Translated from *Uspekhi Khimii*, 48, 1968 - 2006 (1979) U.D.C. 541.515

Inorganic Radical-ions and Their Organic Reactions

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A systematic account is given of the available information about the simplest inorganic radical-ions O_2^-, O^-, O_3^-, CO_2^-, SO_4^-, etc., their reactions with organic substrates are considered, and their possible role in organic reactions is discussed. The bibliography includes 381 references.

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I. INTRODUCTION

The salt-like derivatives of the radical-anion of molecular oxygen became known long before their true nature could be understood. Thus potassium superoxide $K^+O_2^-$ was described by Thenard and Gay-Lussac[1] as early as 1811. It would seem that the idea of the ability of the oxygen molecule to capture a single electron should have arisen for the first time in the study of the mechanism of the oxidation by oxygen, but in reality it was formulated by Bodenstein[2], who discovered the chain mechanism of the interaction of hydrogen with chlorine. Assuming initially that free electrons participate in chain initiation, Bodenstein explained the inhibiting activity of oxygen by the ability of its molecule to capture a single electron, i.e.

$$O_2 + e \rightarrow O_2^- .$$

Heavy alkali metals react with oxygen to form a large number of compounds, among which the "superoxides" MO_2 have been most thoroughly studied in the course of many years[3,4].

There is a striking contrast between the universal distribution of the radical-anion O_2^- in living nature and the small amount of information available about its reactions with organic compounds. However, in recent years a number of unusual reactions of this type were discovered. It was established that the adsorption of oxygen on various metal oxides is accompanied by the formation of the radical-anions O_2^-, O^- and O_3^-.[5] The available data suggest that the adsorbed oxygen radical-anions are responsible for the heterogeneous-catalytic oxidation of various substances by oxygen[5,6]. The formation of the radical-anion CO_2^- may be the first stage in the fixation of carbon dioxide in photosynthesis[7]. Data obtained in a study of the EPR spectra of inorganic radical-anions have been surveyed[8].

The available information about inorganic radical-anions is scattered throughout journals devoted to inorganic, analytical, organic, and physical chemistry, electrochemistry, and biochemistry. Without claiming to cover this field exhaustively, we attempted to compile the most important results obtained in these hitherto divergent disciplines and to deduce possible generalisations.

II. THE RADICAL-ANION OF MOLECULAR OXYGEN

1. Methods of Preparation and Physicochemical Properties

Molecular oxygen has a significant positive electron affinity (0.87 ± 0.13 eV);[9] for this reason, the principal methods for the preparation of superoxide compounds involve the reduction of oxygen. Potassium, rubidium, and caesium superoxides are formed on combustion of these metals in air or in oxygen[10-13]. On combustion, sodium forms a peroxide, since sodium superoxide is thermally unstable and decomposes even at 80–90°C into sodium peroxide and oxygen[14]. The converse reaction takes place at a higher pressure and is used as an industrial method for the preparation of NaO_2.[15]

Among superoxides with ionic structures, the lowest stability is shown by lithium and alkaline earth metal superoxides, which are obtained by ozonising the peroxides of these metals at low temperatures[16,17]. Barium peroxide is stable only below −50°C.[17]

The superoxide radical-anion (SORA), which is short-lived in aqueous solutions, is generated when molecular oxygen captures a hydrated electron[18]:

$$H_2O \xrightarrow{\nu} H^\cdot + {}^\cdot OH + e_{aq}^- + H^+ ,$$

$$H^\cdot + O_2 \rightarrow O_2^- + H^+ ,$$

$$e_{aq}^- + O_2 \rightarrow O_2^- \ (k = 1.9 \cdot 10^{10} \text{ (litre mole}^{-1}\text{ s}^{-1}\text{)}).$$

The most convenient method for the synthesis of sodium and potassium superoxides on a preparative scale involves the reduction of oxygen by solutions of the metals (in liquid ammonia)[19,20] or by ketyls, for example, sodiobenzophenone in tetrahydrofuran[21,22]:

$$Ph_2CO^-Na^+ + O_2 \rightarrow Ph_2CO + NaO_2 .$$

Tetramethyl- and tetraethyl-ammonium superoxides can be obtained by the double decomposition reaction between KO_2 and the corresponding tetraalkylammonium hydroxide[23-25]. In order to obtain Me_4NO_2, tetramethylammonium fluoride can be used instead of tetramethylammonium hydroxide[23]; tetraalkylammonium superoxides can be extracted with liquid ammonia:

$$R_4NX + KO_2 \rightarrow R_4NO_2 + KX ;$$
R=Me or Et; X=OH or F .

Tetramethyl- and tetraethyl-ammonium superoxides are yellow substances melting at 97°[23] and 50°C[25] respectively. In contrast to the thermally stable potassium, rubidium, and caesium superoxides, tetraalkylammonium superoxides decompose vigorously already at 100°C.[23,24]

Convenient methods for the preparative electrochemical reduction of molecular oxygen in aprotic media, leading to the formation of solutions of tetraalkylammonium superoxides, have been developed in recent years[26-31]. A solution of a supporting electrolyte R_4NX in an aprotic solvent (dimethylformamide, dimethyl sulphoxide, pyridine, and acetonitrile) is usually electrolysed at a controlled potential (−1.0 V) in a stream of gaseous oxygen; mercury, platinum, and gold cathodes are used. The resulting coloured solutions give rise to an EPR signal at a low temperature corresponding to the SORA.[26,27,30] It has been shown[32] that the SORA is generated also in the one-electron oxidation of hydrogen peroxide by an alkaline solution of sodium periodate.

Alkali metal superoxides are sparingly soluble in organic solvents. Incidentally, the solubility of KO_2 in dimethyl sulphoxide is sufficient for the measurement of EPR spectra[33]. The low solubility of alkali metal superoxides for a long time inhibited the investigation of their organic reactions. The situation changed significantly after the development of methods for the synthesis of tetraalkyl-ammonium superoxides, which are soluble in aprotic solvents, and also after the discovery in 1975 of the ability of potassium superoxide to dissolve in dimethyl sulphoxide[34] and even in benzene[35] in the presence of crown-ethers.

The crystal lattice of KO_2 is made up of regularly alternating K^+ and O_2^- ions, as in potassium chloride[15]. NaO_2 has a cubic face-centred lattice of the pyrite type[36]. The bond length in the O_2^- radical-anion is 1.29 Å.[37]

The conjugate acid of the SORA as a base is the free hydroperoxy-radical:

$$HO_2^{\cdot} \rightleftarrows H^+ + O_2^- \quad .$$

This radical is a fairly strong acid (pK_a = 4.45,[38] 4.5,[39] 4.88[40]); thus the hydroperoxy-radical exists preferentially in the form of the SORA even in weakly acid media.

2. Chemical Properties

In aqueous solutions alkali metal and tetraalkylammonium superoxides are unstable and rapidly disproportionate to hydrogen peroxide and oxygen[41]:

$$2MO_2 + 2H_2O \rightarrow H_2O_2 + O_2 + 2MOH \ .$$

On passing to strongly alkaline solutions, the rate of disproportionation is greatly reduced[42]. A KO_2 solution in 8 M KOH obtained at −50°C gives rise to the EPR signal of the O_2^- radical-ion[43]. (It is of interest that KO_2 does not react with a solution of hydrogen chloride in dry ether even at room temperature[44].)

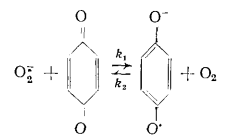
Despite the apparent simplicity of its electronic structure, the radical-anion O_2^- exhibits a varied and in many respects contradictory reactivity. At any rate the widely held view that superoxides with ionic structures can allegedly behave only as strong oxidants has since proved to be clearly untenable.

As a result of its intermediate position in the redox triad

$$O_2 \underset{-e}{\overset{+e}{\rightleftarrows}} O_2^- \underset{-e}{\overset{+e}{\rightleftarrows}} O_2^{2-}$$

the SORA exhibits a dual reactivity: depending on the nature of the substrate, it can behave both as an electron donor and an electron acceptor.

Studies in recent years have shown that the SORA can give up one electron to tetracyanoquinodimethane (TCQ),[33] quinones[45-49], and mono- and di-nitrobenzenes[33,50], converting them into radical-anions (detected by EPR):



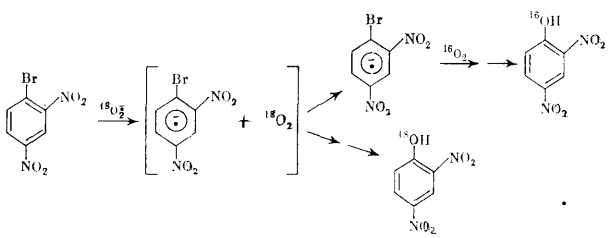
($k_1 = 1.1 \cdot 10^9$ litre mole^{-1} s^{-1}, $k_2 = 10^7$ litre mole^{-1} s^{-1} (Ref.47))

$$TCQ + O_2^- \xrightarrow{-O_2} TCQ^- \ ;$$

$$O_2^- + ArNO_2 \xrightarrow{-O_2} ArNO_2^- \quad .$$

The radical-anions of aromatic nitro-derivatives formed in this process undergo further reactions under the influence of oxygen (and also the excess of SORA); in particular, in the case of dinitrobenzenes one of the nitro-groups is replaced by a hydroxy-group[50].

When halogenonitro- and halogenodinitro-benzenes are acted upon by KO_2 in the presence of a crown-ether, halogen atoms are replaced by hydroxy-groups[50]. It is believed[50] that the first stage in these reactions is not classical nucleophilic substitution, but electron transfer from the SORA to the halogenonitro-derivatives, accompanied by further reactions of the resulting halogenonitrobenzene radical-anions under the influence of oxygen. Owing to the rapid reaction of oxygen, the formation of radical-anions could be demonstrated with the aid of EPR only in the case of *m*-bromonitrobenzene. The one-electron mechanism of the first stage is supported, in particular, by the interaction of $K^{18}O_2$ with 2,4-dinitrobenzene in a solution saturated with $^{16}O_2$. Less than 10% of the resulting 2,4-dinitrophenol contained the ^{18}O isotope[50]:



The reactivity of halogeno-2,4-dinitrobenzenes with respect to KO_2 diminishes in the sequence F > Br ≃ I > Cl,[50] while the sequence F > Cl ≃ Br ≃ I is characteristic of nucleophilic substitution reactions[51].

The fact that the interaction of halogenonitrobenzene radical-anions with oxygen can lead to nitrophenols follows also from kinetic data for the reaction of *p*-chloronitrobenzene with sodium methoxide in the presence of oxygen[52].

An interesting reaction has been observed in a study[33] where it was shown by EPR that treatment of *p*-nitrotoluene with KO_2 leads to the formation of the radical-anion of *p*-nitrobenzaldehyde, which is apparently a product of further reactions of the *p*-nitrotoluene radical-anion in the presence of oxygen and an excess of KO_2.

Among other reactions of the SORA as a one-electron reductant, one may mention the reduction of ferricytochrome *c* to ferrocytochrome *c*,[29] of Nitrotetrazolium Blue

to the corresponding formazan[53], and of tetranitromethane to the nitroformate anion[29,39].

The conjugate acid of the SORA (the $HO_2^{\cdot}$ radical) is a weaker electron donor than the SORA itself[39]:

$$O_2^{\cdot-} + C(NO_2)_4 \rightarrow {}^{-}C(NO_2)_3 + NO_2 + O_2\ ,\quad (k = 1.9 \cdot 10^9\ \text{(litre mole}^{-1}\text{)},$$
$$HO_2^{\cdot} + C(NO_2)_4 \rightarrow {}^{-}C(NO_2)_3 + NO_2 + H^+ + O_2\ ,\quad (k < 1.9 \cdot 10^5\ \text{(litre mole}^{-1}\ \text{s}^{-1}\text{)}).$$

The interaction of the SORA with alkyl halides (tosylates) leads mainly to alkyl peroxides[54-59]. A three-stage reaction mechanism, in which the first stage is bimolecular nucleophilic substitution involving the SORA as the nucleophile, has been proposed[51,52,55]:

$$RX + O_2^{\cdot-} \rightarrow ROO^{\cdot} + X^-\ ,$$
$$ROO^{\cdot} + O_2^{\cdot-} \rightarrow ROO^- + O_2\ ,$$
$$ROO^- + RX \rightarrow ROOR + X^-$$
$$X = Hal,\ \text{or}\ p\text{-}CH_3C_6H_4SO_3-.$$

The above conclusion is based on the inversion of the configuration of the carbon atom linked to the halogen (the tosyl group) in the reaction of KO_2 with optically active halides or tosylates[55,60]. In addition, the sequence of the reactivities of the alkyl halides is the same as in the usual reactions of the S_N2 type (primary > secondary > tertiary; I > Br > Cl).[55,60,61]

The formal S_N2 mechanism does not rule out the possibility of one-electron transfer as one of the stages in the overall reaction[62,63]. In this connection the hypothesis[59] that the initial stage of the reaction under consideration is the reduction of the halide has attracted attention:

$$RHal + O_2^{\cdot-} \rightarrow [Hal^- \cdots R^{\cdot} \cdots O_2] \rightarrow RO_2^{\cdot} + Hal^-\ .$$

This mechanism is quite probable, since, as stated above, the SORA is a fairly effective electron donor and organic halides are capable of accepting an electron (see, for example, Refs. 64–68). The inversion of the configuration is in this case determined solely by the direction of attack on RHal from the side opposite to that of the halogen.

The formation of alcohols[60] as the main products of the reaction of alkyl halides (tosylates) with KO_2 in dimethyl sulphoxide takes place with participation of the solvent[59]. The ROO^- ion, formed "normally", reacts with dimethyl sulphoxide faster than with RX:

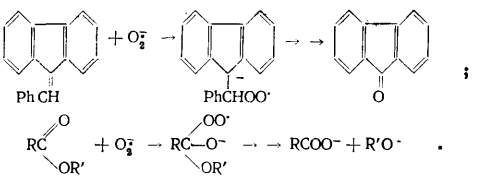
$$ROO^- + Me_2SO \rightarrow \underset{\underset{OOR}{|}}{\overset{\overset{O^-}{|}}{MeSMe}} \rightarrow Me_2SO_2 + RO^-\ .$$

An analogous reaction of the anion of triphenylmethyl hydroperoxide, leading to triphenylmethanol, has been observed[69].

The cleavage of tosylates and methanesulphonates to the corresponding alcohols on treatment with KO_2 in dimethyl sulphoxide, which takes place with complete inversion of the configuration at the carbon atom and which constitutes a synthetic chain procedure in the chemistry of prostaglandins[70,71], apparently also involves the interaction of the corresponding hydroperoxy-anions with dimethyl sulphoxide.

Acid anhydrides[54] and chlorides[44,55,72] are converted into acyl peroxides in high yields on treatment with KO_2, the reaction occuring in a non-aqueous medium. In contrast to the reactions of KO_2 with alkyl and acyl halides, only hexamethyldisiloxane is formed in a high yield by the reaction of chlorotrimethylsilane and KO_2.[44]

The initial nucleophilic addition of the SORA has been postulated in its reactions with benzylidenefluorenone[55] and esters[73,74]:



This mechanism is supported by the finding that, when the acetate derived from (-)(*R*)-2-octanol is cleaved, the configuration of the chiral carbon atom is almost completely preserved[73].

Despite the fact that the electrochemical reduction of the SORA to the O_2^{2-} anion is well known[28,75], there have been so far no studies in which the analogous reaction under the influence of chemical electron donors (DH), i.e. a reaction of the type

$$DH + O_2^{\cdot-} \rightarrow DH^{+\cdot} + O_2^{2-}$$

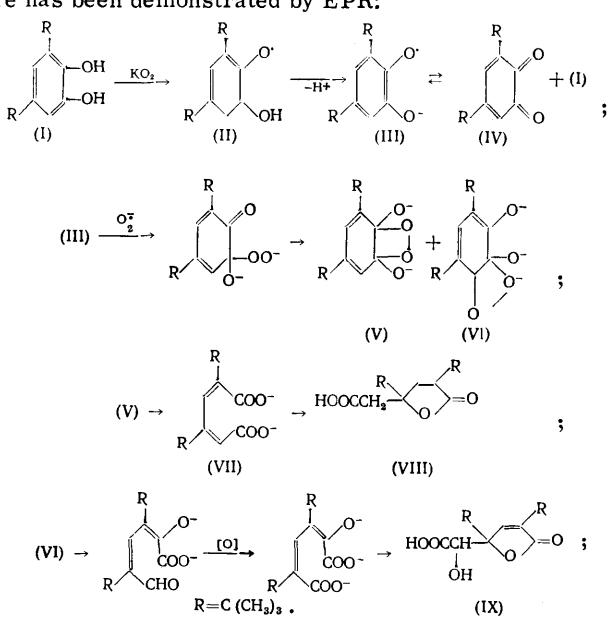
was clearly identified.

The study of reactions of this kind is significantly complicated by the fact that the electron transfer stage is masked by the subsequent rapid processes. For example, electron transfer should be accompanied in certain cases by the recombination or abstraction of a proton under the influence of O_2^{2-}:

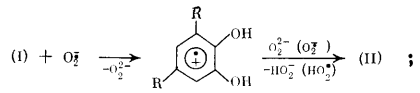
$$DH^+ + O_2^{2-} \rightarrow DHO_2^-\ ;$$
$$DH^+ + O_2^{2-}\,(O_2^{\cdot-}) \rightarrow D^{\cdot} + HO_2^-\,(HO_2^{\cdot})\ .$$

Whereas in the first example the overall result of the reaction is the addition of the SORA to the substrate ($DH + O_2^{\cdot-} \rightarrow DHO_2^-$), the second example can be formally classified as a reaction of the S_H2 type ($DH + O_2^{\cdot-} \rightarrow D + HO_2^-$), i.e. one involving the abstraction of a hydrogen atom.

On treatment with KO_2, 3,5-di-t-butylcatechol (I) is converted largely into a mixture of 3,5-di-t-butyl-*o*-benzoquinone (IV) and compounds (VIII) and (IX).[76] The presence of the radical-anions (III) in the reaction mixture has been demonstrated by EPR:[77]



The intermediate relatively unstable diacid (VII) was isolated on a preparative scale in a low yield[77]. It is extremely likely that the first stage of the process actually consists of two such reactions:



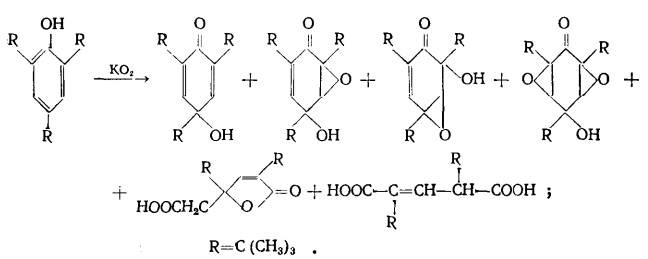
R = C(CH$_3$)$_3$.

Indeed, the abstraction of a hydrogen atom from phenols under the influence of various oxidants is preceded by a stage involving electron transfer from the phenol molecule to the oxidant accompanied by rapid deprotonation of the phenol radical-cation formed[78]. A similar mechanism has been adopted for the abstraction of a hydrogen atom from aliphatic alcohols under the influence of the $SO_4^{\cdot-}$ radical-anion[79,80].

It is of interest to note that the oxidation of alkaline solutions of the catechol (I) by oxygen also leads to *o*-quinone (IV);[81] furthermore, under appropriate conditions the formation of compound (VIII) is also actually possible[82]. Apparently the similarity of the products of the reactions of polyhydric alcohols with oxygen and the SORA is associated with the fact that the SORA is involved in reactions where polyhydric phenols are oxidised by molecular oxygen. The above view is consistent with the data of a number of investigations[83-87], where the ability of polyhydric alcohols to reduce oxygen in the presence of bases was pointed out.

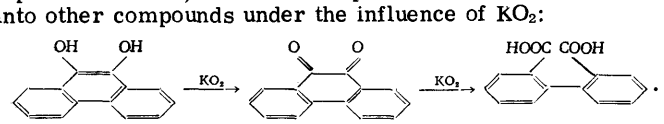
The oxidation of the catechol (I) by atmospheric oxygen in the presence of copper(I) chloride leads to *cis,cis*-di-t-butylmuconic acid[88], which, as stated previously, is also formed on oxidation of the above catechol derivative by KO_2.[73] In this case there is a preliminary activation of oxygen by the formation of its complex with Cu_2Cl_2, in which the reactivity of the dioxygen group in relation to the catechol (I) is probably similar to that of $O_2^{\cdot-}$ in KO_2.

Treatment of 2,4,6-tri-t-butylphenol with potassium superoxide in the presence of 18-crown-6-ether leads to a very complex mixture of products[89]:



R=C(CH$_3$)$_3$.

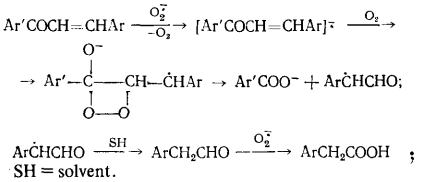
The oxidation of 9,10-dihydroxyphenanthrene under the influence of KO_2 leads to 9,10-phenanthrenequinone and diphenic acid[54,76], which is incapable of further conversion into other compounds under the influence of KO_2:



The cleavage of the fragment –CO–CO– is a fairly general reaction of the SORA and usually leads to carboxylic acids in high yields[54,90,91]. Although San Filippo et al.[91], who investigated the reaction of KO_2 with benzil and its derivatives, speak of the oxidative cleavage of benzils by KO_2, this evidently applies only to the final result, since it is more likely that the reaction actually begins with electron transfer from the SORA to benzil:

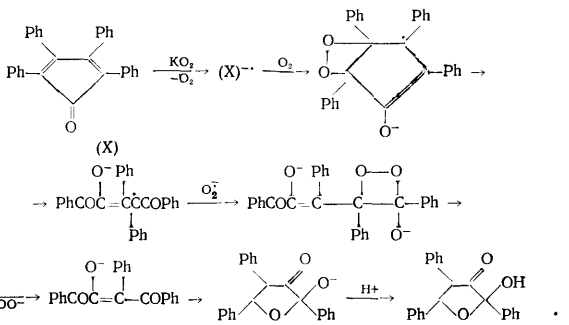


A similar mechanism has been adopted for the cleavage of chalcones[92]:



It has been shown in separate experiments that, on reaction with KO_2, aldehydes can be indeed converted into the corresponding carboxylic acids[54,92].

On treatment with potassium superoxide, tetracyclone (X) is smoothly converted into 2-hydroxy-2,4,5-triphenyl-3-furanone[35,92]:



The cleavage of the C–C bond is also observed when various other carbonyl derivatives are acted upon by the SORA:[91]



It is seen from the examples presented that the SORA is capable of cleaving a very wide range of carbonyl compounds to form carboxylic acids.

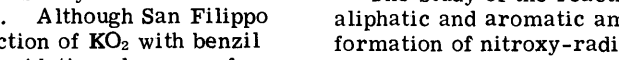
Consideration of the reactions of the SORA with organic substrates accompanied by the cleavage of C–C bonds shows that the key factor in all such reactions is apparently the formation of labile dioxetans, which are known to decompose readily to carbonyl compounds[93].

Ascorbic acid is readily dehydrogenated by the SORA to dehydroascorbic acid[94,95] ($k = 2.7 \times 10^5$ litre mole^{-1} s^{-1})[95].

When 9,10-dihydroanthracene, fluorene, and diphenylmethane are treated with the SORA, the methylene groups are oxidised to carbonyl groups[31,56]. These reactions probably proceed via the abstraction of hydrogen atoms from methylene groups by the superoxide radicals and subsequent transformations of the resulting diarylmethyl radicals under the influence of oxygen and the excess SORA. If the molecule contains an activated methylidyne fragment, then the final product is a hydroperoxide:



The study of the reactions of KO_2 with secondary aliphatic and aromatic amines (by EPR) demonstrated the formation of nitroxy-radicals[33]. The reaction also takes place in the absence of molecular oxygen:



Secondary alcohols (isopropyl alcohol and diphenylmethanol) are oxidised by NaO_2 to ketones (the yields of acetone and benzophenone are 33 and 55% respectively)[96].

It has been found[97] that the SORA is capable of abstracting a hydrogen atom from cysteine; the hydroperoxy radical is not involved in this reaction:

$$RSH + O_2^- \xrightarrow[-HO_2^-]{} RS^\cdot$$

RSH = cysteine.

Under the usual conditions, the reaction of KO_2 with phenylhydrazine in the presence of dicyclohexyl-18-crown-6-ether can serve as a source of phenyl radicals[98]:

$$PhNHNH_2 \xrightarrow{O_2^-} PhN{=}NH \xrightarrow[-HO_2^-]{O_2^-} Ph^\cdot + N_2;$$

$$Ph^\cdot + PhN{=}NH \xrightarrow{-PhH} Ph^\cdot + N_2 \ ;$$

$$Ph^\cdot + PhH \rightarrow \rightarrow Ph{-}Ph \ .$$

On oxidation of other compounds with an N–N bond under the same conditions, the following products are formed[98] (the yields expressed as percentages are indicated in brackets): toluene (54), benzoic acid (15), benzyl alcohol (6), and benzaldehyde (6) from benzylhydrazine; n-octane (32) from n-octylhydrazine; *N*-nitrosodiphenylamine (50) from 1,1-diphenylhydrazine; *N*-methyl-*N*-nitroaniline (33) from 1-methyl-1-phenylhydrazine; azobenzene (98) from 1,2-diphenylhydrazine; benzophenone azine (83) from benzophenone hydrazone; fluorenone (86) from 9-diazofluorene. Many of these reactions apparently begin with the state involving the abstraction of a hydrogen atom from the substrate.

Summarising the foregoing findings, one should note that reactions where the SORA plays the role of a mild reductant, a moderately strong nucleophile, or a free radical exhibiting a moderate dehydrogenating activity are the most characteristic of this species. An interesting feature of the SORA is its ability to react with both π-electron deficient systems (aromatic nitro-compounds) and with compounds having an excess of π electrons (phenols) as well as nucleophiles of the amine type.

3. Reactions Involving the Intermediate Formation of the SORA

Having adopted the view that, after the preliminary binding of the reacting species in complexes, the displacements of the atomic nuclei relative to one another are usually preceded by electron transfer[63], the oxidation of various compounds by oxygen can be represented by the following scheme:

$$RH + O_2 \rightleftarrows RH \cdots O_2 \rightleftarrows [RH^{+\cdot} \cdots O_2^-] \quad (XI);$$

$$(\text{or } [R^\cdot \cdots H^+ \cdots O_2^-]) \rightarrow R^\cdot + HO_2^\cdot \ .$$

In particular, the results of studies on the kinetics of the oxidation of *o*-xylene by oxygen are treated in this way[99]. In this interpretation of the mechanism of the oxidation reaction the tendency towards an increase of the ease of oxidation of organic compounds by oxygen accompanied by an increase of their capacity for electron transfer, which is usually observed, can be naturally accounted for.

Electron transfer to the charge-transfer complex (CTC) (XI) can apparently be induced also by the irradiation of the RH–O_2 system by light whose wavelength corresponds to the absorption band of the charge-transfer process[100–102], for example[102]:

$$C_2H_5OH \cdots O_2 \xrightarrow{h\nu} [C_2H_5\dot{O}H \cdots O_2^-] \rightarrow \text{oxidation products.}$$

One of the types of reactions in which there is a possibility of the formation of the SORA is that of neutral free radicals with oxygen. Thus it has been noted[103] that the radical obtained in the one-electron reduction of the oxidised form of nicotinamide-adenine dinucleotide (NAD^+) in aqueous solutions is much less stable in the presence of oxygen than in its absence. This can be explained by the occurrence of the process

$$NAD^\cdot + O_2 \rightarrow NAD^+ + O_2^- \ (k = 1.9 \times 10^9 \text{ litre mole}^{-1}\,\text{s}^{-1}),$$

apparently accompanied by the decomposition of the resulting SORA under the influence of water.

It is extremely interesting that the rate of reaction with oxygen increases in parallel with the enhancement of the reducing properties of the radical in the sequence $^\cdot CH_2CMe_2OH \simeq {}^\cdot CH_2CH(Me)OH < {}^\cdot CH_2OH < (Me)_2{}^\cdot COH < {}^\cdot COOH$.[104] One of the possible explanations of this behaviour is electron transfer[104]:

$$R^\cdot + O_2 \rightarrow [R^+ \cdots O_2^-] \rightarrow RO_2^\cdot \ .$$

A fairly large number of examples characterising the ability of carbanions and cryptocarbanions to function as electron donors are available at the present time. Significant advances have been made in this field in recent years when it has been shown that this ability is exhibited in many fundamental reactions of organometallic chemistry[105]. The fundamental principle of the one-electron oxidation of carbanions by oxygen was formulated by Russell[69]:

$$R^- + O_2 \rightarrow R^\cdot \cdots O_2^- \begin{cases} \longrightarrow RO_2^- \\ \longrightarrow R^\cdot + O_2^- \end{cases};$$

$$R^\cdot + O_2 \rightarrow RO_2^\cdot \ ;$$

$$RO_2^\cdot + R^- \rightarrow RO_2^- + R^\cdot, \text{ etc.}$$

The formation of free radicals in reactions of organometallic compounds with oxygen has been reliably established[106–108]. Evidently electron transfer from the carbanion to oxygen must be preceded by the coordination of the oxygen atom to the metal atom[108]. A similar mechanism was adopted also for the oxidation with oxygen of various organometallic compounds having a covalent C–metal bond[108].

The oxidation of certain *O*-anions takes place similarly—with electron transfer to oxygen (see Section II, 6). The reaction of fused potassium, rubidium, and caesium hydroxides with oxygen at 410 °C leads to the formation of a mixture of the peroxide and superoxide of the corresponding metal[109]. According to McGrath's results[110], the Favorskii rearrangement includes a stage involving the one-electron reduction of oxygen by the alkali metal enolate.

The following mechanism, involving one-electron transfer from the anion R^-, has been proposed for the low-temperature oxidation of mercaptans by oxygen[111]:

$$RSH \rightleftarrows RS^- + H^+$$

$$RS^- + O_2 \rightarrow RS^\cdot + O_2^- \ ;$$

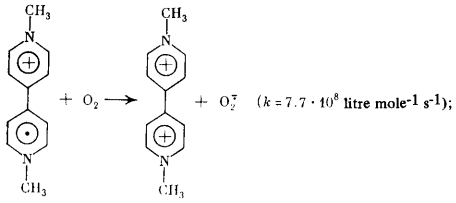
$$2RS^\cdot \rightarrow RSSR \ .$$

The participation of the SORA in the oxidation of mercaptans by oxygen has been demonstrated using a superoxide dismutase test[112] (see below).

It is of interest that, on passing from CH_3OH to tetrahydrofuran, dioxan, diglyme, and further to dimethylformamide, the rate of oxidation of butane-1-thiol increases by a factor of 334 in the presence of sodium methoxide. A possible explanation of this finding, postulating that the influence of the solvent is based on

the enhancement of the nucleophilic properties of CH_3O^- in the above sequence[111] is unconvincing because mercaptans are fairly strong acids and the change in the concentration of the thiolate anion on passing from methanol to dimethylformamide is hardly likely to cause such a large effect. The sharp acceleration of the reaction in highly solvating solvents is apparently associated with the significant decrease of the activation energy for electron transfer on passing from non-polar and weakly solvating media to polar and highly solvating media.

It has been shown by pulse radiolysis that the reaction of a radical-cation with oxygen in aqueous solution proceeds in two stages[113]:

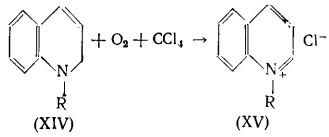


(XII) (XIII)

$$(XII) + O_2^{\cdot-} \longrightarrow (XIII) + O_2^{2-} \quad (k = 6.8 \cdot 10^8 \text{ litre mole}^{-1}\text{ s}^{-1}).$$

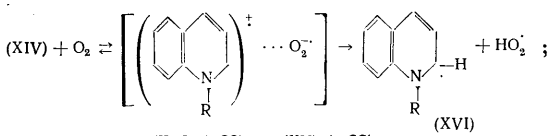
In methanol solution the reaction proceeds in a more complex manner [it is of second order with respect to (XII) and of first order with respect to oxygen][114].

In conformity with the results of kinetic studies, the involvement of the SORA in the oxidation by oxygen of certain aromatic amines in an aqueous medium has also been postulated[115]. An interesting reaction of 1,2-dihydroderivatives of quinoline with CCl_4, which proceeds only in the presence of oxygen and leads to quinolinium salts, has been described[116]:



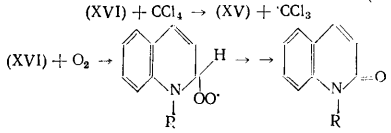
(XIV) (XV)

The oxidation of dihydroquinolines in the absence of a solvent leads to the formation of the corresponding 2-quinolinones[116]. Analysis of literature data leads to the hypothesis that the above oxidation of 1,2-dihydroquinolines proceeds as follows:



(XVI)

$$(XVI) + CCl_4 \rightarrow (XV) + {}^{\cdot}CCl_3$$



Indeed, judging from polarographic reduction data, carbon tetrachloride is a fairly effective electron acceptor ($E_{1/2} = -0.25$ V relative to the saturated calomel electrode[117] in dimethylformamide as a solvent). It is to be expected that radicals of type (XVI) should be fairly strong reducing agents, since it is known, for example, that the radical $(CH_3)_2\dot{C}NH_2$, which contains the α-amino-group, is a strong reductant[118].

4. The Superoxide Radical-Anion and Singlet Oxygen (SO)

The hypothesis of the possible formation of oxygen in an excited state from the SORA has been put forward by Stauff et al.[119]

In a study of the hydrolysis of KO_2 in dimethyl sulphoxide in the presence of singlet oxygen acceptors Khan[120] concluded in 1970 that SO is formed in the disproportionation of the SORA:

$$2O_2^{\cdot-} + 2H^+ \rightarrow H_2O_2 + O_2(^1S).$$

Further investigations of a trapping of the SO formed in this reaction yielded contradictory results[33,121-124], which can be explained[125,126] by the rapid quenching of SO by the superoxide radical-anion, which competes with the capture of SO by the acceptors employed:

$$AO_2 \xleftarrow{A} O_2(^1S) \xrightarrow[-O_2^{\cdot-}]{O_2^{\cdot-}} O_2(^3S);$$

A = SO acceptor.

The mechanism of the formation of SO in the disproportionation of the SORA is still not clear, although one can assume that SO is formed in the one-electron oxidation of the SORA by its protonated form:

$$O_2^{\cdot-} + H\dot{O}_2 \rightarrow O_2(^1S) + HO_2^-,$$

since it has been shown that the oxidation of the SORA by strong one-electron oxidants leads to the formation of SO,[127] while in the reaction

$$2HOO^{\cdot} \rightarrow H_2O_2 + O_2$$

SO is not produced[128].

It is noteworthy that the reactions of dyes in an excited state (Dy^T) with molecular oxygen involving the conversion of the latter into SO, which formally reduce to energy transfer[129,130], can apparently proceed via an electron exchange mechanism with the intermediate formation of a radical-ion pair[131]:

$$Dy^T + O_2(^3S) \rightarrow [Dy^{\cdot+} \cdots O_2^{\cdot-}] \rightarrow Dy + O_2(^1S).$$

This is supported by the fact that the "annihilation" of oppositely charged radical-ions, responsible for the phenomenon of electrochemiluminescence[132], frequently results in the formation of electronically excited molecules:

$$Dy^{\cdot+} + A^{\cdot-} \begin{cases} \rightarrow Dy + A^* \\ \rightarrow Dy^* + A. \end{cases}$$

It has also been shown that the reaction of the SORA with certain radical-cations [the system of species belonging to the type forming the radical-ion pair $[Dy^{\cdot+}...O_2^{\cdot-}]$ leads to the formation of SO:[127]

$$Ferr^{\cdot+} + O_2^{\cdot-} \rightarrow Ferr + O_2(^1S);$$

Ferr = ferrocene.

The formation of radical-ion pairs $(Dy^{\cdot+}...O_2^{\cdot-})$ in the reaction of dyes in triplet states has been postulated on the basis of kinetic data[133,134].

The transition of the dye molecules from the ground to the excited state can be accompanied by a sharp enhancement of the ability of the dye to function as an electron donor. It has been stated, for example, that the oxidation-reduction potential of the P_{700} pigment is +0.4 V in the ground state, while in the excited state it is −0.32 V (the sum $\Delta E_0 \simeq -0.7$ V!).[135]

5. "Covalent" Superoxides

The fact that many transition metal compounds which are effective reductants can be oxidised by oxygen naturally leads to the conclusion that the reaction

$$M^{n+} + O_2 \rightleftarrows M^{(n+1)+} + O_2^- .$$

is possible. This idea was apparently first formulated by Just[136], who investigated the oxidation of iron(II) salts by oxygen. Subsequently the idea of the involvement of the SORA in the oxidation of iron(II) via oxygen was developed by Weiss[137]:

$$Fe^{2+} + O_2 \rightleftarrows Fe^{3+} \cdot O_2^- \xrightarrow{H^+} Fe^{3+} + HO_2^- ;$$
$$HO_2^- + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} ;$$
$$HO_2^- + H^+ \rightarrow H_2O_2 ;$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + OH^- .$$

In subsequent years the problem of the structure of the intermediate oxygen adducts $[MO_2]^{n+}$, formed in the oxidation of transition metal compounds by oxygen and considered by Weiss as SORA derivatives, was at the centre of attention. Some of these adducts are sufficiently stable to be isolated in the pure state. A number of reviews are devoted to the consideration of their properties[138–140]. The interest in oxygen adducts has been aroused mainly by the search for effective synthetic molecular oxygen transferring agents[138] and also by the search for methods of activating oxygen in various oxidation processes[141,142].

The studies in recent years have been characterised by the application of a wide variety of physical methods to the solution of the problem of the structure of metal compounds containing an oxygen molecule as a ligand. The latest advances in this field are discussed below.

In 1964 Weiss suggested that oxygen adducts formed by natural oxygen transferring agents (haemoglobin Hb and myoglobin Mb) should be regarded as iron(III) compounds containing the superoxide ion, i.e. $HbFe^{3+}\cdot O_2^-$ and $MbFe^{3+}\cdot O_2^-$.[143] In support of this hypothesis, Weiss referred particularly to the similarity of the ultraviolet spectra of these adducts and those of methaemoglobin and metmyoglobin derivatives and the fact that oxygen is "activated" in oxyhaemoglobin. Within the framework of Weiss's hypothesis, the diamagnetism of oxyhaemoglobin is explained by the antiferromagnetic interaction in the ion pair $HbFe^{3+}\cdot O_2^-$. Pauling[144] opposed this treatment, stating that oxyhaemoglobin should be regarded as an iron(II) derivative having the formula $HbFe^{2+}=O^+_{O^-}$. Quantum-mechanical calculations[145] support the view that the iron in $HbFeO_2$ is tervalent.

The formation of the $Fe-O_2$ bond in adducts of iron(II) compounds with oxygen can be represented by a correlation diagram (Fig. 1) within the framework of the molecular orbital method[146]. However, one should note that the diagram presented says nothing about the amount of ionic character of the $Fe-O_2$ bond.

The use of physical methods in the solution of the problem of the nature of the bond in oxyhaemoproteins yielded results which are not susceptible to a simple interpretation. Thus studies by the Mössbauer method showed that the chemical shifts of iron in haemoglobin and oxyhaemoglobin are approximately the same[147], which corresponds to approximately identical states of the iron in these compounds. On the other hand, the similarity of the Raman spectra of oxyhaemoglobin and methaemoglobin derivatives was interpreted as a result of the presence of iron(III) in $HbFeO_2$.[148,149] Furthermore, the vibration frequency of the O–O bond is 1107 cm^{-1} in $HbFeO_2$ [150] and 1145 cm^{-1} in KO_2,[151] while in gaseous oxygen it is 1555 cm^{-1}.[152] The study of oxyhaemoglobin by X-ray fluorescence spectroscopy led to the conclusion that there is an unpaired electron at the iron atom in oxyhaemoglobin[153].

The problem of the nature of the $Fe-O_2$ bond, particularly of the amount of its ionic character in oxyhaemoproteins, probably cannot be regarded as finally solved. One can only note that the antiferromagnetic interaction in oxyhaemoproteins, postulated in Weiss's hypothesis, is equivalent to the formation of a new electron pair, giving rise to the $Fe-O_2$ bond owing to the comparatively short $Fe-O_2$ distance, i.e. in fact it corresponds to the absence of the O_2^- radical-anion from oxyhaemoprotein molecules. Naturally, this view in no way predetermines the solution of the problem of the amount of ionic character of the $Fe-O_2$ bond as well as the possibility or impossibility of the dissociation of the adducts $[FeO_2]^{2+}$ into Fe^{3+} and the SORA or the transition of the $Fe^{3+}O_2^-$ ion pair to the triplet state.

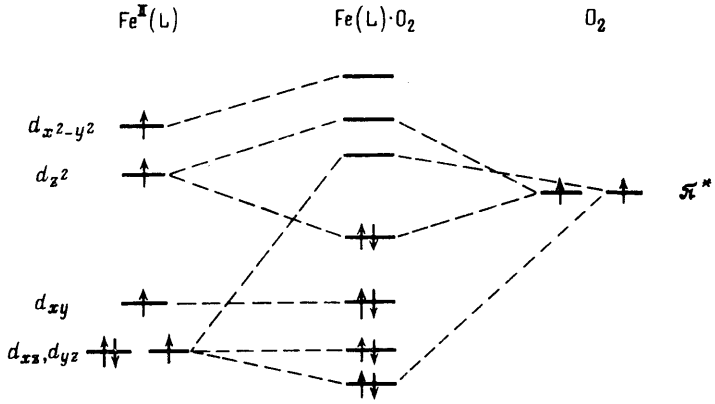


Figure 1. A molecular-orbital model of the coordination of oxygen to iron(II) complexes (L = ligand).

Recently the problem of the nature of the bond between oxygen and the metal atom in the oxygen complexes of transition metals has been vigorously discussed also in relation to octahedral oxygen complexes of bivalent cobalt. X-Ray diffraction data have shown that the oxygen atoms in the oxygen adducts of 1 : 1 cobalt(II) complexes are not equivalent and that the O–O bond length is in many instances close to that observed for the superoxide ion in KO_2.[154–156] The authors of these studies therefore regard these complexes as compounds containing tervalent cobalt and the SORA $\left[-\overset{\diagdown\ \diagup}{Co^{3+}}\cdot O_2^- \right]$.

The results of a study of the oxygen complexes of cobalt by X-ray electronic spectroscopy also agree much better with the formula $Co^{3+}\cdot O_2^-$ than with $Co^{2+}\cdot O_2$.[157,158]

The formula $Co^{3+}\cdot O_2^-$ for the oxygen complexes of cobalt was also adopted by investigators[159,160] who studied such complexes by EPR as well as investigators[161,162] who carried out quantum-mechanical *ab initio* calculations on the oxygen complexes of cobalt by the LCAO-MO-SCF method.

However, Tovrog et al.[146] published very recently a study where it is stated (these views are shared also by the authors of the present review) that the treatment of the oxygen complexes of cobalt(II) as $Co^{3+}\cdot O_2^-$ is only qualitatively correct, since the real degree of electron transfer is usually less than unity and varies in the range 0.1–0.8.

The formation of a complex between cobalt(II) compounds and oxygen has been regarded[146,162] as a result of the pairing of the spin of the electron in the d_z orbital of Co^{2+} with the spin of the electron in the π^* orbital of the oxygen atom. Depending on the strength of the ligand field around the cobalt atom, the complex approaches more or less closely the limiting case described by the formula $Co^{3+}\cdot O_2^-$.[146] The mixing of the Co^{2+} and O_2 orbitals can be represented by the diagram in Fig. 2: we have $Co^{3+}\cdot O_2^-$ for $\alpha = 0$ and $Co^{2+}\cdot O_2$ for $\alpha = \beta$.

Analogous problems concerning the nature of the metal–oxygen bond arise also for the oxygen complexes of Cu^+, Cr^{2+}, Ir^+, Ni^0, Pt^0, Pd^0, etc. For example, the ease of oxidation of copper(I) compounds has been explained by the formation of a π-complex, which is subsequently converted into a copper derivative of the SORA:[163]

$$Cu^+ + O_2 \rightleftarrows [Cu^+ \rightarrow O_2] \rightleftarrows Cu^{2+}\cdot O_2^- .$$

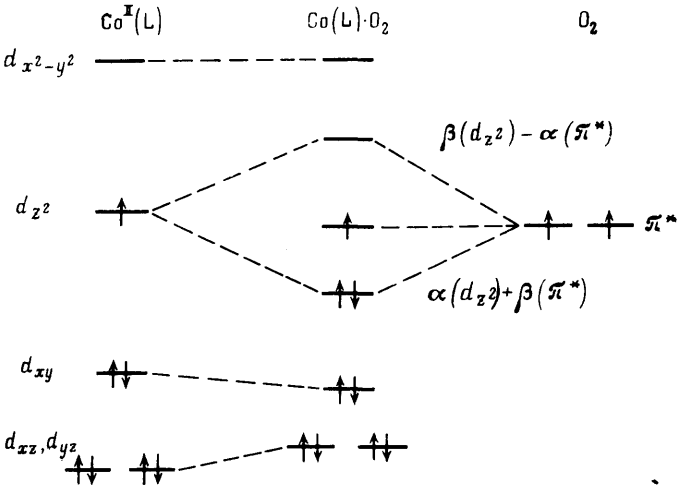


Figure 2. A molecular-orbital model of the coordination of oxygen to cobalt(II) complexes.

In the complexes $Ir(Hal)(CO)(PPh_3)_2.O_2$ the length of the O–O bond varies markedly depending on the nature of the halogen[164,165]: for Hal = Cl, it amounts to 1.30 ± 0.03 Å, while for Hal = I it is 1.47 ± 0.02 Å. Accordingly, La Placa and Ibers[164] regard these complexes as $Ir^{2+}(Cl)(CO)(PPh_3)_2\cdot O_2^-$ and $Ir^{3+}(I)(CO)(PPh_3)_2\cdot O_2^{2-}$. As a result of the difference between the structures of these complexes, reversible binding of oxygen is possible only for the complex $Ir(Cl)(CO)(PPh_3)_2$.[165]

In considering the problem of the way in which oxygen complexes of metals can serve as sources of the SORA, we shall point out the following pathways which are possible in principle:

(1) Direct dissociation (ionisation) of the complex:

$$M^{n+} + O_2 \rightleftarrows [MO_2]^{n+} \rightleftarrows M^{(n+1)+} + O_2^- .$$

On the basis of kinetic data, it is stated[166] that the oxygen complex of Cu^+ in an aqueous acetonitrile medium is capable of dissociating via the above mechanism, but the dissociation with formation of oxygen takes place at a rate which is higher by a factor of approximately 26 than the dissociation with formation of the O_2^- radical-ion.

(2) In protic media there is a possibility of indirect formation of the SORA:[34,166,167]

$$[MO_2]^{n+} + H^+ \rightarrow [MOOH]^{(n+1)+} \rightleftarrows M^{(n+1)+} + HO_2^\cdot ;$$
$$HO_2^\cdot \rightleftarrows H^+ + O_2^- .$$

In this case the formation of $HO_2^\cdot$ is significantly facilitated by the presence of anions capable of forming stable complexes with $M^{(n+1)+}$. Accordingly, the Fe^{2+}–pyrophosphate-anion–O_2 system is greatly superior, as regards the efficiency of the generation of the SORA in aqueous solution, to the analogous systems containing, instead of pyrophosphate, anions which are weaker complex-forming agents in relation to Fe^{3+}.[168]

Few data are as yet available concerning reactions of dioxygen transition metal complexes. Their study is complicated by different oxidation-reduction reactions of the substrate and its oxidation products, for example:

$$M^{(n+1)+} + RH \rightarrow M^{n+} + R^\cdot + H^+ ;$$
$$M^{(n+1)+} + ROOH \rightarrow M^{n+} + ROO^\cdot + H^+ ;$$
$$M^{n+} + ROOH \rightarrow M^{(n+1)+} + RO^\cdot + OH^- .$$

However, it has been established that the formation of complexes between oxygen and transition metal compounds alters significantly the reactivity of oxygen[140,142].

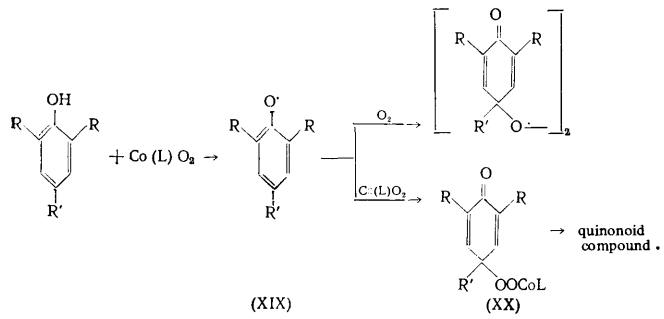
Presumably oxygen complexes of transition metal compounds containing the superoxide-like dioxygen ligand should be capable of abstracting hydrogen atoms from fairly reactive organic compounds. Indeed the available literature data confirm this view[169–173]. For example, in a study of the kinetics of the oxidation of cumene by oxygen, catalysed by the *o*-phenanthroline complex of copper, it was possible to show that the reaction of the oxygen complex of copper with cumene plays an important role in this process[171]:

$$\underset{\text{(XVII)}}{[Cu(phen)]^+} + O_2 \rightleftarrows \underset{\text{(XVIII)}}{[Cu(phen)]^{2+}\cdot O_2^-} ;$$
$$\text{(XVIII)} + RH \rightarrow \text{(XVII)} + HO_2^\cdot + R_2^\cdot ;$$
$$R^\cdot + O_2 \rightarrow RO_2^\cdot ;$$
$$RO_2^\cdot + RH \rightarrow ROOH + R^\cdot, \text{ etc.}$$

R = $PhCMe_2$; phen = *o*-phenanthroline.

It is appropriate to mention here that the abstraction of a hydrogen atom from cumene takes place also under the influence of alkali metal superoxides[31]. The oxidising properties of O_2 complexes with cobalt(II) compounds have been demonstrated convincingly also in relation to the complex $[Co(3\text{-MeO-Salen})\cdot O_2]^{2+}$.[174] This complex readily oxidises thiols, ascorbic acid, hydroquinone, and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine. In the last two instances it was shown by EPR that semiquinone radicals and the *N,N,N',N'*-tetramethyl-*p*-phenylenediamine radical-cation are formed respectively.

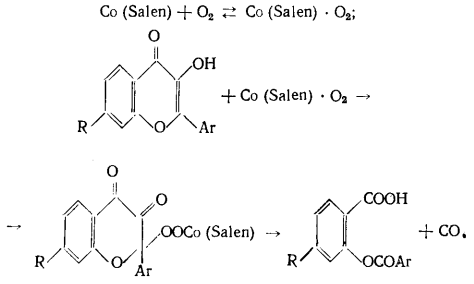
It has been demonstrated that cobalt complexes capable of reversible binding of oxygen behave as homogeneous catalysts of the oxidation of substituted phenols by oxygen under mild conditions, which leads to a mixture of various quinonoid compounds[175-177].



(XIX) (XX)

Complex (XX), where R = R′ = t-C_4H_9 and L = bis-(3-salicylideneaminopropyl)amine dianion, was isolated in the reaction of 2,4,6-tri-t-butylphenol with a stoichiometric amount of CoL and oxygen[177]. Compound (XX) is also formed as a result of the recombination of two radicals—(XIX) and $Co(L)O_2$.

The *N,N′*-bis(salicylidene)ethyleneaminate complex of cobalt(II) [Co(Salen)], which is an effective oxygen transferring agent, catalyses at room temperature the oxidation of hydroxyflavones, simulating the enzymic oxidation of quercetin[178]:



It is of interest to note that the ability of various metal compounds having reducing properties to activate molecular oxygen by its partial reduction is apparently not unique. It appears almost self-evident that, in principle, there should exist activators of molecular oxygen which do not contain reducing metals at all. Thus, in the oxidation of cumene with oxygen, magnesium-phthalocyanine exhibits a catalytic activity[179]:

$$Pc + O_2 \rightleftarrows Pc \cdots O_2 \rightleftarrows Pc^{+} \cdots O_2^{-} \quad (XXI),$$

$$RH + (XXI) \rightarrow Pc + R^{\cdot} + HO_2^{\cdot};$$

R = $PhCMe_2$; Pc = magnesium-phthalocyanine.

The ability of the substrate to form complexes with oxygen clearly depends not only on the nature of the metal but also on the nature of its ligand environment and is thus a general property of the enzyme-like molecule. The study of metal complexes with ligands capable of undergoing ready and reversible one-electron transitions, which only partly involve the valence shell of the metal, is therefore particularly promising. Complexes with paramagnetic ligands are of special interest at the present time.

6. The Role of the SORA in Biochemical Processes

The study of the role of the SORA in living systems was stimulated by the studies of McCord and Fridovich[29,180-182] carried out in 1968–1970. Subsequent investigations initiated a new field in biochemistry—the biochemistry of the SORA. It became clear that the SORA plays an important role in all aerobic cells.

Molecular oxygen plays the role of a readily available electron acceptor in various biochemical oxidation reactions. As a result of such processes, the electrons of the oxidised substrates are passed to the electron transferring enzymes and then further to oxygen molecules, which are converted into the SORA.

The high reactivity of the SORA and of the hydroperoxy-radical, which always accompanies it in aqueous solutions, as well as the possibility of the formation of hydroxy-radicals in systems of this kind are responsible for the toxic effect of the SORA on living tissues[29,183-188]. In 1969 McCord and Fridovich discovered the first example of enzymes which protect living systems from the toxic activity of the SORA by its catalytic disproportionation[29]:

$$O_2^{\cdot-} + 2H^{+} \xrightarrow{\text{enzyme}} H_2O_2 + O_2;$$

$$H_2O_2 \xrightarrow{\text{catalase}} H_2O + O_2.$$

This enzyme proved to be the copper-containing protein erythrocuprein, which had been known already for more than thirty years[189]. Other proteins, fulfilling an analogous function and given the general name of superoxide dismutases (SOD), were discovered subsequently. The active centres of the SOD are usually copper atoms: certain simple copper compounds also possess superoxide dismutase properties[190,191]. However, SOD containing metals other than copper are also known[192,193]. Vigorous research in recent years established the presence of SOD in living objects such as human cells[189,194,195], animal livers[196], plant leaves[179,198], wheat grains[199], and rod cells in animal eyes[200], yeasts[193,201], guinea pig leucocytes[202], etc.

The following sequence of reactions has now been adopted as the mechanism of the enzymic disproportionation of the SORA:[203,204]

$$E + O_2^{\cdot-} \rightarrow E^{-} + O_2 \quad (k = 1.2 \pm 0.2 \cdot 10^9 \text{ litre mole}^{-1} \text{ s}^{-1});$$

$$E^{-} + O_2^{\cdot-} \xrightarrow{2H^{+}} E + H_2O_2 \quad (k = 1 - 3 \cdot 10^9 \text{ litre mole}^{-1} \text{ s}^{-1});$$

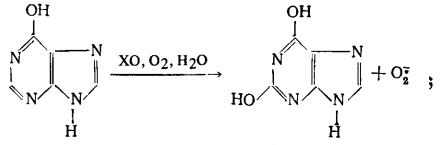
$$E^{2-} + O_2^{\cdot-} \xrightarrow{2H^{+}} E^{-} + H_2O_2 \quad (k = 1.2 \pm 0.2 \cdot 10^9 \text{ litre mole}^{-1} \text{ s}^{-1});$$

E = erythrocuprein.

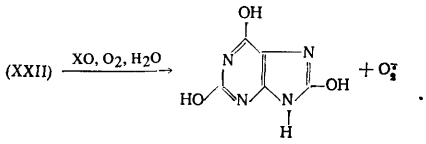
It is extremely significant that, in contrast to spontaneous dissociation, enzymic dissociation does not lead to the formation of toxic singlet oxygen[188].

Following the discovery of the superoxide dismutase properties of erythrocuprein and other proteins, biochemists and organic chemists acquired a valuable test, which makes it possible to confirm or disprove the involvement of the SORA in a particular process. The system believed to generate the SORA is usually treated with compounds capable of reacting with the SORA; these are normally ferricytochrome *c* [29] and Nitrotetrazolium Blue,[53,183] which are reduced by the SORA to ferrocytochrome *c* ($k = 1.4 \times 10^6$ litre $mole^{-1}$ s^{-1};[205] $HO_2^{\cdot}$ does not reduce ferricytochrome *c* [205]) and formazan respectively, as well as adrenalin, which is oxidised by the SORA to adrenochrome[85]. If the system does indeed induce any of these reactions and catalytic amounts of SOD inhibit it fully (or significantly), it is concluded that the SORA is formed in the given system.

The formation of the SORA has been established in many enzymic and non-enzymic systems. The enzymic system which has been most thoroughly investigated and most frequently used for the generation of the SORA consists of a mixture of xanthine with a catalytic amount of xanthine oxidase (XO), which converts xanthine into uric acid in the presence of oxygen[32,180,181,206]. Hypoxanthine can be used instead of xanthine[185]:



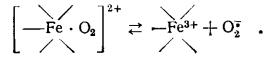
(XXII)



It is believed that oxygen is reduced to the SORA by the reduced form of the isoalloxazine ring of the flavin-adenine dinucleotide associated with xanthine oxidase[207,208].

Oxygen is also reduced to the SORA when it is treated by the reduced form of a simpler flavin compound—flavin mononucleotide[182,208,209]. The formation of the SORA in the reaction of reduced flavins with oxygen was demonstrated directly by EPR.[210]

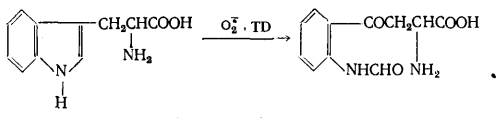
Misra and Fridovich[211], who discussed the problem of the possible generation of the SORA from the oxygen complexes of haemoproteins, noted that even their simple dissociation might lead to the SORA:



The properties of the SORA suggest the possibility of its formation from oxyhaemoglobin. Thus, in contrast to haemoglobin and methaemoglobin, the denaturation of oxyhaemoglobin by heat is accompanied by oxidation of its sulphydryl groups[212]. Catechol, hydroquinone[213], and aniline[214] exhibit a catalytic effect on the $HbFe.O_2 \rightarrow$ MetHbFe transition (as already mentioned, polyhydric phenols are capable of binding the SORA).

It has been possible to show that the autoxidation of haemoglobin in the presence of adrenalin leads to the oxidation of the latter to adrenochrome, which is inhibited by the addition of SOD.[211] These data indicate the formation of the SORA from oxyhaemoglobin. Other haemoproteins are also capable of generating the SORA from oxygen. Thus it has been concluded that the SORA is formed by the autoxidation of certain cytochromes[215,216].

The involvement of the SORA in the cleavage of tryptophan to formylkynurenine, catalysed by tryptophan 2,3-dioxygenase (TD), has also been demonstrated[217]:



The reaction is inhibited by SOD and the addition of electrochemically generated Bu_4NO_2 to a mixture of tryptophan and the enzyme leads to the rapid formation of formylkynurenine in an amount proportional to that of the added Bu_4NO_2.[217]

Horseradish peroxidase is also capable of reducing oxygen to the SORA.[218] The generation of the SORA by proteins containing non-haem iron (ferredoxins) has been demonstrated both with the aid of SOD[219] and by the direct detection of SORA with the aid of EPR.[206,220] Copper proteins are apparently likewise capable of generating the SORA from oxygen in certain instances[221].

It is extremely significant that photosynthesis is also accompanied by the generation of the SORA.[222-226] It is believed that it is formed on reduction of oxygen with ferredoxins and is consumed in the dehydrogenation of ascorbic acid. The familiar Hill reaction[227], which involves methylviologen as an electron acceptor, similarly leads to the formation of the SORA as a result of the reduction of oxygen by the methylviologen radical-cation[94,228].

The involvement of the SORA in the autoxidation of phenylhydrazine[229], mercaptans[112], and polyhydric phenols[87,230] and in the reaction of oxygen with the reduced form of phenazinium methosulphate has also been demonstrated with the aid of SOD.[231]

Phenothiazine derivatives, whose metabolism in the organism reduces to their conversion into S-oxides, give rise to S-oxides also on treatment with the SORA, which may indicate the involvement of the latter in the metabolism of medicinal substances derived from phenothiazine[232].

The enzymic reduction of nitro-compounds, which proceeds via the formation of their radical-anions, is inhibited by oxygen apparently in consequence of the reaction[233]

$$RNO_2^{\cdot-} + O_2 \rightarrow RNO_2 + O_2^{\cdot-} .$$

The inhibiting effect of SOD has been observed in the study of its influence on hydroxylation by a number of model non-enzymic systems[234,235]. SOD acts similarly also on a number of enzymic hydroxylation processes[236-239]. One can therefore assume that hydroxylation is in such cases a SORA-dependent process. However, the fact that the inhibition of hydroxylation by SOD is not complete may indicate the simultaneous operation of other, SORA-independent hydroxylation mechanisms. In addition to all other species involved in this process, the hydroxylating agents can be the $HO_2^{\cdot}$ radical and the hydroxy radical generated, for example, via the mechanism[235,240]

$$O_2^{\cdot-} + H_2O_2 \rightarrow O_2 + {}^{\cdot}OH + OH^- .$$

Studies in recent years[241,242] indicated the important role of the SORA in the mechanism of the bactericidal action of human leucocytes. The phagocytosis of latex particles or *Propionibacterium Shermanii* leads to chemiluminescence[243]. The addition of SORA oxidants (Nitrotetrazolium Blue or cytochrome *c*) lowers its intensity; SOD inhibits both chemiluminescence[244] and the reduction of oxidants by SORA[243]. These findings show that the bactericidal action of leucocytes is a SORA-dependent process. However, the direct bactericidal agent is not SORA, but the singlet oxygen formed from it. This is confirmed by the greater resistance to phagocytosis of bacteria containing carotenoids [powerful $O_2(^1S)$ quenching agents] compared with the analogous bacteria which do not contain them[245]. In this case the NADPH–NADPH oxidase system (NADPH is reduced nicotinamide-adenine dinucleotide phosphate) is responsible for the generation of the SORA.

The involvement of the SORA has also been postulated in various lipid oxidation processes[123,246-248], because the latter can be inhibited by SOD. Like the bactericidal

action of leucocytes, the oxidation of lipids is apparently caused by the singlet oxygen formed in the disproportionation of the SORA.[123] This is indicated by the inhibition of the oxidation of lipids by 1,3-diphenylisobenzofuran, which is an effective acceptor of singlet oxygen[123].

III. OTHER OXYGEN RADICAL-ANIONS

1. The Radical-Anion of Atomic Oxygen (ORA)

The properties of the ORA ($O^{\cdot-}$) have been little studied hitherto, in contrast to its conjugate acid—the hydroxy-radical. However, the data already available indicate a significant difference between the properties of the ORA and the hydroxy-radical[249].

The EPR signal of $O^{\cdot-}.nH_2O$, which consists of a broad singlet line, has been observed following the ultraviolet irradiation of frozen alkaline solutions in hydrogen peroxide[250].

The usual method for the generation of the ORA involves the radiolysis of aqueous solutions of alkali saturated with nitrous oxide[251]. Nitrous oxide then behaves as an acceptor of hydrated electrons and decomposes with formation of the ORA:

$$H_2O \xrightarrow{\gamma} H^{\cdot} + {}^{\cdot}OH + e^-_{aq} + H^+ \ ;$$
$${}^{\cdot}OH + OH^- \rightarrow O^{\cdot-} + H_2O \ ;$$
$$N_2O + e^-_{aq} \rightarrow N_2O^{\cdot-} \rightarrow N_2 + O^{\cdot-} \ .$$

Nitrous oxide can be replaced by ammonium persulphate[252]:

$$S_2O_8^{2-} + e^-_{aq} \rightarrow SO_4^{3-} + SO_4^{\cdot-} \ ;$$
$$SO_4^{\cdot-} + 2OH^- \rightarrow SO_4^{2-} + O^{\cdot-} + H_2O \ .$$

The rate of reaction of the hydroxy-radical with potassium hexacyanoferrate(III) falls markedly with increase of the pH of the medium, which has been interpreted as a result of the dissociation of the hydroxy-radical, leading to the less active ORA:[253,254]

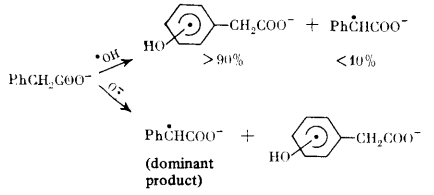
$${}^{\cdot}OH \rightleftarrows O^{\cdot-} + H^+ \ ;$$
$$Fe(CN)_6^{4-} \xrightarrow{{}^{\cdot}OH(O^{\cdot-})} Fe(CN)_6^{3-} \ ;$$
$$pK = 11{,}9 \ .$$

The main pathway in the destruction of the ORA in aqueous solution involves recombination to the peroxide ion[253]:

$$O^{\cdot-} + O^{\cdot-} \rightarrow O_2^{2-} \quad (2k = 2 \cdot 10^9 \text{ litre mole}^{-1}\,\text{s}^{-1}).$$

Kinetic parameters have now been obtained for a number of reactions in which the ORA behaves as an electron or hydrogen atom acceptor. The rate constants for the one-electron oxidation of the Br^-, I^-, SCN^-, Fe^{2+}, $Fe(CN)_6^{4-}$, and $C_6H_5O^-$ ions as well as aniline by the radical-anion $O^{\cdot-}$ are in the range $(0.03-3)\times 10^9$ litre mole^{-1} s^{-1}. Reactions involving the abstraction of hydrogen atoms from a number of organic substrates (CH_3OH, CH_3CN, polymethylbenzenes, pyrrolidine) are characterised by rate constants in the range $(0.22-21)\times 10^9$ litre mole^{-1} s^{-1}.[257-260]

Comparison of the reactivities of the ORA and the hydroxy-radical in reactions with organic compounds shows that the ORA is usually less reactive than the conjugate acid. At the same time, in reactions involving the abstraction of atomic hydrogen from organic compounds the reactivity of the ORA is only slightly inferior to that of the $^{\cdot}OH$ radical, but the rates of addition of the ORA to aromatic systems are smaller by 2–3 orders of magnitude than in the case of the hydroxy-radical. This leads to a significant change of the relative rates of the competing processes on passing from acidic and weakly alkaline media to strongly alkaline media. Thus, whereas at pH values corresponding to acidic and weakly alkaline media the dominant pathway in the reactions with many aromatic derivatives is addition of the hydroxy-radical to the aromatic ring, on passing to high pH values the abstraction by atomic oxygen radical-anions of hydrogen atoms which are not linked directly to the aromatic ring predominates[259,261,262].



Using an ionic cyclotron resonance mass-spectrometer, a study has been made of the reactions of the ORA with unsaturated hydrocarbons involving the abstraction of a proton:

$$CH{\equiv}CH + O^{\cdot-} \rightarrow C_2H^- + {}^{\cdot}OH \ ;$$
$$MeCH{=}CH_2 + O^{\cdot-} \rightarrow C_3H_5^- + {}^{\cdot}OH \ .$$

which can sometimes be accompanied by the subsequent abstraction of a hydrogen atom:

$$CH_2{=}CH_2 + O^{\cdot-} \rightarrow C_2H_3^- + H_2O \ ;$$
$$CH_2{=}CF_2 + O^{\cdot-} \rightarrow CF_2C^{\cdot-} + H_2O$$

which formally corresponds to the abstraction of the H_2^+ radical-cation from the substrate[263].

The oxidation of acetone by hydroxy-radicals and the ORA leads to different products[264]:

$$Me_2CO + {}^{\cdot}OH \rightarrow MeCOCH_2^{\cdot} \xrightarrow{O_2,\ H_2O} \rightarrow MeCOCOOH \ ;$$
$$Me_2CO + O^{\cdot-} \rightarrow Me{-}\underset{\displaystyle {}^{\cdot}O\quad O^-}{\overset{\displaystyle |\quad |}{C}}{-}Me \rightarrow MeCOO^- + Me^{\cdot} \ ;$$
$$Me^{\cdot} \dashrightarrow \rightarrow CH_2O \ .$$

2. The Ozone Radical-Anion (OzRA)

The ozone molecule exhibits a very high electron affinity (2.14 ± 0.15 eV,[265] 2.09 eV[266]), readily combines with an electron, and is converted into the OzRA ($O_3^{\cdot-}$). The OzRA salts of alkali metals (Na, K, Ru, Cs) and the $N(CH_3)_4^+$ cation[267-269] have been isolated in a pure state. They are usually obtained by treating solid alkalis[267,268] or alkali metal superoxides[270-272] with ozonised oxygen:

$$O_3 + MOH \rightarrow M^+O_3^{\cdot-} + {}^{\cdot}OH \ ;$$
$${}^{\cdot}OH + MOH \rightarrow M^+O^{\cdot-} + H_2O, \quad M = Na, K, Rb, Cs, \text{ or } NMe_4 \ ;$$
$$M^+O^{\cdot-} + O_3 \rightarrow M^+O_3^{\cdot-} + O_2 \ ;$$
$$M^+O_2^{\cdot-} + O_3 \rightarrow M^+O_3^{\cdot-} + O_2 \ .$$

Alkaline earth metal ozonides, which are stable only at low temperatures, can be obtained by the ozonisation of the peroxides of these metals[273,274].

Aqueous solutions of alkali containing nitrous oxide and oxygen are used to generate the OzRA in studies by pulse radiolysis[275-277]:

$$H_2O \xrightarrow{\gamma,\ N_2O,\ OH^-} O^{\cdot-} \ ;$$
$$O^{\cdot-} + O_2 \rightarrow O_3^{\cdot-} \ (k = 2.5 \cdot 10^9 \text{ litre mole}^{-1}\,\text{s}^{-1}) \text{ (Ref.275).}$$

Alkali metal ozonides are orange or red crystalline compounds whose lattice is made up of regularly alternating alkali metal ions and O_3^- species. It has been found that[278] the O–O bond length in the O_3^- radical-anion is 1.19 Å and the O–O–O angle is 100°.†

Alkali metal ozonides dissolve in liquid ammonia, forming paramagnetic solutions. The maximum of the O_3^- absorption band is near 450 nm (liquid ammonia)[269,280] and in the region of 430–438 nm (water)[275–277].

The OzRA salts are rapidly decomposed by water via the mechanism[281]

$$MO_3 + H_2O \rightarrow {}^{\cdot}OH + O_2 + MOH\,.$$

It has been noted that this reaction can serve as a powerful source of hydroxy-radicals, which are formed in the absence of metal cations capable of forming complexes with them[282].

Low temperatures and a highly alkaline medium increase the stability of the OzRA in an aqueous medium (the half-life in 8 M KOH at −50°C is 12 min)[43].

Virtually nothing is known about the organic reactions of alkali metal ozonides. It has been noted that solid KO_3 is capable of initiating the chain oxidation of acetaldehyde by oxygen, which is distinguished by an unusual chain length (more than 10^4 CH_3CHO molecules react per KO_3 molecule)[283]. The mechanism of the reactions of ozone with organic compounds has been comparatively little studied[284]. The initial stage in the oxidation of saturated hydrocarbons RH by ozone is a simple bimolecular reaction[285,286]. The most probable products under these conditions are the R˙ and ˙OH radicals and oxygen[287–291]. Like the oxidation of hydrocarbons by oxygen, their reaction with ozone apparently includes an electron transfer stage, which precedes the formation of weak CTC:[292–294]

$$RH + O_3 \rightleftarrows RH \ldots O_3 \rightleftarrows [RH^{+\cdot} \ldots O_3^-] \rightarrow [R^{\cdot} + O_2 + {}^{\cdot}OH] \longrightarrow \begin{cases} \longrightarrow ROH + O_2 \\ \longrightarrow R^{\cdot} + O_2 + {}^{\cdot}OH. \end{cases}$$

Whereas in the reaction with oxygen the abstraction of a hydrogen atom by a triplet oxygen molecule can serve as an alternative mechanism, such an explanation is altogether impossible for the diamagnetic ozone.

At low temperatures, where the thermal oxidation reaction does not occur, the irradiation of ozone solutions in saturated hydrocarbons leads to their photochemical oxidation[294]. This apparently entails a photoinduced electron transfer to the CTC. Analysis of the composition and ratio of the oxidation products (alcohols, ketones) indicates the similarity of the mechanisms of the photochemical and thermal reactions of ozone with saturated hydrocarbons. In addition, both reactions of ozone with isomeric decalins proceed with approximately the same degree of retention of the configuration of the oxidation products[294].

The first stage in the oxidation with ozone of various organometallic compounds[108] as well as organic compounds containing heteroatoms[284] (amines, sulphides, nitroxy-radicals) also involves the formation of the OzRA as a result of electron transfer from the substrate to ozone.

The oxidation of trimesitylvinyl alcohol to the radical (XXIII) under the influence of ozone has been described[295]:

$$Mes_2C{=}C(OH)\,Mes + O_3 \rightleftarrows Mes_2C{=}C(OH)\,Mes \ldots O_3 \rightarrow$$
$$\rightarrow \left[\left(Mes_2C{=}\overset{OH}{\overset{|}{C}}Mes\right)^{\ddagger} \ldots O_3^-\right] \rightarrow Mes_2\dot{C}COMes\,.$$
(XXIII)

† In free ozone the O–O bond length is 1.26 Å and the O–O–O angle is 127°.[279]

The epoxidation of olefins and aromatic compounds by ozone begins in the same way:

$$\text{>C=C<} + O_3 \rightleftarrows \text{>C=C<} \ldots O_3 \rightleftarrows \left[\left(\text{>C–C<}\right)^{\ddagger} \ldots O_3^-\right] \rightarrow$$
$$\rightarrow \left[\left(\text{>C=C<}\right)^{\ddagger} \ldots O^- \ldots O_2\right] \rightarrow \text{>C(O)C<} + O_2\,.$$

In fact, as already mentioned, the OzRA is capable of dissociating into the ORA and O_2 ($k = 3.3 \pm 0.3 \times 10^3$ s^{-1}; 25°C).[257]

In aqueous solutions of alkali, ozone decomposes via the mechanism[296]

$$O_3 + OH^- \rightarrow O_3^- + {}^{\cdot}OH\,;$$
$${}^{\cdot}OH + OH^- \rightarrow O^- + H_2O\,;$$
$$2O^- + H_2O \rightarrow O + 2OH^-\,;$$
$$O^- + O \rightarrow O_2^-\,;$$
$$2O_3^- + H_2O \rightarrow HO_2^- + OH^- + O_2\,.$$

The formation of the ˙OH radicals and the ORA is responsible for the extremely effective oxidising properties of ozone in an alkaline medium in relation to organic compounds (the final oxidation products are CO_2 and H_2O).[297] In the $O_3^- \rightleftharpoons O_2 + O^-$ system the most active species is the ORA, so that many reactions of the OzRA are in fact reactions of the ORA.

IV. THE CARBON DIOXIDE RADICAL-ANION

The existence of the carbon dioxide radical-anion (CRA) CO_2^- was demonstrated at the beginning of the 1960s in a study of the EPR spectra of alkali metal formate crystals subjected to γ- or X-irradiation[298–300].

In contrast to the carbon dioxide molecule, the CRA is non-linear[299,301]; the O–C–O angle is approximately 135°. The EPR spectrum of the CRA in aqueous solution (singlet line with $g = 2.0040$) has been observed in two investigations[104,302]. The available data concerning the magnitude of pK for the equilibrium $^{\cdot}COOH \rightleftharpoons CO_2^- + H^+$ are contradictory: 2.8 (Gutlbauer and Getoff[303]) and 1.4 (Buxton and Sellers[304]).

Since the CO_2 molecule apparently has a negative electron affinity (−0.36 eV according to the results of a quantum-mechanical calculation[301]) its direct chemical reduction proceeds with difficulty and is not at present used to generate the CRA. The simplest method of generating the CRA in an aqueous medium involves the interaction of hydroxy-radicals with formates. Hydrogen peroxide is usually reduced by Ti^{3+} salts in the presence of formate ions[104,305]:

$$Ti^{3+} + H_2O_2 \rightarrow Ti^{4+} + {}^{\cdot}OH + OH^-\,;$$
$${}^{\cdot}OH + HCO_2^- \rightarrow CO_2^- + H_2O$$
$(k = 2.7 \cdot 10^9$ litre mole^{-1} s^{-1}).

The CRA is unstable and is rapidly converted into formate, bicarbonate, and oxalate anions and carbon monoxide[306–309]. The formation of the formate anion under these conditions undoubtedly begins with the protonation of the CRA. The subsequent stages may involve the reduction of the carboxy-radical and the protonation of the resulting formate anion. It has been suggested that the carbonate ion and carbon monoxide can be formed via a bimolecular reaction[306,309], but the possibility of the

unimolecular fragmentation of the CRA cannot be ruled out either:

$$CO_2^{\cdot-} + H_2O \rightleftarrows {}^{\cdot}COOH + OH^-;$$
$${}^{\cdot}COOH + CO_2^{\cdot-} \xrightarrow[-CO_2]{} {}^{-}COOH;$$
$${}^{-}COOH \begin{cases} \longrightarrow HCOO^- \\ \xrightarrow{H^+} HCOOH \end{cases};$$
$$2CO_2^{\cdot-} \rightarrow CO_3^{2-} + CO;$$
$$CO_3^{2-} + H^+ \rightarrow HCO_3^-;$$
$$2CO_2^{\cdot-} \rightarrow (-COO^-)_2.$$

The electrochemical reduction of carbon dioxide in dimethyl sulphoxide, which takes place at high cathodic potentials (−1.9 to −2.0 V) according to coulometric measurements, may consist in the transfer of one electron (gold cathode) or between one and two electrons (mercury cathode) to the CO_2 molecule[306]. The main products are carbon monoxide and the bicarbonate anion.

The CRA is also formed when hydrated electrons, generated in the radiolysis of water, are accepted by carbon dioxide[310]:

$$CO_2 + e_{aq}^- \rightarrow CO_2^{\cdot-} \quad (k = 7.7 \cdot 10^9 \text{ litre mole}^{-1}\text{ s}^{-1}).$$

In this case the formation of the CRA is demonstrated, in particular, by the fact that in the presence of aliphatic alcohols they are carboxylated to α-hydroxyacids[311]:

$$H_2O \xrightarrow{\gamma} H^{\cdot} + {}^{\cdot}OH + e_{aq}^- + H^+;$$
$$e_{aq}^- + CO_2 \rightarrow CO_2^{\cdot-};$$
$$RCH_2OH + {}^{\cdot}OH \xrightarrow[-H_2O]{} R\dot{C}HOH;$$
$$R\dot{C}HOH + CO_2^{\cdot-} \rightarrow RCH(OH)COO^-.$$

The CRA can also be generated by the one-electron oxidation of the oxalate anion. Examples of such reactions known at the present time are associated with the decomposition of tervalent manganese[312] and cobalt[313] oxalates and the chain oxidation of oxalate anions by persulphates[314]:

$$[M(C_2O_4)_n]^{(2n-3)-} \rightarrow M^{2+} + (n-1)C_2O_4^{2-} + CO_2^{\cdot-} + CO_2;$$
$$S_2O_8^{2-} \rightleftarrows 2SO_4^{\cdot-};$$
$$SO_4^{\cdot-} + C_2O_4^{2-} \rightarrow SO_4^{2-} + CO_2^{\cdot-} + CO_2;$$
$$CO_2^{\cdot-} + S_2O_8^{2-} \rightarrow CO_2 + SO_4^{\cdot-} + SO_4^{2-} \text{ etc.}$$

Reactions in which the CRA behaves as a one-electron reductant are most characteristic of this radical-anion. Thus, when a solution of manganese(III) oxalate is decomposed thermally in the presence of oxygen, an appreciable amount of H_2O_2 is formed[312], apparently from superoxide radical-anions:

$$CO_2^{\cdot-} + O_2 \rightarrow CO_2 + O_2^{\cdot-} \quad (k = 4.6 \cdot 10^9 \text{ litre mole}^{-1}\text{ s}^{-1}) \text{ (Ref.315)}.$$
$$2O_2^{\cdot-} + H_2O \rightarrow H_2O_2 + O_2.$$

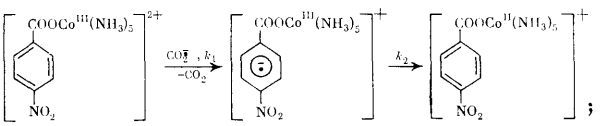
The interaction of the CRA with alkyl halides[316,317] and also with compounds having an N–halogen bond[318] leads to the dissociative capture of an electron by halide molecules; the free radicals formed in this process have been identified by EPR:[317,318]

$$RX + CO_2^{\cdot-} \rightarrow R^{\cdot} + X^- + CO_2;$$
$$MeCONHBr + CO_2^{\cdot-} \rightarrow MeCONH^{\cdot} + Br^- + CO_2.$$

Apparently all iodo-derivatives as well as sufficiently reactive bromides and chlorides react with the CRA.[317]

The ability of the CRA to transfer an electron to the *p*-nitrophenyl diazonium cation[319], quinones[315,320], aliphatic nitro-compounds[319], nitrobenzene[321], acetaldehyde, acetone and certain other carbonyl compounds[322], maleimide[323], riboflavin[324], and a number of dyes[325] has been demonstrated.

Under the influence of the CRA, the complexes of tervalent cobalt and ruthenium are reduced to the corresponding derivatives of the bivalent metals[326–328]. The reduction of the CRA by *p*-nitrobenzoatopentammine-cobalt(III) ion is of particular interest[328]. In this case it was possible to detect by ultraviolet spectroscopy the primary reduction product [the radical-ion (XXIV)], which is converted by an intramolecular electron transfer into the final product—the *p*-nitrobenzoatopentammine-cobalt(II) complex:



(XXIV)

$k_1 = 1.9 \cdot 10^9$ litre mole^{-1} s^{-1}; $k_2 = 2.6 \cdot 10^3$ s^{-1}.

Certain reactions are known[319] which can be classified as free-radical additions of the CRA to multiple bonds (demonstrated with the aid of EPR):

$$RCH{=}\overset{+}{N}(O^-)O^{\cdot} + CO_2^{\cdot-} \rightarrow RCH(CO_2^-)\text{—}N(O^-)O^{\cdot};$$
$$R^1R^2C{=}NOH + CO_2^{\cdot-} \rightarrow R^1R^2C(CO_2^-)NHO^{\cdot}.$$

In connection with the recent hypothesis of the possible involvement of the CRA in photosynthetic processes[7], the following considerations may be noted.

(1) The reduction to the CRA constitutes an extremely effective means of activating carbon dioxide.

(2) Since the fixation of carbon dioxide is a dark process, the problem arises of the nature of the reductant capable of reducing CO_2 molecules, which are fairly difficult to reduce. In this connection, one can postulate the possibility of the reduction of carbon dioxide to the CRA even by comparatively weak reductants when the molecules of the latter and CO_2 are located in different parts of the homogeneous systems at whose boundary the electrical double layer is capable of exerting a catalytic effect on electron transfer to CO_2. For example, it has been stated that pyrenesulphonic acid, which is incapable of being reduced by the CRA in a homogeneous medium, is readily reduced in the solubilised state (positively charged micelles) by the CRA present in the aqueous phase[329].

The electrical double layer apparently has an analogous influence in the photochemical oxidation of water by chlorophyll in the octane–water system (under homogeneous conditions, water is not oxidised)[330].

(3) The oxalic acid present in the leaves of certain plants can be a product of the dimerisation of the CRA.

V. THE $SO_4^{\cdot-}$ RADICAL-ANION

The formation of the sulphate radical-anion (SRA) $SO_4^{\cdot-}$ was first postulated as the initial stage in oxidation by alkali metal persulphates:

$$S_2O_8^{2-} \rightleftarrows 2SO_4^{\cdot-}.$$

Subsequently this view became generally accepted. The SRA is formed fairly rapidly only on heating aqueous solutions of persulphates to 80–100°C. At lower temperatures the CRA can be conveniently generated either

photochemically[331] or by treating persulphates with reductants (Fe^{2+}, Ti^{3+}, etc.)[332,333]:

$$S_2O_8^{2-} \xrightarrow{h\nu} 2SO_4^{\cdot-} ;$$

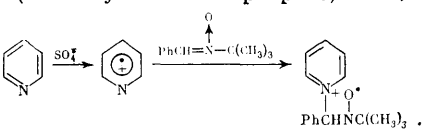
$$S_2O_8^{2-} + M^{n+} \rightarrow SO_4^{\cdot-} + SO_4^{2-} + M^{(n+1)+} .$$

An anisotropic EPR signal ($g_1 = 2.004$; $g_2 = 2.012$; $g_3 = 2.030$), apparently due to the SRA, was detected in a study of crystalline barium sulphate labelled with the radioactive isotope ^{35}S.[334] The EPR signal of the SRA in solution has been detected[302].

The chemical properties of the SRA show that it is a powerful one-electron oxidant. Aromatic compounds are readily oxidised by this species to radical-cations[333,335,336]:

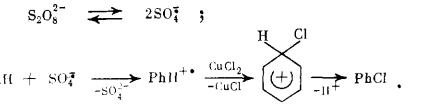
$$ArH + SO_4^{\cdot-} \rightarrow ArH^{+\cdot} + SO_4^{2-} .$$

Direct evidence for the formation of the radical-cations in the reaction of the SRA with aromatic compounds was obtained with the aid of EPR.[336] Even pyridine[337] and its derivatives[338] can be oxidised to radical-cations by treatment with the SRA. The formation of the pyridinium radical-cation was demonstrated with the aid of a spin-trapping agent (2-methyl-2-nitrosopropane)[337,338]:

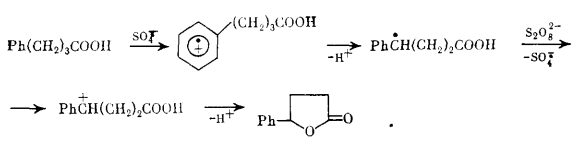


An interesting method for the chlorination of benzene and its homologues is based on the oxidation of these compounds to radical-cations; it consists in heating them with a mixture of sodium persulphate and copper(II) chloride in an aqueous acetonitrile medium[335]:

$$S_2O_8^{2-} \rightleftharpoons 2SO_4^{\cdot-} ;$$



A convenient method has been proposed for the synthesis of the lactone of γ-hydroxy-γ-phenylbutyric acid, based on the oxidation of γ-phenylbutyric acid[339]:



The interaction of the SRA with certain saturated compounds also begins with the abstraction of an electron from the latter[79,80,340]:

$$R^1R^2CHOH + SO_4^{\cdot-} \xrightarrow[-SO_4^{2-}]{} R^1R^2\dot{C}HOH \xrightarrow[-H^+]{} R^1R^2CHO \xrightarrow[-R^1R^2CHOH]{R^1R^2CHOH} R^1R^2\dot{C}OH$$

$$R_2S_2 + SO_4^{\cdot-} \xrightarrow[-SO_4^{2-}]{} R_2S_2^{\cdot+} .$$

Previously the reaction with alcohols was treated as abstraction of an α-hydrogen atom by the $SO_4^{\cdot-}$ radical-anion[341,342].

Alkoxy-radicals are also formed in the photochemical oxidation of alcohols by paraquat dichloride[343] and iron(III) compounds[344] as well as quinones[345].

In the reaction with the SRA various alcohols, having the general formula $PhCH_2CR_2OH$, undergo oxidative fragmentation[80,333] (demonstrated by the spin-trapping method[80]):

$$PhCH_2CR_2OH \xrightarrow{SO_4^{\cdot-}} [PhCH_2\dot{C}R_2 \rightarrow PhCH_2^{\cdot} + R_2CO .$$

The reaction of the SRA with the nitromethane anion leads to the nitromethyl radical[346]:

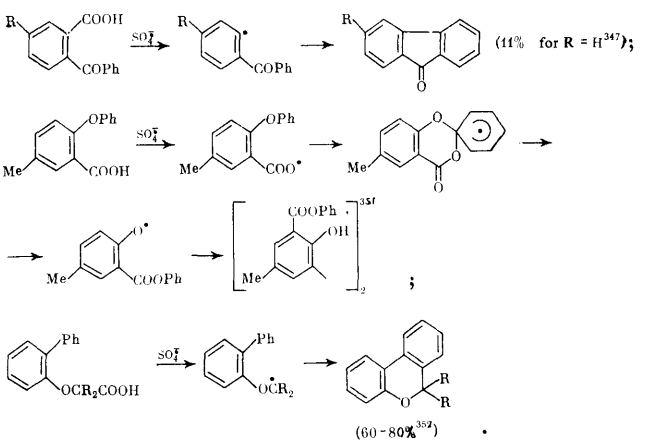
$$\underset{(XXV)}{CH_2{=}\overset{+}{N}(O^-)O^-} + SO_4^{\cdot-} \xrightarrow[-SO_4^{2-}]{} {}^{\cdot}CH_2NO_2 \xrightarrow{(XXV)} O_2NCH_2CH_2N(O^-)O^{\cdot} .$$

The SRA has found an important application in a simple and convenient method for the generation of alkyl and aryl radicals in aqueous solutions by the oxidative decarboxylation of carboxylic acids[333,347-350]:

$$RCOO^- \xrightarrow{SO_4^{\cdot-}} RCOO^{\cdot} \xrightarrow{-CO_2} R^{\cdot} ;$$

R = alkyl or aryl.

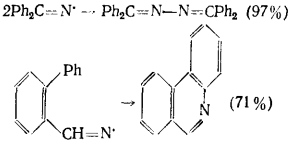
In many instances the free radicals formed in the oxidation of carboxylic acids cyclise or fragment, which can be of definite synthetic interest:



Oxidative decarboxylation under the influence of the SRA can be used for the generation of iminyl radicals[353,354]:

$$R^1R^2C{=}NOCH_2COOH \xrightarrow[-CO_2]{SO_4^{\cdot-}} R^1R^2C{=}NOCH_2^{\cdot} \xrightarrow{-CH_3O} R^1R^2C{=}N^{\cdot} ;$$

$$2Ph_2C{=}N^{\cdot} \rightarrow Ph_2C{=}N{-}N{=}CPh_2 \ (97\%) ;$$



Apart from the reactions in which the SRA behaves as an oxidant, reactions involving the addition of the SRA to unsaturated compounds are also known[333]:

$$CH_2{=}CHCH_2OH \xrightarrow{SO_4^{\cdot-}} CH_2\dot{C}HCH_2OH ;$$
$$\quad\quad\quad

SRA in relation to carboxylate anions than in relation to neutral molecules of unsaturated acids. Hence it follows that the SRA is an electrophilic anion[333], which differentiates it sharply from organic radical-anions[355].

VI. OTHER INORGANIC RADICAL-IONS

A large number of other relatively unstable inorganic radical-anions have been described. Although very little is known about the organic reactions of these species, some of them are of considerable interest for organic chemistry. These include the relatively unstable molecular halogen ions $X_2^{\cdot-}$. Presumably the $X_2^{\cdot-}$ radical-anions should arise in organic reactions with participation of halogens acting as electron acceptors. For example, the reaction of tetramethylhydrazine with iodine is treated in this way[356]:

$$Me_2NNMe_2 + I_2 \rightleftarrows Me_2NNMe_2 \ldots I_2 \rightleftarrows [Me_2NNMe_2]^{\cdot+} + I_2^{\cdot-} .$$

Another pathway leading to halogen radical-anions involves the reaction of the halide ion with the atomic halogen:

$$X^{\cdot} + X^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X_2^{\cdot-}$$

($k_1 = 2.1 \cdot 10^{10}$ litre mole^{-1} s^{-1}; $k_{-1} = 1.1 \cdot 10^5$ s^{-1}; $K = 1.9 \cdot 10^5$ litre mole^{-1} (Ref.357) (X = Cl)).

In practice the $X_2^{\cdot-}$ radical-anions are usually generated by the radiolysis of aqueous solutions of alkali metal halides[358-361].

Halogen radical-anions are apparently effective oxidants[103]. The oxidation of bicarbonate or carbonate ions by the hydroxy-radical[362] or the $SO_4^{\cdot-}$ radical-anion[363] as well as the flash photolysis of the salt (XXVI) [364,365] lead to the radical-anion $CO_3^{\cdot-}$:

$$HCO_3^- (CO_3^{2-}) + {}^{\cdot}OH \rightarrow CO_3^{\cdot-} + H_2O\,(OH^-) \ ;$$

$$CO_3^{2-} \xrightarrow[-SO_4^{2-}]{SO_4^{\cdot-}} CO_3^{\cdot-} \ ;$$

$$\text{(XXVI)} \quad [Co(NH_3)_4CO_3]ClO_4 \xrightarrow{h\nu} CO_3^{\cdot-} + Co + 4NH_3 + ClO_4^- \ .$$

The pK for the equilibrium $HCO_3^{\cdot} \rightleftharpoons H^+ + CO_3^{\cdot-}$ is 9.5.[366,367]

The chemical properties of the $CO_3^{\cdot-}$ radical-anion are of considerable interest, since its formation is to be expected in living organisms exposed to ionising radiation (from the hydroxy-radical and the bicarbonate anion). In addition, another possible pathway leading to the formation of the carbonate radical-anion may involve the photochemical oxidation of the carbonate ion by quinones[368].

It has been found that this radical-anion reacts with alcohols, abstracting an α-hydrogen atom[365], and with aromatic compounds[369]; in the latter case it apparently adds to the aromatic ring.

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Thus inorganic radical-anions and in the first place the oxygen and sulphate radical-anions, are extremely promising for synthetic and theoretical organic chemistry. The study of the properties of inorganic radical-ions constitutes an essential stage in the investigation of both photosynthetic and respiratory processes; without it, there can be no effective attempt at a functional modelling of these processes.

The chemistry of unstable inorganic radical-ions leads to new possibilities for the investigation of the mechanisms of reactions of organic substrates with inorganic reagents, including those of various heterogeneous-catalytic processes.

During the preparation of the review for the press, a number of interesting studies on the chemistry of the oxygen radical-anion were published[370-381].

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