyrin, phthalocyanate [phthalocyanine?], and other complexes are used as catalysts of the oxidation of substrates by molecular oxygen. Thus, in catalysis by manganese(III) aquo-ions, the latter oxidise the substrates, forming at the same time radicals and manganese(II).[62–65] In the subsequent stages, manganese(II) is oxidised by the reaction products to manganese(III), i.e. the catalytic process includes the redox reactions:

$$Mn(III) \underset{-e}{\overset{+e}{\rightleftarrows}} Mn(II)$$

and a radical-chain or a radical-ion (non-chain) mechanism of the oxidation of substrates by molecular oxygen. The role of manganese(III) ions consists in preparing the substrate (by converting it into a radical) for the subsequent interaction with oxygen.

Catalysis by manganese(II) aquo-ions occurs apparently only when the substrate has a chelating capacity and a metal–substrate complex effectively reacting with oxygen is formed during the process. The oxidation of the substrate proceeds most probably within the coordination sphere of the metal–substrate complex under the influence of the manganese ions in the highest oxidation states.[65,147–149]

Coordination compounds of manganese are more effective catalysts of the oxidation of substrates by molecular oxygen. In such processes the initial stage involves the formation of an intermediate compound incorporating the complex catalyst and O_2, in which the latter is in fact activated. The mechanism of the activation of O_2 has not been ultimately elucidated. It has been suggested that there is no spin density and no appreciable negative charge on the oxygen in such an intermediate complex, so that O_2 is bound in a quasi-singlet state ($^1\Delta_g$).[88] One may therefore expect

the manifestation by the oxygen in such complexes of the chemical reactivity characteristic of O_2 in its singlet state.§

The composition of the intermediate active oxygen complex formed has been given in a number of studies[83,91] as $L_n(Mn(II)^{\delta+}\ldots O_2^{\delta-}$. For example, the mechanism of chain initiation in the oxidation by molecular oxygen of a series of organic substrates (8-pentadecanone, hexadecanone) in the presence of manganese stearate has been expressed as follows:

$$MnSt_2 + O_2 \longrightarrow MnSt_2^{\delta+}\ldots O_2^{\delta-},$$

$$MnSt_2^{\delta+}\ldots O_2^{\delta-} + RH \longrightarrow \begin{cases} MnSt_2OH + RO, \\ MnSt_2OOH + R. \end{cases}$$

In most studies, it is assumed that the process proceeds via a stage involving the formation of a ternary catalyst–O_2–substrate complex, the decomposition of which leads to the formation of the reaction products.[88]

If the substrates are oxidised with trivalent manganese compounds used as the catalysts, an additional reductant (usually tetrahydroborate) is introduced into the system. The process mechanism under such conditions becomes appreciably more complex, which hinders its rigorous justification. It has been established reliably that in such cases the manganese(III) compounds are initially reduced to manganese(II) compounds, after which the substrate–O_2–catalyst ternary complex is formed. A process of this kind occurs in the oxidation of cholesterol, androst-5-en-5β-ol, and a number of aliphatic olefins in the presence of porphyrin complexes of manganese(III).

The general mechanism can be represented in the following form:[90,151]

$$TPPMn(III) + NaBH_4 \rightleftarrows TPPMn(II) + P_1,$$

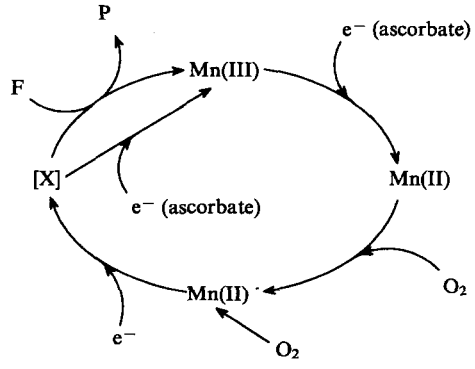
$$TPPMn(II) + S + O_2 \rightleftarrows S{-}O{-}O{-}Mn(II)TPP,$$

$$S{-}O{-}O{-}Mn(II)TPP \longrightarrow TPPMn(III) + P_2,$$

$$S{-}O{-}O{-}Mn(II)TPP \longrightarrow P_3,$$

$$TPPMn(II) \longrightarrow P_4,$$

where P_1 are the $NaBH_4$ reaction products, P_2 the olefin oxidation products, P_3 and P_4 the catalyst reaction and dehydration products respectively, [and TPP is tripyhenylphosphine]. A similar mechanism has been proposed also for the oxidation of olefins in the Mn(III)(TPP)–O_2–ascorbic acid–olefin system;[87] and the formation of a complex between O_2 and the catalyst, and the fact that $O_2^{\cdot-}$ and H_2O_2 are not involved in the process have been demonstrated. The mechanism can be represented by a sequence of stages.



[Mn(II) and Mn(III) are understood as the corresponding complexes with TPP, F is the olefin, and P is its oxidation product]. Competition between the ascorbate ion and the substrates for the active species [X] is postulated.

The mechanisms of substrate oxidation presented above are of the inner-sphere type. Complete schemes for the oxidation of substrates with formation of the experimentally established final products have been put forward in a number of studies[88,89,93] taking into account the operation of the inner-sphere mechanism. Such mechanisms must be regarded as tentative, because they have been set up purely speculatively in order to express clearly the possible pathways leading to the formation of the oxidation products.

Substrates may be oxidised by oxygen also via an outer-sphere mechanism, for example in the oxidation of hydrazine [the Mn(III)–Hm–O_2–N_2H_4 system, where Hm = haemoglobin]:

$$Mn(III){-}Hm + O_2 \rightleftarrows Mn(III)_2Hm\ldots O_2,$$

$$Mn(III)_2Hm\ldots O_2 + N_2H_4 \longrightarrow Mn(III)Hm + N_2 + 2\,H_2O.$$

An outer-sphere mechanism operates also in the Mn(II)–L–O_2–leuco-base (LO) systems:[10]

$$MnL_2 + O_2 \rightleftarrows MnL_2O_2,$$

$$MnL_2O_2 + LO \longrightarrow MnL_2 + LO \text{ oxidation products}$$

(L = Phen, Bipy).

A distinctive feature of this process is that it occurs in neutral aqueous media and that the rate of oxidation of the leuco-base increases appreciably when the system is irradiated with UV light (λ = 314–334 nm).

An outer-sphere mechanism (without the activation of O_2 in the coordination sphere of the complex catalyst) also operates in the liquid-phase oxidation of organic substances in the presence of initiators or when manganese(III) complexes, which react effectively with the substrate, are used as the catalysts.[84,97]

It is noteworthy that occasional studies on the oxidation reactions of organic substances by molecular oxygen in the presence of manganese ions and coordination compounds do not permit the development of a unique point of view on their mechanisms. At the same time, one may conclude that such systems may be used for the synthesis of certain organic compounds of practical interest.

Many studies devoted to the liquid-phase oxidation of organic compounds by molecular oxygen in the presence of manganese ions had preparative aims. For example, optimum conditions have been found {[$MnSt_2$] = 16.5 mmol litre^{-1}, 393 K} for the oxidation of 8-pentadecanone by oxygen, in which the yield of caprylic and oenanthic acids (51.9%) is a maximum.[88]

The main products of the liquid-phase oxidation of *n*-pentane in solution in acetic acid in the presence of 10^{-3} mole of manganese acetate per mole of *n*-pentene are lower aliphatic carboxylic acids.[152]

Preparative methods of synthesis of new organic substances with manganese complexes used as catalysts have also been described in a number of other studies.[10,84,89,92–94,96,147] The manganese(II)–ligand–H_2O_2 systems, in which ȮH radicals are generated, can be used to obtain aldehydes (ketones) from the corresponding alcohols.[103,104,116] By virtue of their high effectiveness in the hydrogen peroxide decomposition reactions, manganese(II) complexes are suitable for the elimination of H_2O_2 at high concentrations from waste waters.[153]

§ Questions concerning the activation of O_2 by coordination compounds have been considered in detail in a number of communications.[126,131,150]

V. Manganese compounds as catalysts of processes in the environment

One of the consequences of the increasing amount of anthropogenic waste discharged into the atmosphere is the precipitation of acid rain, the main components of which are sulfuric and nitric acids. The oxidation processes in the atmosphere, leading, for example, to sulfur(IV) (in the form of SO_2) and sulfur(VI) (in the form of H_2SO_4) are usually accelerated catalytically by transition metal ions and compounds, particularly those of manganese and iron. The concentrations of the latter in rain water are usually $\sim 2.6 \times 10^{-7}$ and $\sim 3.8 \times 10^{-6}$ M respectively.[154] This is sufficient to exert a strong catalytic effect on many processes.[10, 149, 155] The oxidants are usually O_2, H_2O_2, or their reactive activation products — the $\dot{O}H$ and $H\dot{O}_2$ radicals.

Metal (manganese, iron) complexes participate in the oxidation of sulfur(IV) by ozone in the aqueous phase of the atmosphere.[156, 157] Furthermore, compounds of these metals may concentrate in the moist aerosol particles and there is therefore a possibility of an appreciable increase in the rate of oxidation of SO_2.

The mechanisms of this process under laboratory conditions and in the real atmospheric moisture can differ appreciably (for example, the SO_2 oxidation reactions in the water of a mist, in rain water, or in aerosol water). The rate of oxidation of SO_2 in aerosols diminishes in the following sequence of metal salts:

$$Mn(NO_3)_2 > MnCl_2 > Cu(NO_3)_2 > MnSO_4 > CuSO_4 > CuCl_2.$$

This indicates the strong influence of the nature of the ligand. For example, the formation of complexes with participation of manganese ions and various volatile organic ligands leads to the appearance of fairly effective catalysts activating the molecules of the oxidant (O_2, H_2O_2) and the substrate (SO_2). The rate of the catalytic oxidation of SO_2 depends on a multiplicity of causes: on the ratio of the manganese ions and ligand molecules, on the pH of the medium, and other factors. The observed rates of this oxidation process at different sites and at different times can therefore also be different. However, an appreciable fraction of sulfur dioxide in a water drop within the mist is usually rapidly converted into sulfuric acid. For example, during summer approximately half of the atmospheric SO_2 and NO_2 waste is converted into H_2SO_4 and HNO_3 after 180 and 14 h respectively.[158] The detailed mechanisms of these processes have so far been poorly determined.

The overall reaction involving the catalytic oxidation of sulfur(IV) to sulfur(VI) by oxygen can be as follows:

$$SO_2(aq) + H_2O + \tfrac{1}{2}O_2 \xrightarrow{Mn^{2+}L_n} \longrightarrow H_2SO_4 \rightleftarrows HSO_4^- + H^+.$$

The study of the model $Mn(II) - SO_2(aq) - HSO_3^- - O_2$ system showed that the order of the reaction with respect to manganese is two (there is a possibility of the participation of species of the type of Mn_2^{4+}). A radical-chain mechanism has been postulated:[159]

$$Mn^{2+} + HSO_3^- \rightleftarrows MnHSO_3^+ ,$$

$$2\,Mn^{2+} \rightleftarrows Mn_2^{4+} ;$$

intiation:

$$Mn_2^{4+} + HSO_3^- \xrightarrow{slow} Mn_2HSO_3^{3+} ,$$

$$Mn_2HSO_3^{3+} + O_2 \xrightarrow{fast} 2\,Mn^{2+} + \dot{O}H + SO_4^{\cdot -} ,$$

$$\dot{O}H + HSO_3^- \longrightarrow H_2O + SO_3^{\cdot -} ;$$

branching:

$$SO_4^{\cdot -} + HSO_3^- \longrightarrow HSO_4^- + SO_3^{\cdot -} ,$$

$$SO_3^{\cdot -} + O_2 \longrightarrow SO_5^{\cdot -} ,$$

$$SO_5^{\cdot -} + HSO_3^- \longrightarrow SO_4^{\cdot -} + HSO_4^- ,$$

$$MnHSO_3^+ + HSO_3^- \longrightarrow Mn(HSO_3)_2 ,$$

$$Mn(HSO_3)_2 + O_2 \longrightarrow Mn^{2+} + 2\,HSO_4^- ;$$

termination:

$$SO_5^{\cdot -} + \text{organic compound} \longrightarrow \text{inert products.}$$

This mechanism of the oxidation of sulfur(IV) to sulfur(VI) corresponds to the following rate equation:[159]

$$\frac{d}{dt}[S(VI)] = \left[10 \exp\left(\frac{6.4 - 4\sqrt{I}}{1 + \sqrt{I}}\right)\right][Mn^{2+}]^2 + \left[10 \exp\left(\frac{3.5 - \sqrt{I}}{1 + \sqrt{I}}\right)\right][Mn^{2+}][HCO_3^-] ,$$

where I is the ionic strength.

In contrast to the catalytic oxidation of sulfur(IV) to sulfur(VI) in the presence of iron compounds, in the case of compounds of manganese the catalyst is its dinuclear form Mn_2^{4+} [apparently in the form of some kind of complex, for example, $(MnSO_2)_2^{4+} \cdot O_2$].[160] A powerful oxidant (the $\dot{O}H$ radical), participating in the process, is formed under these conditions.

One of the problems in passing from the model mechanism to the mechanism of the oxidation of SO_2 in the atmosphere is the presence in the latter of both manganese(II) and iron(III) compounds. They exert jointly a much greater catalytic effect than they do separately, as under laboratory conditions. In addition there is a possibility of a difference between the mechanisms due to the difference between the concentrations of the interacting substances under laboratory conditions and in the atmosphere. Thus, at low SO_2 (HSO_3^-) concentrations, the following mechanism of the oxidation of sulfur(IV) by oxygen has been proposed:

$$Mn^{3+} + HSO_3^- \xrightarrow{k_1} HSO_3^{\cdot} + Mn^{2+} , \quad (1)$$

$$HSO_3^{\cdot} + O_2 \xrightarrow{k_2} HSO_5^{\cdot} , \quad (2)$$

$$HSO_5^{\cdot} + HSO_3^- \xrightarrow{k_3} HSO_5^- + HSO_3^{\cdot} , \quad (3)$$

$$HSO_3^- + HSO_5^- \xrightarrow{k_4} 2\,HSO_4^- , \quad (4)$$

$$HSO_5^{\cdot} + HSO_5^{\cdot} \xrightarrow{k_5} S_2O_6^{2-} + 2\,O_2 . \quad (5)$$

Then

$$\frac{d}{dt}[SO_4^{2-}] = k_3 \frac{k_1^{1/2}}{k_5}[HSO_3^-]^{3/2}[Mn]^{1/2} ,$$

if it is assumed that the rate is determined by stage (3).

On raising the concentration of SO_2 (HSO_3^-), the mechanism may change and the reaction

$$HSO_3^{\cdot} + HSO_3^- \xrightarrow{k_6} H_2S_2O_6 + e^- , \quad (6)$$

will appear instead of stage (5). The chain termination stage is now represented by reaction (6) instead of reaction (5) and the rate is determined by stage (2). In this case

$$\frac{d}{dt}[SO_4^{2-}] = k_2 \frac{k_1}{k_6}[Mn^{2+}][O_2] .$$

The catalytic oxidation of SO_2 by oxygen in the presence of the chloride of the tetraolylporphyrin (II) complex of manganese [Mn(III)II] and a reductant can be represented schematically in the following way:[162]

$$SO_2 \cdot H_2O \rightleftharpoons HSO_3^- + H^+ \rightleftharpoons SO_3^{2-} + 2H^+,$$

$$Mn^{3+}\Pi...O_2 \xrightarrow{+e^-} Mn^{3+}\Pi...O_2^- \xleftarrow{Mn^{3+}\Pi} O_2^- \xleftarrow{+e^-} O_2$$

$$+O_2 \uparrow\downarrow -O_2$$

$$Mn^{3+}\Pi \xrightarrow{+e^-} Mn^{2+}\Pi \xrightarrow{+O_2} Mn^{4+}\Pi...O_2^-$$

$$\downarrow +HSO_3^-$$

$$Mn^{3+}\Pi + SO_4^{2-} + HSO_3^{\cdot} + OH^-,$$

$$HSO_3^{\cdot} + O_2 \longrightarrow HSO_5^{\cdot},$$

$$HSO_5^{\cdot} + HSO_3^- \longrightarrow HSO_5^- + HSO_3^{\cdot},$$

$$HSO_5^- + HSO_3^- \longrightarrow 2\,HSO_4^-,$$

$$HSO_4^- + H^+ \rightleftharpoons H_2SO_4.$$

The initiation stage involves the reduction of MnΠ, O_2, or MnΠ ... O_2. The catalyst promotes the coordination and specific reduction of O_2 to the peroxide ions O_2^{2-} and also the generation of the active form of the substrate ($H \cdot SO_3^{\cdot}$ radicals), which is the initiator of the autoxidation of sulfur(IV). The oxide ($Mn^{3+}\Pi$ ... O_2), superoxide ($Mn^{3+}\Pi$ ... O_2^-), and peroxide ($Mn^{4+}\Pi$ ... O_2^{2-}) complexes formed were detected spectrophotometrically.

Hydrogen peroxide plays an even more important role than O_2 as the oxidant in the catalytic conversion of SO_2 into H_2SO_4 in the atmosphere. The H_2O_2 concentration in an atmospheric moisture drop is $\sim 10^{-6}-10^{-4}$ M.[163] Typical catalytic oxidation–reduction systems are then produced:

$$M^{z+} - H_2O_2 - SO_2,\ M^{z+} - L - H_2O_2 - SO_2$$

(M = Mn, Fe, Cu, etc),

in which sulfur dioxide is oxidised to sulfuric acid:

$$SO_2 + H_2O_2 \xrightarrow{Mn^{z+}\ (Mn^{z+}L)} H_2SO_4.$$

Thus in the majority of the aqueous atmospheric systems (pH < 5) the main oxidant for SO_2 is H_2O_2.[164] At pH > 5, other oxidants [OH, O_3, Fe(III)–O_2] begin to play an important role and the contribution of H_2O_2 to the oxidation reaction diminishes. Similar catalytic oxidation–reduction systems arise in atmospheric water with participation of O_3 and O_2.

The conditions in certain model experiments on the catalytic oxidation of SO_2 were close to the atmospheric conditions [the concentrations of the reacting components — Mn(II), SO_2, and H_2O_2, acidity, and temperature].[165] Thus the concentration of manganese(II) was 10^{-6} to 4×10^{-6} M, which corresponds to its content in the atmosphere. Under these conditions, the rate of oxidation of sulfur(IV) is given by

$$-\frac{d}{dt}[S(VI)] = k[S(IV)][Mn(II)].$$

In different studies, the order of the reaction with respect to manganese(II) varied from 1 to 2. The rate constant for this reaction at pH 3–6 remained invariant also for $[Mn(II)]_0 = 10^{-6}$ M and amounted to 5.1×10^3 litre mol^{-1} s^{-1}, which was approximately 6 times greater than the value of k at the same iron(III) concentration. The reaction involving the catalytic oxidation of sulfur(IV) to sulfur(VI) proceeds via the formation of the complex $Mn(II)(HSO_3^-)_x^{2-x}$, the composition of which has not been ultimately determined. It is of interest that similar manganese hydrogen carbonate complexes $[Mn(HCO_3)_2]$ are[10] active catalysts of the decomposition of H_2O_2 with subsequent formation of $HO_2^{\cdot -}$ and $\dot{O}H$ free radicals species. The sequence of metals forming the catalyst is as follows when account is taken of the rate constants for the oxidation of sulfur(IV) to sulfur(VI):

Mn(II) > Fe(III), Cu(II) ≫ non-catalytic reaction.

Thus the non-catalytic and catalytic oxidation of SO_2 to H_2SO_4 by various oxidants (especially H_2O_2) is the most important process leading to the acidification of rain water. Apparently the key catalysts of this process (together with iron compounds) are manganese compounds and the rates of formation of SO_4^{2-} (mol litre^{-1} s^{-1}) in model experiments are described by the expressions

$$\frac{d}{dt}[SO_4^{2-}] = 0.142[Mn(II)] \text{ at } [SO_2] > 4 \times 10^{-5}\text{ M},$$

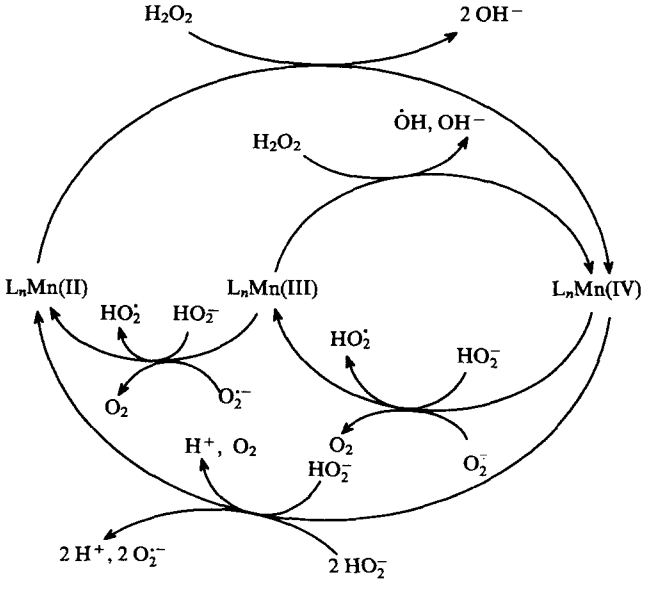
$$\frac{d}{dt}[SO_4^{2-}] = 0.142[Mn][SO_2]^{3/2} \text{ at } [SO_2] < 4 \times 10^{-5}\text{ M}.$$

The mechanism of the oxidation of SO_2 in the atmosphere apparently involves free radical species.

In the atmosphere, 20%–40% of the acidity is caused by the oxidation of NO_x to nitric acid.[166] This reaction can also occur under the influence of catalysts.[167–170] However, the number of reliable data concerning the mechanism of this process is much smaller than for the mechanism of the oxidation of sulfur and they will not therefore be considered here.

VI. Conclusion

Many coordination compounds of manganese(II) with ligands containing nitrogen, oxygen, and both nitrogen and oxygen can be regarded as functional models of catalase (they catalyse the decomposition of H_2O_2 to O_2), peroxidase (they catalyse reactions involving the oxidation of organic and inorganic compounds by hydrogen peroxide oxidation products), superoxide dismutase (they catalyse the destruction of superoxide radical-ions O_2^-), and oxidase (they activate O_2 in the oxidation reactions of various compounds). The set of oxidation–reduction reactions which can occur in Mn(II)–ligand–H_2O_2 systems with participation of the complex catalyst is reflected by the following general scheme:



In each specific case, the mechanism of the decomposition of H_2O_2 by manganese complexes includes a definite set of oxidation–reduction reactions (presented above). The operation of a radical-ion (chain or cyclic) or ion-molecule mechanism is determined by the ligand environment of Mn^{2+} and the process

conditions. A clear relationship between the composition of the complex, the ligand environment in which the manganese ion exists, its reactivity, and the mechanism of the catalytic action has not so far been established.

The catalase-active coordination compounds of manganese(II) possess also a definite peroxidase activity because the catalytic decomposition of hydrogen peroxide generates ȮH radicals and manganese(IV) and manganese(III) compounds which have a high oxidising capacity. If a radical-chain mechanism of the decomposition of hydrogen peroxide operates in the systems with generation of ȮH radicals, the latter make the main contribution to the oxidation of the substrates. When an ion-molecule or a radical-ion cyclic mechanism of the decomposition of hydrogen peroxide operates, the oxidant consists mainly of manganese(IV) compounds. Substrates with relatively weak complex-forming capacity in relation to Mn^{2+} {$pK_s < 3$ for $K_s[L]/K_s[S] \gg 1$} are oxidised via an outer-sphere mechanism in the Mn(II)–ligand–H_2O_2 systems. Substrates forming fairly stable compounds with Mn^{2+} {$3 < pK_s < 8$ for $K_s[L]/K_s[S] \geqslant 1$} are oxidised within the coordination sphere of the complex catalyst (inner-sphere oxidation mechanism). If reactive substrate radicals are formed in the reaction volume, molecular oxygen participates in the oxidation process under aerobic conditions and the role of H_2O_2 reduces to the preparation of the substrate, by converting it into an active radical, for subsequent oxidation by molecular oxygen.

The liquid-phase catalytic oxidation by molecular oxygen in the presence of coordination compounds of manganese proceeds as a rule in non-aqueous media. Oxygen is activated mainly as a consequence of the formation of an intermediate active catalyst–O_2 compound and the mechanism of the oxidation of the substrate is then of the outer-sphere type. A ternary complex of the type $MnL_n–O_2–S$ is sometimes formed in the course of the process. In such cases an inner-sphere mechanism of the oxidation of the substrate operates. The factors determining the operation of a particular oxidation mechanism, which permit a purposeful search for catalytically active manganese compounds and also characterise the role of the substrate and the medium in the liquid-phase oxidation by molecular oxygen, have by no means been fully established.

The high reactivity of individual manganese complexes can be used to develop catalymetric analytical methods (tens of such methods are already known) for preparative purposes (for the synthesis of particular organic compounds via liquid-phase oxidation) and for the solution of other applied problems (-elimination of organic contaminants from waste waters, etc.). The role of manganese compounds as catalysts of the processes occurring in the environment has been demonstrated on model systems for the conversion of sulfur(IV) (as SO_2) into sulfur(VI) (as H_2SO_4), which play an important role in the formation of acid rain.

References

1. S V Khangulov, V V Barynin, V R Melik-Adomyan, A I Grebenko, N V Voevodskaya, L A Blyumenfel'd, S N Dobryakov, V B Il'yasova *Bioorg. Khim.* **12** 741 (1986)
2. S V Khangulov, N V Voevodskaya, V V Barynin, A I Grebenko, V R Melik-Adomyan, *Biofizika* **32** 960 (1987)
3. G M Chenial *Ann. Rev. Plant. Physiol.* **21** 467 (1970)
4. G M Chenial, I F Martin *Biochim. Biophys. Acta* **197** 219 (1970)
5. M Galvin *Science* **184** 375 (1974)
6. M Pick, I Raboni, F Yost, J Fridovich *J. Am. Chem. Soc.* **96** 7329 (1974)
7. B B Keele, J M McCord, J Fridovich *J. Biol. Chem.* **245** 6176 (1970)
8. I A Chernavin, in *Fiziologiya i Biokhimiya Mikroelementov v Katalize* (The Physiology and Biochemistry of Microelements in Catalysis) (Moscow: Vys. Shkola, 1970) p. 70
9. A Ya Sychev *Okislitel'no-Vosstanovitel'nyi Kataliz Kompleksami Metallov* (Oxidation-Reduction Catalysis by Metal Complexes) (Kishinev: Shtiintsa, 1976)
10. A Ya Sychev, V G Isac *Koordinatsionnye Soedineniya Margantsa* (Coordination Compounds of Manganese) (Kishinev: Shtiintsa, 1990)
11. R P Pantaler, L D Alfimova, A M Bulgakova *Zh. Anal. Khim.* **30** 1834 (1975)
12. S L Davydova, N N Plate, T P Brin *Zh. Fiz. Khim.* **42** 258 (1968)
13. N M Reibel' *Zh. Fiz. Khim.* **40** 1112 (1966)
14. G F Reshetnikova, A G Muftakhov, N V Kapitsa, in *Tezisy Dokladov III Vsesoyuznogo Soveshchaniya po Khimii Koordinatsionnykh Soedinenii Kobal'ta, Margantsa, Nikelya. Tbilisi, 1974* (Abstracts of Reports at the IIIrd All-Union Conference on the Chemistry of the Coordination Compounds of Cobalt, Manganese, and Nickel. Tbilisi, 1974) p. 168
15. J H Wang *J. Am. Chem. Soc.* **77** 4715 (1955)
16. R P Pantaler, L E Alfimova, M E Globus, A M Bulgakov *Zh. Neorg. Khim.* **22** 1559 (1977)
17. W Langenbeck, K Dehler *Chem. Ber.* **89** 2458 (1956)
18. W Langenbeck, M Augustin, F H Richter *J. Prakt. Chem.* **27** 64 (1965)
19. W Langenbeck, M Augustin, F H Richter *Chem. Ber.* **94** 831 (1961)
20. H W Krause *Chem. Ber.* **95** 777 (1962)
21. D T Richens, D T Sawyer *J. Am. Chem. Soc.* **101** 3681 (1979)
22. E R Nightingale *Anal. Chem.* **31** 146 (1959)
23. M A Suwyn, R E Hamm *Inorg. Chem.* **6** 142 (1967)
24. T E Jones, R E Hamm *Inorg. Chem.* **13** 1940 (1974)
25. M Oishi, Y Mishida, S Kida *Chem. Lett.* 409 (1982)
26. J Dolezal, O Gurtler *Talanta* **15** 299 (1968)
27. A Ya Sychev, V G Isac *Zh. Fiz. Khim.* **47** 593 (1973)
28. A Ya Sychev, V G Isac *Zh. Fiz. Khim.* **47** 244 (1973)
29. A Ya Sychev, V G Isac, Dao Van Lap *Zh. Fiz. Khim.* **51** 363 (1977)
30. A Ya Sychev, V G Isac, Dao Van Lap *Zh. Fiz. Khim.* **52** 107 (1978)
31. A Ya Sychev, V G Isac, Chan Thi Thanh Phuong *Izv. Akad. Nauk Mold. SSR, Ser. Biol. Khim. Nauk* **6** 66 (1984)
32. A Ya Sychev, V G Isac, Chan Thi Thanh Phuong *Zh. Fiz. Khim.* **58** 332 (1984)
33. A Ya Sychev, V G Isac, U Pfanmueller *Zh. Fiz. Khim.* **57** 760 (1983)
34. A Ya Sychev, S S Budnikov, V G Isac *Izv. Akad. Nauk Mold. SSR, Ser. Biol. Khim. Nauk* **2** 54 (1986)
35. A Ya Sychev, V G Isac, Chan Thi Thanh Phuong *Zh. Fiz. Khim.* **58** 2331 (1984)
36. D G Batyr, V G Isac, A A Kirienko *Koord. Khim.* **10** 1372 (1984)
37. V G Isac, A Ya Sychev *Okislitel'no–Vosstanovitel'nyi Kataliz Kompleksami Perekhodnykh Metallov* (Oxidation–Reduction Catalysis by Transition Metal Complexes) (Kishinev: Izd. Mold. Gos. Univ., 1984)
38. D G Batyr, V G Isac, A A Kirienko, S V Kil'mininov *Disproportionation of Hydrogen Peroxide in the Mn(II)–triethylenetetramine–H_2O_2 System* (Moscow, 1984) Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI), N 5779-84
39. D G Batyr, V G Isac, A A Kirienko, N B Unkulitsa *Koord. Khim.* **9** 1085 (1983)
40. V G Isac, A A Kirienko *Izv. Akad. Nauk Mold. SSR, Ser. Biol. Khim. Nauk* **4** 82 (1981)
41. D G Batyr, V G Isac, A A Kirienko *Koord. Khim.* **10** 1372 (1984)
42. D G Batyr, V G Isac, S O Travin, A A Kirienko *Koord. Khim.* **12** 1065 (1986)
43. D G Batyr, V G Isac, S V Kil'mininov *Kinetics and Fundamental Mechanism of the Disproportionation of H_2O_2 by Coordination Compounds of Manganese(II) and Glycine* (Moscow, 1985) Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI), N8353-V (1985)
44. D G Batyr, V G Isac, S V Kil'mininov, Yu A Kharitonov *Koord. Khim.* **13** 3 (1987)
45. D G Batyr, V G Isac, S V Kil'mininov *Koord. Khim.* **13** 367 (1987)
46. D G Batyr, V G Isac, S V Kil'mininov *Koord. Khim.* **13** 1371 (1987)
47. D G Batyr, V G Isac, S V Kil'mininov, Chan Thi Thanh Phuong *Izv. Akad. Nauk Mold. SSR, Ser. Biol. Khim. Nauk* **6** 46 (1986)
48. Ya D Tiginyanu, A Ya Sychev, V M Berdnikov *Zh. Fiz. Khim.* **45** 1723 (1971)
49. Ya D Tiginyanu, A Ya Sychev, V M Berdnikov *Zh. Fiz. Khim.* **45** 2533 (1971)
50. Ya D Tiginyanu, Doctoral Thesis in Chemical Sciences, Moscow State University, Moscow, 1984
51. Ya D Tiginyanu, V M Berdnikov *Zh. Fiz. Khim.* **59** 349 (1985)

52. V G Isac, A Ya Sychev *Oxidation–Reduction Catalysis of the Disproportionation of Hydrogen Peroxide by Coordination Compounds of Manganese. The Catalase Activity* (Kishinev: Mold. Gos. Univ., 1985) Article deposited at MoldNIINTI, N 568-M (1985)
53. V G Isac, Abstract of Doctoral Thesis in Chemical Sciences, Rostov-on-Don, 1990
54. V G Isac, A Ya Sychev, L B Voziyan *Catalytic Properties of Mn(II) Complexes of Triethanolamine* (Kishinev: Mold. Gos. Univ., 1986) Article deposited at MoldNIINTI, N 655-M (1986)
55. V G Isac *Manganese Complexes of 8-Hydroxyquinoline in the Catalytic Decomposition of H_2O_2* (Kishinev: Mold. Gos. Univ., 1990) Article deposited at the MoldNIINTI, N 1159-M (1990)
56. D G Batyr, V G Isac, S V Kil'mininov *Coordination Compounds of Manganese(II) and Glycine* (Kishinev: Mold. Gos. Univ., 1989) Article deposited at MoldNIINTI, N 1145-M (1989)
57. Ya D Tiginyanu, A P Moravskii, V F Shuvalov, V M Berdnikov *Kinet. Katal.* **24** 1038 (1983)
58. E N Rizkolle, J J Anis, L H Knafil *Polyhedron* **109** 7865 (1987)
59. P N Bolasubramanion, E S Schmidt, T C Bruice *J. Am. Chem. Soc.* **109** 7865 (1987)
60. Chan Thi Thanh Phuong, Abstract of Candidate's Thesis in Chemical Sciences, Kishinev, 1984
61. G Davies, L J Kirschenbaum, K Kustin *Inorg. Chem.* 7 146 (1968)
62. C F Walls, D Mays *J. Chem. Soc. A* 665 (1968)
63. M Constantini, A Droward, M Jouref, B Brossard, I Varagnat *J. Mol. Catal.* 7 98 (1980)
64. J Reinado *Analyst* **112** 771 (1987)
65. E G Denisov, N I Mitskevich, V E Agabekov *Mekhanizmy Zhidkofaznogo Okisleniya Kislorodsoderzhashchikh Soedinenii* (The Mechanisms of the Liquid-Phase Oxidation of Oxygen-Containing Compounds) (Minsk: Nauka i Tekhnika, 1975)
66. O S Fedorova *React. Kinet. Catal. Lett.* **8** 371 (1978)
67. N N Lebedev, N G Digurov, T V Bukharina, in *Tezisy Vsesoyuznoi Konferentsii po Zhidkofaznomu Okisleniyu Organicheskikh Soedinenii. Okislenie-86* (Abstracts of Reports at the All-Union Conference on the Liquid-Phase Oxidation of Organic Compounds. Oxidation-86) (Lvov, 1986) Vol. 1, p. 114
68. V G Isac, U Pfanmueller, A Ya Sychev *Zh. Fiz. Khim.* **57** 1969 (1983)
69. A Ya Sychev, U Pfanmueller, V G Isac *Zh. Fiz. Khim.* **57** 1974 (1983)
70. A Ya Sychev, U Pfanmueller, V G Isac *Zh. Fiz. Khim.* **57** 2217 (1983)
71. D G Batyr, V G Isac, S V Kil'mininov *Koord. Khim.* **12** 949 (1986)
72. D G Batyr, V G Isac, A A Kirienko, Yu Ya Kharitonov *Koord. Khim.* **12** 435, (1986)
73. V G Isac, A Ya Sychev *Peroxidase Properties of Manganese(II) Compounds. General Features* (Kishinev: Mold. Gos. Univ., 1988) Article Deposited at MoldNIINTI, N 916-M (1988)
74. D G Batyr, V G Isac, A A Kirienko, S V Kil'mininov *Izv. Akad. Nauk Mold. SSR, Ser. Biol. Khim. Nauk* **5** 46 (1985)
75. D G Batyr, V G Isac, A A Kirienko, I G Povar *Koord. Khim.* **11** 266 (1985)
76. D G Batyr, V G Isac, A A Kirienko, I G Povar *Koord. Khim.* **11** 628 (1985)
77. A Ya Sychev, V G Isac, Chang Thi Thanh Phuong *Zh. Fiz. Khim.* **59** 771 (1985)
78. A Ya Sychev, V G Isac, Chang Thi Thanh Phuong *Zh. Fiz. Khim.* **59** 773 (1985)
79. Ya D Tiginyanu, V P Lozovan *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **21** 1314 (1978)
80. Ya D Tiginyanu, V P Lozovan *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **18** 1229 (1978)
81. Ya D Tiginyanu *Koord. Khim.* **2** 933 (1976)
82. D G Batyr, V G Isac, S V Kil'mininov, S M Fedorova *Peroxidase Properties of Coordination Compounds of Manganese(II) and Glycine. The Outer-Sphere Mechanism of the Oxidation of Substrates* (Kishinev: Mold. Gos. Univ., 1990) Article deposited at MoldNIINTI, N 1167-M (1990)
83. O P Dmitrieva, V E Agabekov, N I Mitskevich *Dokl. Akad. Nauk Beloruss. SSR* **25** 329 (1981)
84. R V Kucher, L I Opeida, T V Novikova *Dokl. Akad. Nauk Ukr. SSR* **5** 37 (1987)
85. I I Korsak, V E Agabekov, V I Bondurko, et al. *Vestsi Akad. Navuk Beloruss. SSR, Ser. Khim. Navuk* **2** 21 (1980)
86. I I Korsak, V E Agabekov, N I Mitskevich *Vestsi Akad. Navuk Beloruss. SSR, Ser. Khim. Navuk* **1** 37 (1979)
87. I Tobushi, N Koga *J. Am. Chem. Soc.* **101** 6456 (1974)
88. E A Lukashova, A B Solov'eva, A L Chugreev, N S Enikolopyan *Dokl. Akad. Nauk SSSR* **294** 1167 (1987)
89. A B Solov'eva, V I Mel'nikov, K K Livnitskii *Izv. Akad. Nauk SSSR Ser. Khim.* **10** 2327 (1983)
90. E A Lukashova, A B Solov'eva, G Ya Malinovskii *Kinet. Katal.* **26** 56 (1985)
91. N S Enikolopyan, K A Bogdanova, K A Askarov *Usp. Khim.* **52** 20 (1983) [*Russ. Chem. Rev.* **52** 13 (1993)]
92. A B Solov'eva, T I Karakazova, K A Bogdanova *Dokl. Akad. Nauk SSSR* **269** 160 (1983)
93. N G Ariko, T P Kenigsberg, N I Mitskevich *Neftekhimiya* **22** 653 (1982)
94. St Lunâk, S Veprek-Siska *React. Kinet. Katal. Lett.* **16** 305 (1981)
95. N P Butina, V S Pshezhetskii, D I Stom *Vysokomol. Soedin.* **626** 813 (1984)
96. A R Eichhorn (Ed.) *Inorganic Chemistry* [G L Eichhorn, Inorganic Biochemistry?] (Translated into Russian) (Moscow: Mir 1978) p. 82
97. V D Komisarov, E T Denisov *Kinet. Katal.* **10** 513 (1969)
98. T P Vorob'eva, E G Isac, A P Purmal', A Ya Sychev *Zh. Fiz. Khim.* **48** 1731 (1974)
99. A Ya Sychev, U Pfanmueller, V G Isac *Zh. Fiz. Khim.* **57** 1690 (1983)
100. E R Stadtman, B S Berlett, P B Chock *Proc. Natl. Acad. Sci. USA* **87** 384 (1990)
101. M B Yim, B S Berlett, P B Chock, E R Stadtman *Proc. Natl. Acad. Sci. USA* **87** 394 (1990)
102. V G Isac, A Ya Sychev, Chan Thi Thanh Phuong, in *Sintez, Modifikatsiya i Issledovaniya Polimernykh i Koordinatsionnykh Soedinenii* (The Synthesis, Modification, and Study of Polymeric and Coordination Compounds) (Kishinev: Sitiintsa, 1989) p. 36
103. I E Kalinichenko, E N Matveeva, A G Pilipenko *Kinet. Katal.* **23** 626 (1982)
104. Yu I Skurlatov, Doctoral Thesis in Chemical Sciences, Moscow State University, Moscow, 1980
105. V G Isac, A Ya Sychev *Peroxidase Properties of Manganese(II) Compounds. II. Oxidation of Organic Dyes by OH Radicals* (Kishinev: Mold. Gos. Univ., 1988) Article Deposited at MoldNIINTI, N 911-M (1988)
106. V G Isac, A Ya Sychev *Peroxidase Properties of Manganese(II) Compounds. VI. Inner-Sphere Oxidation of Organic Dyes* Kishinev (Kishinev: Mold. Gos. Univ., 1988) Article deposited at MoldNIINTI, N 915-M (1988)
107. A Ya Sychev, V G Isac, U Pfanmueller *Zh. Fiz. Khim.* **53** 2790 (1979)
108. A Ya Sychev, Mai Hui Him, V G Isac *Zh. Fiz. Khim.* **58** 906 (1984)
109. V G Isac, A Ya Sychev *Izv. Akad. Nauk Mold. SSR, Ser. Biol. Khim. Nauk* **3** 74 (1987)
110. A Ya Sychev, V G Isac *Peroxidase Properties of Manganese(II) Componds. III. The Influence of Molecular Oxygen* (Kishinev: Mold. Gos. Univ., 1988) Article deposited at MoldNIINTI, N 912-M (1988)
111. A Ya Sychev, V G Isac *Peroxidase Properties of Manganese(II) Compounds. IV. Oxidation by Manganese(IV) Compounds* (Kishinev: Mold. Gos. Univ., 1988) Article deposited at MoldNIINTI, N 923-M (1988)
112. D G Batyr, V G Isac, A A Kirienko, S V Kil'mininov *Koord. Khim.* **12** 949 (1986)
113. K B Yatsimirskii *Kineticheskie Metody Analiza* (Kinetic Analytical Methods) (Moscow: Khimiya, 1967)
114. S U Kreingol'd *Katalimetriya v Analize Reaktivov i Veshchestv Osoboi Chistoty* (Catalymetry in the Analysis of Reagents and Specially Pure Substances) (Moscow: Khimiya, 1983)
115. H Muller, M Otto, G Werner *Catalytic Methods in Trace Analysis* (Translated into Russian) (Moscow: Mir, 1983)
116. A K Lavrukhina, L V Yukina *Analiticheskaya Khimiya Margantsa* (Analytical Chemistry of Manganese) (Moscow: Nauka, 1974)
117. A Ya Sychev, V G Isac, U Pfanmueller *Zh. Anal. Khim.* **33** 1351 (1978)
118. P Bartkus, S Kalesnikaite, L Siaurukaite, E Jasinskiene *Nauch. Tr. Vyssh. Uchebn. Zaved. Lit. SSR, Khim. Khim. Tekhnol.* **8** 37 (1967)
119. S U Kreingol'd, E A Bozhevol'nov, N S Petrovskaya *Metody Analiza Khimicheskikh Reaktivov i Preparatov* (Methods for the Analysis of Chemical Reagents and Preparations) (Moscow: Izd. IREA, 1966) No. 13
120. P Bartkus, E Jasinskiene *Nauch. Tr. Vyssh. Uchebn. Zaved. Lit. SSR, Khim. Khim. Tekhnol.* **11** 25 (1969)

121. V I Martsokha, S U Kreingol'd, L I Sosenkova, in *Sbornik Nauchnykh Trudov VNII Lyuminoforov i Osobo Chistykh Veshchestv* (Collected Reports from the All-Union Institute of Phosphors and Specially Pure Substances) (Moscow, 1977) No. 16, p. 49
122. Chen Gnochu, Fansi Huasjua *Anal. Chem.* **15** 910 (1987)
123. A Ya Sychev, V G Isac, U Pfanmueller *Izv. Akad. Nauk Mold. SSR, Ser. Biol. Khim. Nauk* **4** 88 (1979)
124. P Bartkus, E Jasinskiene *Zh. Anal. Khim.* **23** 1622 (1968)
125. V G Isac, A Ya Sychev *Peroxidase Properties of Manganese(II) Compounds. VIII. Application of the Results in Catalymetry* (Moscow: Mold. Gos. Univ., 1988) Article deposited at MoldNIINTI, N 917-M (1988)
126. Yu I Bratushko *Koordinatsionnye Soedineniya 3d-Perekhodnykh Metallov s Molekulyarnym Kislorodom* (Coordination Compounds of 3*d* Transition Metals with Molecular Oxygen) (Kiev: Naukova Dumka, 1987)
127. E Bayer, P Schretzmann *Structure and Bonding* (Translated into Russian) (Moscow: Mir, 1969)
128. Yu I Bratushko, Abstract of Doctoral Thesis in Chemical Sciences, Kiev, 1991
129. B M Hoffman, C J Wechler, F Basolo *J. Am. Chem. Soc.* **98** 5473 (1976)
130. R D Jones, D A Summervile, F Basolo *J. Am. Chem. Soc.* **100** 4416 (1978)
131. K D Magers, C G Smith, D G Sawyer *J. Am. Chem. Soc.* **100** 989 (1978)
132. A B P Lever, J P Wilshire, S K Quan *Inorg. Chem.* **21** 761 (1981)
133. S D Miller, F D Oliver *J. Inorg. Nucl. Chem.* **34** 1873 (1972)
134. C J Borehan, B Chiswell *Inorg. Chem. Acta* **24** 77 (1977)
135. A Dedien, M M Rohmer *J. Am. Chem. Soc.* **99** 8050 (1977)
136. H D Burcett, V F Newberry, W E Hill, S D Worda *J. Am. Chem. Soc.* **105** 4097 (1983)
137. Li Guang-Nian, Li Guang-Qing *Acta Chem. Sci.* **43** 1053 (1985)
138. K B Yatsimirskii, Yu I Bratushko *Teor. Eksp. Khim.* **18** 367 (1982)
139. N Herron, D H Busch *Inorg. Chem.* **22** 3470 (1983)
140. I Ocura, N K Thuan, T Kaii *J. Mol. Catal.* **5** 125 (1979)
141. I A Duncan, A Harriman, G Parter *J. Chem. Soc., Faraday Trans. 2* **76** 227 (1980)
142. D J Cookson, T D Smith, J F Boas, R Pilbrow *J. Chem. Soc., Dalton Trans.* 1791 (1976)
143. T Yarino, T Matsushito, I Masuda, K Shinra *J. Chem. Soc., Chem. Commun.* 1317 (1970)
144. K Togokichi *Nippon Kagaku Zasshi* **80** 575 (1960)
145. M E Bodini, D T Sawyer *J. Am. Chem. Soc.* **98** 8366 (1976)
146. D T Richens, C G Smith, D T Sawyer *Inorg. Chem.* **18** 707 (1979)
147. A Y Sychev, I M Reibel', L P Podgornaya *Zh. Fiz. Khim.* **43** 676 (1969)
148. I L Benet, F H Hernande, J M Eseriche, R M Zaez *Analyst* **111** 1325 (1986)
149. H S Hertog, E Kooyman *J. Mol. Catal.* **6** 357 (1966)
150. A Ya Sychev, S O Travin G G Duka, Yu I Skurlatov *Kataliticheskie Reaktsii i Okhrana Okruzhayushchei Sredy* (Catalytic Reactions and Protection of the Environment) (Kishinev: Shtiintsa, 1983)
151. A B Solov'eva, A I Samokhvalova, E I Karakozova *Kinet. Katal.* **25** 1080 (1984)
152. S P Prokipchuk, B V Ivakh, in *Tezisy Dokladov 6 Vsesoyuznoi Nauchnoi Konferentsii po Okisleniyu Organicheskikh Soedinenii v Zhidkoi Faze. Okislenie-86* (Abstracts of Reports at the 6th All-Union Conference on the Oxidation of Organic Compounds in the Liquid Phase. Oxidation-86) (Lvov, 1986) Vol. 2, p. 43
153. V G Isac, A Ya Sychev, L B Voziyan, in *Mezhvuzovskii Sbornik* (Intercollegiate Collection) (Kishinev, 1991) p. 89
154. G Gravenhorst, S Beilke, M Betz, H-M Gheovgii, in *Effects of Acid Precipitation on Terrestrial Ecosystems* (Eds T C Hutchinson, M Havis) (New York: Plenum, 1980) p. 41
155. F E Brickman, G J Olson, W P Iverson, in *Atmospheric Chemistry* (Ed. E D Goldberg) (Berlin: Springer, 1982) p. 231
156. H Harirson, T V Larson, C S Monkman *Atmos. Environ.* **16** 1039 (1982)
157. M R Hoffman, D J Jasov, in *SO_2, NO_2 and NO Oxidation Mechanisms: Atmospheric Considerations* (Ed. G Calbert) (Boston: Ann Arbor Science, 1984) p. 101
158. G E Zaikov, S A Maslov, V L Rubailo *Kislotnye Dozhdi i Okruzhayushchaya Sreda* (Acid Rain and the Environment) (Moscow: Khimiya, 1991)
159. A Huss, P K Lim, C A Eckert *J. Phys. Chem.* **86** 4224 (1982)
160. M J Matteson, W Stober, H Luther *Ind. Eng. Chem., Fundam.* **6** 677 (1969)
161. S A Penkett, in *Chemistry of Multiphase Atmospheric Systems* (Ed. W Jaeschke) (Berlin: Springer, 1986) p. 507
162. V V Volod'ko, A A Revin *Kinet. Katal.* **32** 1362 (1991)
163. R G Zika *J. Geophys. Res.* **87** 5015 (1982)
164. D W Gunz, M R Hoffman *Atmos. Environ.* **24** 1601 (1990)
165. T Ibusuki, H M Barnes *Atmos. Environ.* **18** 145 (1984)
166. F W Lurmann, J R Yong, G M Hidy, in *Chemistry of Multiphase Atmospheric Systems* (Ed. W Jaeschke) (Berlin: Springer, 1986) p. 773
167. L W Richards *Atmos. Environ.* **17** 397 (1983)
168. C L Jones, J H Seinfeld *Atmos. Environ.* **21** 2370 (1987)
169. B G Heikes, A M Tompson *J. Geophys. Res.* **88** 10883 (1983)
170. W R Stockwell, J L Calvert *J. Geophys. Res.* **88** 6673 (1983)