U.D.C. 541.459

Modern Views on the Nature of Inorganic Peroxy-compounds

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A general account is given of the literature data on the molecular oxygen anions O_2^{2-}, O_2^-, and O_3^- characterising the structures of simple peroxy-compounds: peroxides, superoxides, and ozonides. The principal studies published in recent years dealing with the structure of complex peroxy-compounds are briefly summarised. The nomenclature for organic peroxy-compounds proposed by other authors is critically discussed and a scheme is put forward for classification and nomenclature based on the latest data on the structures of such compounds.
The bibliography includes 93 references.

Until recently, in order to define the concept of "an inorganic peroxy-compound" it was thought sufficient to indicate compounds corresponding to this concept and containing the peroxo-group, the so called "oxygen bridge".

Detailed studies of the structures and properties of many compounds corresponding to the above concept, begun in the 1930's with active participation of Soviet scientists, showed that the term "inorganic peroxy-compounds" is applicable to a very wide class of compounds and combines at least nine groups of compounds differing in the type of bond not only between the "oxygen bridge" and the atoms of the elements constituting the peroxy-compound but also in the type of bond between the oxygen atoms in the bridge itself.

Some workers, including Hein[1], tend to regard all inorganic peroxy-compounds as complex, dividing them into three groups: polyoxides, peroxo-acids, and peroxy-hydrates. However, the authors include in the group of polyoxides, together with H_2O_2, H_2O_3, and H_2O_4, also peroxy-compounds the crystal lattices of which consist of metal ions (belonging mainly to subgroups IA and IIA of the Periodic System) and the corresponding molecular anions O_2^{2-} (peroxides), O_2^- (superoxides), and O_3^- (ozonides).

It has been shown recently[2] that compounds of this type, for example Rb_2O_2, dissociate completely in the $LiNO_3-KNO_3$ eutectic mixture into ions according to the mechanism $M_2O_2 \rightarrow 2M^+ + O_2^{2-}$ and RbO_2 dissociates[3] according to the mechanism $RbO_2 \rightarrow Rb^+ + O_2^-$.

In the neutral molecule of hydrogen peroxide H_2O_2, the peroxide ion O_2^{2-} does not exist as such. This means that hydrogen atoms are not attracted to any appreciable degree by the peroxo-group via electrostatic forces. Hydrogen peroxide is the first member of the homologous series of hydrogen polyoxides H_2O_2, H_2O_3, H_2O_4, ..., the molecules of which comprise, like sulphanes, zig-zag chains of oxygen atoms joined by single bonds with a length of about 1.5 Å.

The change in the type of bond in the peroxo-group on passing from hydrogen peroxide to other peroxy-compounds depends mainly on the change in the electronegativity of the element forming the peroxy-compound. The negative dissociation energy of the O_2^{2-} ion and the high energy required to complete the process $O_2 \rightarrow O_2^{2-}$ are the reasons why this ion can be stabilised only by highly electropositive elements (Li–Cs, Ca–Ba). To some extent this applies also to O_2^- and O_3^- ions.

To a first approximation, one may assert that the linkage between atoms of elements having an electronegativity lower than that of hydrogen and the "oxygen bridge" formed by the above molecular anions is predominantly ionic. The peroxy-compounds of elements with an electronegativity higher than that of hydrogen contain a peroxo-group (both as such and in the form of H_2O_2 molecules and HO_2 radicals). The peroxo-group may be present in the compound both as a bidentate ligand and as a "bridge".

On the basis of the differences in the structures of inorganic peroxy-compounds, it is useful to retain in their classification the subdivision into simple and complex compounds and to isolate in a special group the hydrogen polyoxides despite the clear genetic relation between H_2O_2 and metal peroxides.

For a deeper understanding of the structure of inorganic peroxy-compounds, it is necessary to examine in somewhat greater detail the electronic structure of molecular oxygen anions.

Molecular Oxygen Anions

In order to represent the electronic structure of the above molecular anions, it is necessary to recall that the oxygen molecule has an unusual structure, the details of which have still not been completely elucidated. The former representation of the double-bonded oxygen structure O=O in which the two oxygen atoms complete their stable octets by exchanging two electrons [:Ö: :Ö:] has been disproved by spectroscopic and magnetic measurements. The oxygen molecule is paramagnetic, which implies the presence of unpaired electrons. Therefore the oxygen molecule has been regarded as a kind of biradical, the structure of which may be represented by the electronic scheme [:Ö–Ö:] with an even number of electrons (twelve) but with only one single bond and two unsaturated valences. Two electrons are unpaired, which is the reason for the paramagnetism of the oxygen molecule. The low reactivity of oxygen in relation to that of free radicals is evidence against this scheme. Moreover, experimental data show that the dissociation energy of the oxygen molecule into atoms is 118 kcal mole^{-1}, which greatly exceeds the value necessary to dissociate a simple covalent bond. Hence it follows that in this case the unpaired electrons stabilise the bond between the oxygen atoms. This unusual case has been treated[4,5] as a three-electron bond. On the basis of these hypotheses, the oxygen molecule in the ground $^3\Sigma$ state can be approximately described by the formula [:O⋯⋯O:] with one single and two three-electron bonds. The O=O bond length is 1.207 Å.[6]

The structure of the oxygen molecule may be represented as follows in terms of the molecular orbital method:

$$[KK(z\sigma)^2(y\sigma^*)^2(x\sigma^*)^2(w\pi)^4(v\pi^*)^2].$$

Consequently in the ground state of the oxygen molecule there are four bonding electrons in excess relative to the antibonding electrons and the bond order is two.

The addition of a single electron to the oxygen molecule leads to the formation of the singly-charged negative ion O_2^- which enters into the composition of superoxides. The electronic structure of the O_2^- ion may be represented by the formula $[:\ddot{O}:\!\!-\!\!-\ddot{O}:]$,[5,7] and in terms of the molecular orbital method by the formula

$$[KK(z\sigma)^2(y\sigma^*)^2(x\sigma)^2(w\pi)^4(v\pi^*)^3].$$

The electron adds to the antibonding orbital and the bond order diminishes by 1/2. Evidently the singly-charged negative superoxide ion has an odd number of electrons (thirteen) with one single and one three-electron bond†. This is consistent with the paramagnetism and colour of the peroxy-compounds containing this ion. More detailed information about the electronic structure of the O_2^- ion in the free state and in the lattices of alkali metal halides has been given by Zeller et al.[8]

The electron affinity of the oxygen molecule ($O_2 + e \rightarrow O_2^-$) determined by a thermochemical method[9] proved to be 0.87 ± 0.13 eV, i.e. the addition of an electron to the oxygen molecule involves an energy change of 20 ± 3 kcal mole^{-1}. However, the value of $E_{O_2^-}$ determined by other methods is much lower.

The dissociation energy of the O_2^- ion into O^- and O has been estimated from the Raman spectra of KO_2 as 2.99 eV, i.e. about 69 kcal mole^{-1}.[10] Consequently the O_2^- ion is less stable than the oxygen molecule. The O–O bond length in the O_2^- ion is greater than in the oxygen molecule. Earlier a value of 1.28 Å was adopted[10] but subsequent studies showed that it is in the range 1.82–1.35 Å.[12] The O_2^- ion has the form of an ellipsoid of rotation, the length of the major axis of which is 4.55 Å. The radius of each oxygen atom in O_2^- may be assumed to be 1.59 Å.[13] The major half-axis of the O_2^- ion is therefore 2.27 Å and the minor half-axis (or the transverse radius) is 1.52 Å.[7]

The absorption spectrum of O_2^- ions in an aprotic solvent has a maximum at 240 nm.[14]

The addition of two electrons to the oxygen molecule or of one electron to the O_2^- ion is not accompanied by evolution of energy, as in the formation of the O_2^- ion, but by its absorption,

$$O_2 + 2e \rightarrow O_2^{2-} - 110 \text{ kcal mole}^{-1},$$
$$O_2^- + e \rightarrow O_2^{2-} - 130 \pm 3 \text{ kcal mole}^{-1},$$

and the formation of the doubly charged negative O_2^{2-} ion[15,16], which forms part of peroxides‡.

In contrast to the O_2^- ion, which is known to occur in a free state[18] and which is capable of prolonged existence in aprotic solvents[19], the O_2^{2-} ion is known only in the crystal lattices of peroxides, where it is stabilised by cations with large radii. The appearance of the O_2^{2-} ion in aqueous solution is also possible: $H_2O_2(\text{liq.}) \rightarrow 2H^+ + O_2^{2-} - 56$ kcal mole^{-1}, but not in the gas phase, since in the latter case the formation of O_2^{2-} is exothermic: $H_2O_2(\text{gas}) \rightarrow 2H^+ + O_2^{2-} - 886$ kcal mole^{-1}. The electronic structure of O_2^{2-} may be represented by the formula $[:\ddot{O}-\ddot{O}:]^{2-}$,[4,20]§ and in molecular orbital terms by

$$[KK(z\sigma)^2(y\sigma^*)^2(x\sigma)^2(w\pi)^4(v\pi^*)^4].$$

The addition of two electrons to the antibonding orbital leads to a decrease of the bond order to unity. Evidently the doubly charged negative peroxide ion has an even number of electrons (fourteen) and one single bond. This is consistent with the diamagnetism and the lack of colour of peroxy-compounds containing this ion. The dissociation energy of the O_2^{2-} ion has been estimated as -125 kcal mole^{-1},[21] while according to other data[22] it is -53.4 kcal mole^{-1}. Consequently the O_2^{2-} ion is less stable than the O_2^- ion and the oxygen molecule. The O–O bond length in O_2^{2-} is 1.40 Å, i.e. longer than in the O_2^- ion and in the oxygen molecule. Like O_2^-, the O_2^{2-} ion has the shape of an ellipsoid of rotation but with a somewhat less extended major axis, whose length is 4.19 Å. The radius of both O^- and O_2^{2-} is 1.35 Å. The major half-axis of the O_2^{2-} ion is therefore 2.09 Å and the minor half-axis (or the transverse radius) is 1.23 Å.[21,23]

The probable distribution of electrons in the three perpendicular 2*p* orbitals according to the quantum-mechanical representation of the electronic structure of the oxygen molecule and O_2^- and O_2^{2-} ions is illustrated schematically in Fig. 1.[24]

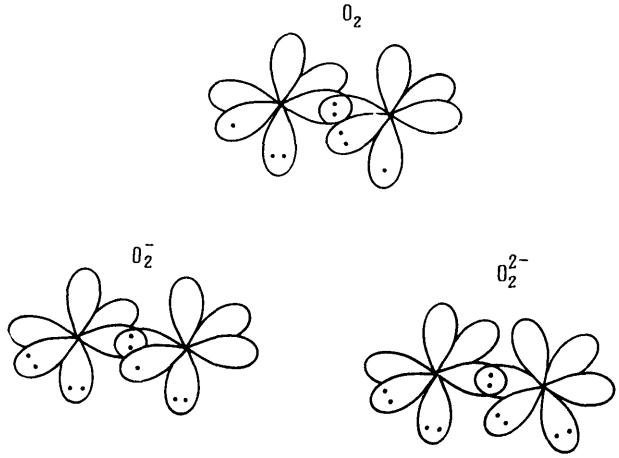


Figure 1. Schematic illustration of the probable distribution of electrons in three perpendicular 2*p* orbitals according to the quantum-mechanical representation of the electronic structure of the oxygen molecule and the O_2^- and O_2^{2-} ions.

In order to represent the electronic structure of the O_3^- ion, one must recall that the structure of ozone $:\!\underset{:O:}{\overset{}{O}}\!:$ proposed previously is in conflict with its enthalpy of formation, which amounts to +34.0 kcal mole^{-1}. If this structure is adopted, then ΔH_{298} for the formation of ozone

† The pernitride ion $[:\ddot{N}\!\!-\!\!-\ddot{N}:]^{3-}$ has a similar electronic structure.

‡ The affinity of the oxygen molecule for two electrons quoted by Vedeneev et al.[17] (-175 ± 15 kcal mole^{-1}), obtained with the aid of the Born–Haber cycle on the basis of an approximate estimate of the lattice energies of alkaline earth metal peroxides, is inaccurate.

§ The O_2^{2-} has a structure which is isoelectronic with that of the fluorine molecule and is analogous to the structure of the disulphide ion $[:\ddot{S}-\ddot{S}:]^{2-}$.

should be 77.9 kcal mole^{-1}. According to Pauling [4,6], the electronic structure of the ozone molecule may be represented by a formula with eighteen electrons (Table 1). Then the structure of one of the terminal oxygen atoms in the ozone molecule resembles that of the fluorine atom; it completes its octet by sharing one electron pair with a neighbouring oxygen atom. Such an atom may be regarded as a negative ion $:\ddot{O}\cdot^-$ forming one covalent bond. The central atom may be regarded as a positive oxygen ion $:\dot{O}^+$ forming three covalent bonds: one single bond with the left-hand side oxygen atom and one double bond with the right-hand side oxygen atom. The angle at the vertex is 116°4′ according to Trambarulo [25] and 127°3′ according to Hughes [26].

Table 1. Principal characteristics of the bond types in the molecules of oxygen and ozone and their molecular anions.

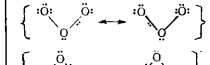
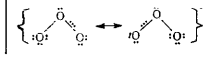
Formula	Electronic structure	O–O bond length, Å	Bond dissociation energy, kcal mole^{-1}	Electron affinity E, kcal mole^{-1}
O_2	:O ⋮÷ O:	1,207	118	20±3
O_2^-	[:O ⋯ O:]$^-$	1.32—1.35	69	130±3
O_2^{2-}	[:Ö–Ö:]$^{2-}$	1.49	—125	—
O_3		1.278	25.1	44±10
O_3^-		(1.19—1.22)	—	—

Table 1 presents two structures for the ozone molecule. This implies that the two terminal oxygen atoms are equivalent. Using the terminology of the resonance theory, one may say that each bond in the ozone molecule is a hybrid of a single and a double bond.

The addition of one electron to the ozone molecule results in the evolution of energy, $O_3 + e \rightarrow O_3^-$ + 66.5 kcal mole^{-1}, [25,27] or, according to later data, +44 ± 10 kcal mole^{-1}, [28] and the formation of the singly-charged negative ion O_3^- which enters into the composition of ozonides. The electron structure of the O_3^- ion may be represented by the formula quoted in Table 1. Evidently the singly-charged negative ozonide ion has an odd number of electrons (nineteen), in agreement with the paramagnetism and colour of compounds containing it. The dissociation energy of the O–O bond in the O_3^- ion is unknown, but it is probably lower than the dissociation energy of this bond in the ozone molecule itself, giving O_2 and O, which amounts to 25.1 kcal mole^{-1}. [9] Consequently in the series of molecular oxygen anions, the O_3^- anion is least stable, though, according to not altogether reliable data [29,30], its O–O bond length is smaller than in the other ions discussed above and even in the oxygen molecule itself. It is 1.19–1.22 Å, [29,30] while in ozone it is 1.278 Å [25] or, according to later data [26], 1.260 Å. The angle at the vertex of the O_3^- ion is 100°. [29]

Table 1 presents the principal characteristics of the bond types in oxygen and ozone molecules and their molecular anions.

Simple Inorganic Peroxy-compounds

Inorganic peroxy-compounds, the crystal lattices of which contain the above oxygen anions O_2^{2-}, O_2^-, O_3^- and also the hydroperoxide anion HO_2^- should be classified as simple peroxy-compounds.

Simple inorganic peroxy-compounds can be divided into four groups: (1) peroxides, the crystal lattices of which contain the peroxide ions O_2^{2-}; (2) superoxides incorporating the superoxide ions O_2^-; (3) ozonides incorporating the ozonide ion O_3^-; (4) hydroperoxides.

The crystal lattices of hydroperoxides, which have the general formula EOOH, contains the hydroperoxide ion HO_2^-. In these compounds the peroxo-group is linked by an ionic bond to the atom of the element E and by a covalent bond to the hydrogen atom. The ionic character of hydroperoxides has been demonstrated experimentally only for the compound NH_4OOH. [31,32] It is also confirmed by the fact that hydrogen peroxide is a weak acid with $K = [H^+][HO_2^-]/H_2O_2 = 2.24 \times 10^{-12}$.

It is noteworthy that certain hydroperoxides may be regarded as peroxyhydrates and others as peroxo-acids. For example, NaOOH may be represented as the peroxyhydrate $Na_2O_2.H_2O_2$, and the compound $(OH)_3TiOOH$ may be regarded as a peroxo-acid.

Compounds in which the peroxo-group is linked to the atom of the element forming the peroxy-compound by a coordinate bond involving the π bonding orbitals of the O_2^{2-} ion should be included among complex peroxy-compounds, which will be described in detail in the next section. Complex peroxy-compounds include also peroxide hydrates, adducts of peroxides and salts with hydrogen peroxide, and compounds containing in the inner sphere H_2O_2 molecules or HO_2 radicals.

A characteristic property of peroxy-compounds, both simple and complex, is their capacity to form hydrogen peroxide on interaction with dilute solutions of acids and also to evolve oxygen readily in an active form on thermal decomposition or under the influence of water and other chemical agents. The "superoxide" oxygen evolved by peroxides has come to be referred to as "active". Other inorganic compounds which can serve as sources of oxygen, for example nitrates, chlorates, perchlorates, permanganates, and certain oxides [33], do not evolve oxygen under the action of water; they do so only on heating to high temperatures and in the presence of catalysts. Potassium dichromate, manganese dioxide, and lead dioxide evolve oxygen only on interaction with concentrated sulphuric acid solutions.

The difference in the type of bond between the oxygen atoms in the "bridges" of peroxides and hydroperoxides on the one hand and in superoxides and ozonides on the other is clearly revealed on hydrolysis. Peroxides and hydroperoxides are hydrolysed according to the equations $M_2O_2 + H_2O \rightarrow 2MOH + H_2O_2$ and $MOOH + H_2O \rightarrow MOH + H_2O_2$ (where M is the metal atom) with formation of hydrogen peroxide, which is quantitatively titrated with acid permanganate. The formation of hydrogen peroxide on hydrolysis of peroxides and hydroperoxides indicates a clear genetic relation between these compounds and hydrogen peroxide. Therefore peroxides and hydroperoxides have long been regarded as salts of hydrogen peroxide with two and one metal atoms.

Superoxides are hydrolysed with formation of an intermediate HO_2 radical (the hydroperoxyl) according to the equations

$$\begin{array}{l} 2MO_2 + 2H_2O \rightarrow 2MOH + 2HO_2, \\ 2HO_2 \rightarrow H_2O_2 + O_2, \\ \hline 2MO_2 + 2H_2O \rightarrow 2MOH + H_2O_2 + O_2, \end{array}$$

Consequently two-thirds of the active oxygen, constituting the "superoxide oxygen", is evolved as O_2 and can be determined gas-volumetrically and one-third of the active oxygen, which constitutes the "peroxide oxygen", is evolved as H_2O_2 and can be titrated with acid permanganate. Ozonides are hydrolysed without the formation of H_2O_2 according to the equation $MO_3 + H_2O \rightarrow MOH + OH + O_2$.

The reactions occurring on hydrolysis of superoxides and ozonides reveal a clear genetic relation, noted by Kazarnovskii, between superoxides and the H_2O radical and between ozonides and the hypothetical radical HO_3 (the hydro-ozonyl).[34]

The term peroxide was introduced in the Russian nomenclature by D.I. Mendeleev, who wrote, emphasising the lack of similarity in the reactions of the peroxides MO_2 and the salt-forming oxides of the same composition, that "the concept of peroxides is indefinite if one includes among them not only H_2O_2, Na_2O_2, and BaO_2 but also MnO_2 and PbO_2".[35] The definitions of "peroxide" quoted in the textbook of Gess [Hess?][36] and Shcheglov[37] suffer from this lack of clear-cut significance. Unfortunately certain contemporary chemists both in the USSR and abroad continue to employ the term peroxides for quadrivalent lead and manganese oxides the molecules of which contain the oxide ion O^{2-} with the electron structure $[:\ddot{O}:]^{2-}$. The nitrogen (IV) oxide N_2O_4, in the molecule of which there is no peroxo-group and the oxygen atom is linked covalently to the nitrogen atom, is also incorrectly called a peroxide.

The principal feature distinguishing peroxide from oxides of the type MO_2 is the reaction with dilute acids. As mentioned above, the former form H_2O_2, and the latter can, for example, evolve chlorine from hydrochloric acid.

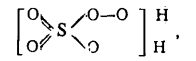
The term hydroperoxide (gidroperekis') was adopted in the Russian literature as the translation of the German term Hydroperoxyd[38].

The term superperoxide (nadperekis') was introduced into the Russian nomenclature in 1948 [39] and is more apt than the term "tetroxide" adopted previously[40], since it has been shown[4,7] that there is no O_4^{2-} ion in the molecules of these compounds. The term superperoxide has become firmly established in the Russian chemical nomenclature[41-43]. In 1947 the term "dioxide" was proposed for these compounds[44], as in the German nomenclature[45], and later the term "superoxide" ["superoksid"][46], a translation of the corresponding English term, was suggested by Neuman[47]. This term was adopted[48] in 1953 in the English, French (superoxyde), German (Superoxyd), and Italian (superossido) nomenclature, but in 1957 the International Union of Pure and Applied Chemistry approved the terms hyperoxide and hyperoxyde[49,50] on the basis of the term Hyperoxyd proposed by Remy[51] for the German nomenclature. While there names are justified by the fact that in the above languages we have the terms oxide, oxyde, Oxyd, and ossido and also peroxide, peroxyde, Peroxyd, and perossido, in the Russian nomenclature the terms "superoksid" (superoxide) and "giperoksid" (hyperoxide) are in no way justified, since the terms "okis'" (oxide) and "perekis'" (peroxide)[52] have been generally adopted for the lower degrees of oxidation and not "oksid" (oxide) and "peroksid" (peroxide), as suggested by some workers[53-56]. Moreover the Russian suffix "nad" corresponds to the Latin suffix super and the Greek suffix $\upsilon\pi\epsilon\rho$. Therefore the term "nadperekis'" (superperoxide) is quite acceptable¶. Evidently, on the basis of the same considerations, the term "nadokis'" (superoxide) was proposed[52]. However, it is close in significance to the term "perekis'" (peroxide) and does not reflect the fact that the relevant compounds contain more active oxygen than a peroxide. The proposed term "superoksid" (superoxide) for peroxides of the type M_2O_2 is quite inappropriate[56].

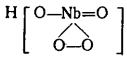
The term "inorganic ozonide" was introduced by Kazarnovskii[57] and has been adopted by the International Union of Pure and Applied Chemistry[49,50].

Complex peroxy-compounds may be divided into five groups.

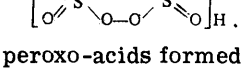
1. Peroxo-acids and their salts, in which the peroxo-group† enters into the composition of the complex anion. Mononuclear peroxo-acids and their salts are known, for example, peroxomonosulphuric acid:



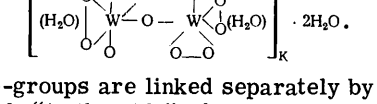
and peroxomononiobic acid:



as well as polynuclear peroxo-acids and their salts. In these compounds the atoms of elements in Groups IV–VI of the Periodic System—the non-metals carbon, nitrogen, phosphorus, and sulphur or the metals titanium, vanadium, chromium, niobium, molybdenum, tantalum, and tungsten—usually function as the coordinating species. In polynuclear peroxo-acids formed by non-metals, the atoms of the coordinating element are linked via a peroxo-group, as, for example, in peroxodisulphuric acid:



In polynuclear peroxo-acids formed by transition elements, the linkage between the atoms of the coordinating element is formed via one oxygen atom, as, for example, in potassium tetraperoxotungstate[59,60] or tetraperoxomolybdate[61]:

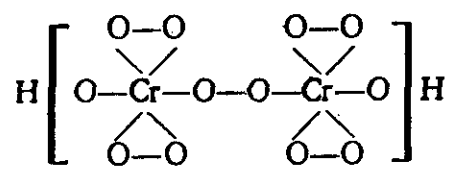


The peroxo-groups are linked separately by two covalent π bonds "to the side" of each atom of the coordinating element. The O–O bond length is 1.50 Å in the tungsten compound[60] and 1.48 Å in the molybdenum compound[61]. The peroxy-complexes of titanium[62], in which the O–O bond length is 1.45 Å, have the same structure.

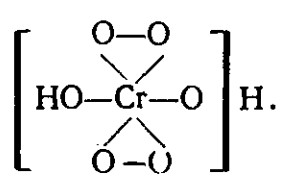
¶ If the term "oksid" (oxide) proposed by the authors of projects for the Russian nomenclature[53,54] and Kazarnovskii[55] is approved, the above remarks concerning the term "superoksid" (superoxide) will be no longer valid and the terms "perekis'" (peroxide) and "gidroperekis'" (hydroperoxide) should be replaced by "peroksid" (peroxide) and "gidroperoksid" (hydroperoxide).

† At the XXIInd Congress of the International Union of Pure and Applied Chemistry, the term "peroxido-group" was adopted instead of "peroxo-group"[58].

The presence of a linkage between the atoms of the coordinating element via an "oxygen bridge" in polynuclear peroxo-acids of certain other transition elements appeared controversial. For example, until recently[63] it was believed that there exist polynuclear peroxochromates with the composition $M_2[Cr_2O_{12}]$ to which the formula of pentaperoxodichromic acid was attributed:



However, according to later data[64,65], the mononuclear structure of oxomonohydroxodiperoxochromic acid was established for this compound:

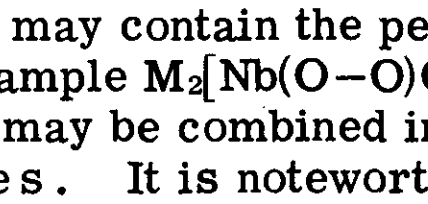


The O–O bond length in derivatives of chromium peroxo-acids is 1.40–1.47 Å.[65] The O–O bond length in peroxoacid derivatives of non-metals, for example, in the compounds $(NH_4)_2S_2O_8$ and $Cs_2S_2O_8$, is 1.46 Å.[66]

2. P e r o x y - c o m p l e x e s w h i c h a r e n o t p e r o x o a c i d s o r t h e i r d e r i v a t i v e s. These can also be divided into mononuclear and polynuclear. The mononuclear compounds may contain the peroxo-group in the inner sphere, for example $M_2[Nb(O{-}O)Cl_5]$, and $M_2[Mo(O{-}O)_2OCl_4]$, and may be combined in the subgroup of p e r o x o - c o m p l e x e s. It is noteworthy that, whereas the oxo-group always behaves as a monodentate ligand, the peroxo-group, owing to the greater length of the O – O bond, can behave as a bidentate ligand and can promote the formation of compounds with a coordination number of seven and particularly eight. This possibility diminishes in the series Cr < Mo ≃ W and V < Nb ≃ Ta. The possibility of the existence of a peroxo-ligand and other ligands around the central atom of the complex depends both on the nature of the central atom and on the conditions in the medium where the compound is synthesised. It depends on the pH of the solution and on the oxidation–reduction properties of the ions involved in the reaction.

Mononuclear peroxy-complexes also include compounds with hydrogen peroxide molecules in the inner sphere, for example $[Fe(H_2O)_5(H_2O_2)]^{3+}$. Compounds of this kind constitute the group of p e r h y d r o - c o m p l e x e s. Finally hydroperoxy-radicals may be coordinated in the inner sphere, as, for example, in $K_3[Co(CN)_5OOH]$. Compounds of this type constitute the subgroup of h y d r o - p e r o x o - c o m p l e x e s.

Compounds of the type

$Na_2[B_2(O)_2(OH)_4]\cdot 6H_2O$,  $\cdot 6H_2O$,

$[(NH_3)_5Co{-}O{-}O{-}Co(NH_3)_5](NO_3)_5$ and others

may serve as an example of polynuclear peroxy-complexes which are not peroxo-acids.

The bond length in the first compound is 1.47 Å[67] and in the last 1.45 ± 0.06 Å.[68] In contrast to derivatives of binuclear peroxo-acid derivatives of transition elements, in these compounds the linkage between the metal atoms is formed via an "oxygen bridge".

The comparatively recently discovered complex peroxy-compounds formed by the addition of oxygen to certain reactive d^8 and d^{10} complexes of iridium, rhodium, platinum, palladium, and nickel are of some interest. For example, the iridium complex $IrO_2Cl(CO)(PPh_3)_2$, in which the O–O distance is 1.30 ± 0.003 Å, i.e. close to the O–O distance in the O_2^- anion, has been isolated[69–71]. However, this compound is diamagnetic like all other similar derivatives. It is interesting to note that the O–O bond length in iridium complexes of this kind and their capacity for combination with oxygen increase with increasing capacity of the other ligands to lose electrons.

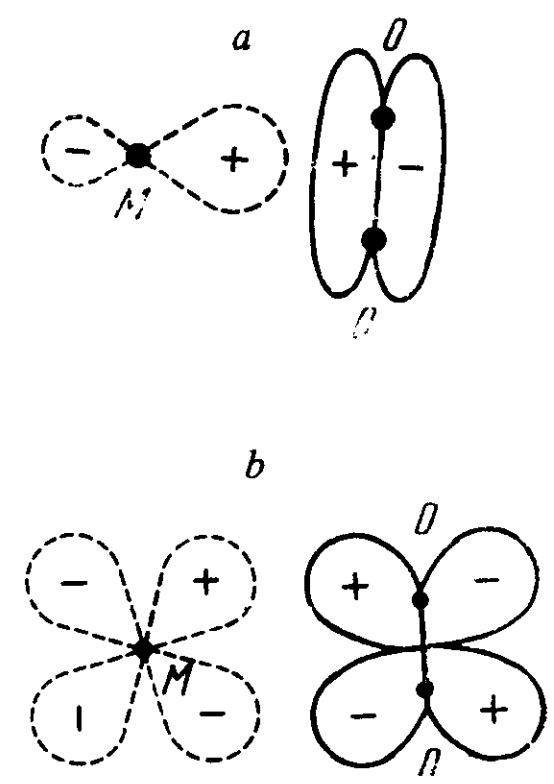


Figure 2. *a*) Transfer of π electrons from the donor (oxygen) to free *d* orbitals of the metal; *b*) transfer of *d* electrons from the metal to the antibonding orbital of the donor.

For example, in the iodide complex $IrO_2I(CO)(PPh_3)_2$, the O–O distance is 1.51 Å, i.e. close to the O–O distance in the O_2^{2-} anion, while in the phosphine chelate complex $IrO_2(PAr_2)_4$ [probably $IrO_2(P_2Ar_4)$, (Ed. of Translation)] the distance is 1.66 Å, i.e. greater by 0.17 Å than in the O_2^{2-} molecular anion. The reason for the increase of the O–O bond length should probably be sought in the fact that these compounds have a metal–oxygen bond $(L)_nM\begin{smallmatrix}\nearrow O\\ \leftarrow \|\\ \searrow O\end{smallmatrix}$ of the π type[72]. In this bond type, one may expect a transfer of π electrons from the donor (oxygen) to the free *d* orbitals of the metal, as shown schematically in Fig. 2*a*, and also a transfer of the *d* electrons of the metal to the antibonding orbital of the donor, as shown schematically in Fig. 2*b*. The overall effect is the transfer of electrons from the bonding to the antibonding orbital of the donor via the metal. This is reflected in a decrease of bond energy and consequently in an increase of bond length. The stronger the linkage between the donor and the metal, the greater the bond length.

The most important property of these complexes is their capacity to oxidise substrates under unusually mild conditions[73].

3. P e r o x i d e h y d r a t e s —adducts of peroxides and water of crystallisation, for example $CaO_2.8H_2O$.

4. P e r o x y h y d r a t e s —molecular compounds, resembling hydrates, containing hydrogen peroxide of crystallisation, for example $CaO_2.2H_2O_2$ and $K_2CO_3.3H_2O_2$.

The analogy between the peroxyhydrates of peroxides and their hydrates is not rigorous. In the former the hydrogen peroxide molecules are linked to O_2^{2-} ions by strong hydrogen bonds, forming infinite chains. The nature of peroxyhydrates of peroxides is close to that of compounds of the type KF.HF.[74] Molecular compounds with H_2O_2 are also formed by ammonia and certain organic compounds with basic properties.

5. Hydrates of peroxyhydrates—molecular compounds containing both water and hydrogen peroxide of crystallisation, for example $BaO_2.H_2O_2.2H_2O$ and $Na_2SO_4.0.5H_2O_2.H_2O$.

The term "peroxoacid" ("peroksokislota") is the English term recommended by the International Union of Pure and Applied Chemistry[48]. The necessity to introduce into the Russian nomenclature this term, in the place of the previously adopted "nadkislota" ("peracid") proposed by Mendeleev[75] arose due to the following considerations.

For example, the compound $H_2S_2O_8$ is at present called persulphuric acid (nadsernaya kislota) in the Russian nomenclature. The terms "sulphuric acid" ("sernaya kislota" and "sulphurous acid" ("sernistaya kislota") have been adopted for oxyacids of sulphur. They emphasise that in the first compound sulphur is in the hexavalent state and in the second in the quadrivalent state. The term "persulphuric acid" is unwittingly associated with the idea that in this compound sulphur has a valence higher than six, which is not the case. Moreover, the compound H_2SO_5 is nowadays called monopersulphuric acid (mononadsernaya kislota). It would be quite logical to assume, as rightly pointed out by Gussein-zade[76], that the prefix "mono" indicates the number of peroxo-groups in the compound, since otherwise it should be referred to as permonosulphuric acid (nadmonosernaya kislota). In fact, in the above example the prefix "mono" indicates the number of sulphur atoms. Like the preceding compound, $H_2S_2O_8$ contains one peroxo-group but two sulphur atoms, which is not reflected in its name (persulphuric acid). The use of the terms "peroxomonosulphuric" and "peroxodisulphuric" for the compounds H_2SO_5 and $H_2S_2O_8$ removes this inconsistency. If in any other peroxoacid the number of peroxo-groups is greater than unity, as, for example, in peroxochromic acid H_3CrO_8 where there are four such groups, it should be designated as a tetraperoxoacid, i.e. tetraperoxomonochromic acid.

As regards the nomenclature of peroxoacid salts, it is noteworthy that the terms persulphates, percarbonates, perborates, etc. which persist in the chemical literature, are very inapt and lead to the incorrect idea that they resemble the salts of certain oxygen-containing acids, such as perchlorates, permanganates, perrhenates, etc., where the prefix "per" indicates merely the highest degree of oxidation of the element and not the presence of the peroxo-group. Certain salts of oxygen-containing acids (for example, perchlorates and permanganates) also serve as sources of oxygen in thermal decomposition. However, in contrast to the thermal decomposition of peroxoacid derivatives, their decomposition involves a change in the valence of the elements forming these compounds. For example, whereas in the thermal decomposition of potassium peroxodisulphate according to the equation $K_2S_2O_8 \rightarrow K_2SO_4 + SO_3 + 0.5O_2$ sulphur retains a valence of six in the decomposotion products, in the thermal decomposition of potassium perchlorate or permanganate according to the equations $KClO_4 \rightarrow KCl + 2O_2$ and $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$, the chlorine in the decomposition products has passed from the heptavalent to the univalent state and the manganese from the heptavalent to the hexavalent and quadrivalent state. The terms peroxosulphates, peroxocarbonates, etc. are correct for peroxoacid salts. According to crystal structure data[67], infrared and NMR spectroscopy[77], and magnetic measurements[78,79], "perborates" may be divided into two groups: those containing water may be referred to as diperoxodiborotetrahydroxo-salts and the anhydrous compounds may be designated by the term peroxoborates.

The general term peroxy-complexes is not open to objection. The term peroxyhydrate has also been recommended by the International Union of Pure and Applied Chemistry[48]. It is to be preferred to the terms "perhydrate"[90] and "hydroperoxate" proposed by American workers[81].

The difference in the type of bond between the "oxygen bridge" and the element forming the peroxy-linkage in peroxoacids and their salts compared with peroxides, superoxides, and ozonides is also shown in hydrolysis. For example, in the hydrolysis of peroxodisulphuric acid $H_2S_2O_8$ or peroxodisulphate salts, peroxomonosulphuric acid H_2SO_5 is formed initially without the formation of hydrogen peroxide, according to the equation $H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4$ and then peroxomonosulphuric acid yields hydrogen peroxide according to the equation $H_2SO_5 + H_2O \rightarrow H_2SO_4 + H_2O_2$. However, at room temperature the hydrolysis is very slow and involves considerable loss of active oxygen. Although on heating the rate of reaction does increase, there is a simultaneous increase of the amount of oxygen evolved. Consequently, the quantitative determination of active oxygen in these compounds cannot be achieved by permanganate titration and iodometric titration is employed.

Peroxy-complexes which are not peroxoacids or derivatives of peroxoacids hydrolyse in most cases with formation of hydrogen peroxide, but certain mononuclear peroxy-complexes, for example $[(NH_3)_5Co-O-O-Co(NH_3)_5]^{5+}$ are extremely stable in relation to water and give rise to H_2O_2 only in an acid medium.

When peroxyhydrates react with water, hydrogen peroxide of crystallisation passes to the solution and may be determined quantitatively by permanganate titration in an acid medium.

A new class of peroxides—organometallic peroxides—the composition of which includes one or several metal atoms, peroxy-groups, and organic residues, are of special interest[82]. For example silicon, germanium, tin, and lead are capable of forming symmetrical peroxides of the type R_3MOOMR_3, in which the linkage between the atoms of the element is achieved via an "oxygen bridge".

Table 2 presents a scheme for the classification and nomenclature of inorganic peroxy-compounds proposed by the author of this review[83-85] and supplemented by taking into account the latest data on their structure.

The methods of synthesis of each group of peroxy-compounds quoted in Table 2 are different. Hydroperoxides are synthesised mainly via alkoxides in an anhydrous medium. Peroxides are synthesised by the reaction of oxides with oxygen or via solutions of the hydroxides and hydrogen peroxide. Superoxides are synthesised mainly via the metals, by their combustion in oxygen at the normal pressure, and also by the action of oxygen on peroxides at the normal or elevated pressure. Ozonides are obtained by the reaction of ozone with hydroxides or superoxides with subsequent extraction by liquid ammonia. Peroxoacids and the peroxoacid salts of

Table 2. Classification and nomenclature of inorganic peroxy-compounds.

Type	Group			Formula
Simple	Hydrogen polyoxides			H_2O_2, H_2O_3, H_2O_4
	Hydroperoxides			M^IOOH
	Peroxides			$M^I_2O_2$
	Superoxides			M^IO_2
	Ozonides			M^IO_3
Complex	Peroxoacids and their salts	Mononuclear		$[E^{IV}O_4]^{2-}$; $[E^VO_5]^{3-}$; $[E^{VI}O_5]^{2-}$; $[E^{VI}O_6]^{2-}$
		Polynuclear	With peroxo-bridges	$[O_2E^{IV}-O-O-E^{IV}O_2]^{4-}$; $[O_2E^V-O-O-E^VO_3]^{4-}$; $[O_2E^{VI}-O-O-E^{VI}O_2]^{2-}$
			With oxo-bridges	$[(O-O)_2OE^{VI}-O-E^{VI}O(O-O)_2]^{2-}$
	Peroxy-complexes	Mononuclear	Peroxo-	$[M(O-O)_x(L)_y]^n$
			Perhydro-	$[M(H_2O_2)_x(L)_y]^n$ $n=0,\pm1,2,3...$
			Hydroperoxo-	$[M(HO_2)_x(L)_y]^n$
		Polynuclear		$[(L)_yMO-OM(L)_y]^n$
	Peroxide hydrates			$M^I_2O_2\cdot xH_2O$
	Peroxyhydrates	of peroxides		$M^I_2O_2\cdot xH_2O_2$
		of salts		$M^I_nEO_m\cdot x\cdot H_2O_2$
	Peroxyhydrate hydrates	of peroxides		$M^I_2O_2\cdot xH_2O_2\cdot yH_2O$
		of salts		$M^I_nEO_m\cdot x\cdot H_2O_2\cdot yH_2O$
Organometallic	Hydroperoxides			$R_nM(OOH)_m$
	Substituted hydroperoxides			$R_nM(OOR)_m$; $M(OOR)_n$
	Peroxides	Homoradical		R_nMOOMR_n
		Heteroradical		$R_nMOOMR^1_n$
		Heteroelemental		R_nMOOCR_n

M = metal, E = element, L = ligand, and R = organic group.

typical elements are synthesised predominantly by the electrolytic method. The peroxoacids of transition elements and their salts are synthesised via solutions of oxygen-containing acids of these elements and of hydrogen peroxide. Peroxy-complexes which are not derivatives of peroxoacids are obtained mainly with the aid of solutions of hydrogen peroxide, but in many cases oxidation with molecular oxygen is employed. The addition of molecular oxygen to the coordinating element in compounds of certain transition metals may be represented schematically as follows:

$$M^{n+} + O_2 \xrightarrow{I} M^{n+}(O_2) \xrightarrow{II} M^{n+2}(O_2^{2-}).$$

Oxygen carriers are formed reversibly via mechanism I, while mechanism II involves the irreversible formation of peroxy-complexes where the metal passes to a higher valence state and in the case of binuclear complexes μ-peroxo-compounds are produced.

Peroxyhydrates and their hydrates are formed exclusively from hydrogen peroxide solutions. Organometallic compounds form organometallic peroxo-derivatives on reaction with peroxy-compounds or on oxidation with molecular oxygen.

The difference between the structures of inorganic peroxy-compounds is responsible for the difference between their physical properties and reactivities and hence for the possibility of employing them under a wide variety of conditions.

The above data concerning the radical differences between the molecular oxygen anions and the different states of the peroxo-group in complex peroxy-compounds demonstrate that inorganic peroxy-compounds cannot be characterised by the words "these are compounds incorporating an oxygen bridge". Additional evidence showing that this definition is not altogether satisfactory comes from the elucidation of the structure of the compound F_2O_2, which has been incorrectly called[15] fluorine peroxide. It has been established[86,87] that in the oxygen fluoride F_2O_2 the fluorine atoms are joined by the "oxygen bridge" O–O, although this compound does not exhibit the properties of peroxides. The O–O bond length in this compound (1.22 Å) differs little from the bond length in the oxygen molecule. On coming into contact with ice, F_2O_2 (m.p. 64.3°) explodes with evolution of oxygen[88]. The energy of the dissociation of F_2O_2 into 2OF is 62.3 ± 20 kcal mole^{-1}.[89]

The so called dioxygenyl compounds incorporating the O_2^+ ion, for example the compounds $O_2^+PtF_6^-$[90] and $O_2^+BF_4^-$[91] are not peroxides either. The formation of the O_2^+ ion is accompanied by the evolution of 286 kcal mole^{-1} and the energy of dissociation into $O^+ + O$ is 153.48 ± 0.05 kcal mole^{-1}.[92] The interatomic distance in the O_2^+ molecular ion, which is formed on removal of one electron from the $\nu\pi^*$ level, is reduced to 1.1227 Å compared with 1.2074 Å in the oxygen molecule, while, as stated above, on formation of peroxide anions the above distance increases owing to the introduction of additional electrons in the same level[93].

REFERENCES

1. F. Hein, "Chemische Koordination Lehre", Leipzig, Hirzel Verlag, 1950, p. 131.
2. A. Chretien and P. Allamagny, Compt. rend., 260, 1425 (1965).
3. P. Allamagny, Rev. Chim. Min., 2, 645 (1965).
4. L. Pauling, "The Nature of the Chemical Bond" (Translated into Russian), Goskhimizdat, Moscow, 1947, p. 330.
5. L. Pauling, "General Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1964.

6. L. Pauling, "The Nature of the Chemical Bond", Ithaca, New York, Cornell Univ. Press, 1960, p.354.
7. V.V. Kasatochkin and V.N. Kotov, Zhur. Fiz. Khim., 8, 320 (1936); Dokl. Akad. Nauk SSSR, 47, 199 (1945).
8. H.R. Zeller et al., Helv. Phys. Acta, 40, 845, 873 (1967).
9. V.I. Vedeneev et al., "Energiya Razryva Khimicheskoi Svyazi" (Chemical Bond Dissocation Energy), Izd. Akad. Nauk SSSR, Moscow, 1962, p. 207.
10. J.A. Creighton and E.R. Lippincott, J. Chem. Phys., 40, 1779 (1964).
11. A.P. Altschuller, J. Chem. Phys., 28, 1254 (1958).
12. F. Halverson, Phys. and Chem. Solids, 23, 207 (1962).
13. N.G. Vannerberg, in "Progress in Inorganic Chemistry" (Edited by F.A. Cotton), Interscience Publ., New York, 1962, p. 137.
14. G. Czapski and B. Halperin, Israel J. Chem., 5, 185 (1967).
15. S.A. Shchukarev, "Lektsii po Obshchemu Kursu Khimii" (A General Chemistry Course of Lectures), Izd. Leningrad. Gos. Univ., Leningrad, 1964, Vol. 2, p. 103.
16. K.B. Yatsimirskii, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 2, 481 (1959).
17. A.V. Vedeneev et al., Zhur. Fiz. Khim., 26, 1808 (1952).
18. A. Barton, Phys. Rev., 26, 360 (1925).
19. M. Prover and B. White, Chem. Comm., 183 (1965); Electrochim. Acta, 11, 1061 (1966); J. Chem. Soc. B, 816 (1970); Chem.-Ing.-Techn., 42, 185 (1970).
20. J.D. Bernal, E. Dyatlova, et al., Z. Kryst., 92, 344 (1935).
21. D.G. Tuck, J. Inorg. Nuclear Chem., 26, 1528 (1964).
22. M.M. Pavlyuchenko and T.I. Popova, Dokl. Akad. Nauk Beloruss. SSR, 7, 156 (1963).
23. H. Foeppl, Z. anorg. Chem., 291, 49 (1957).
24. N.G. Vannerberg, "The Formation and Structure of Peroxycompounds of Group IIA and IIB Elements", Goeteborg, Upsala, Almquist, 1959.
25. R. Trambarulo, J. Chem. Phys., 21, 851 (1953).
26. R.H. Hughes, J. Chem. Phys., 24, 131 (1956).
27. G.P. Nikol'skii and I.A. Kazarnovskii, Dokl. Akad. Nauk SSSR, 72, 713 (1950).
28. R.H. Wood and L.A. D'Orazio, J. Phys. Chem., 69, 2562 (1965).
29. L.V. Azarov and J. Corvin, Proc. Nat. Acad. Sci. U.S.A., 49, 1 (1963).
30. K. Herman and P. Giguére, Canad. J. Chem., 43, 1746 (1965).
31. A. Simon and K. Keishman, Naturwiss., 42, 14 (1955).
32. A. Knop and P. Giguére, Canad. J. Chem., 37, 1794 (1959).
33. "Nouveau Traite de Chimie Minerale", Masson, Paris, 1960, Vol. 13, p. 174.
34. P. Smith, Chem. Ind. (London), 1299 (1954).
35. D.I. Mendeleev, Zhur. Russ. Fiz.-khim. Obshch., 3, 284 (1871).
36. G.I. Gess [H.I. Hess?], "Osnovaniya Chistoi Khimii" (Foundations of Pure Chemistry), Sixth Edition, Tip. Akad. Nauk, St. Petersburg, 1845, p. 584.
37. N.P. Scheglov, "Nachal'nye Osnovaniya Khimii" (Fundamental Principles of Chemistry), Tip. Glazunova, St. Petersburg, 1830.
38. M.E. Pozin (Editor), "Perekis' Vodoroda i Perekisnye Soedineniya" (Hydrogen Peroxide and Peroxy-compounds), Goskhimizdat, Moscow, 1951.
39. A.F. Wells, "Structural Inorganic Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1948, p. 346.
40. I.A. Kazarnovskii, Zhur. Fiz. Khim., 14, 326 (1940).
41. K.V. Astakhov and A.G. Getsov, Dokl. Akad. Nauk SSSR, 81, 43 (1951).
42. T.V. Rode, Dokl. Akad. Nauk SSSR, 90, 1075 (1953).
43. I.I. Vol'nov, Zhur. Neorg. Khim., 1, 1938 (1956).
44. I.A. Kazarnovskii, Zhur. Fiz. Khim., 21, 248 (1947).
45. A. Helms and W. Klemm, Z. anorg. Chem., 241, 106 (1939).
46. I.A. Kazarnovskii and L.I. Kazarnovskaya, Zhur. Fiz. Khim., 3, 293 (1951).
47. E.W. Neuman, J. Chem. Phys., 2, 31 (1934).
48. International Union of Pure and Applied Chemistry, "Extrait des Comptes Rendus de la 17-me Conference", Stockholm, 1953, p. 101.
49. IUPAC Report of the Commission on the Nomenclature of Inorganic Chemistry, 1957; J. Amer. Chem. Soc., 82, 5530 (1960).
50. IUPAC Rapport de la Commission de Chimie Minerale, 1957; Bull. Soc. chim. France, 580 (1960).
51. H. Remy, Angew. Chem., 68, 613 (1956).
52. S.M. Aria, Candidate's Thesis, Leningrad State University, 1948.
53. B.V. Nekrasov, "Osnovy Obshchei Khimii" (Fundamentals of General Chemistry), Izd. Khimiya, Moscow, 1965.
54. G.P. Luchinskii, "Proekt Pravil Nomenklatury Neorganicheskikh Soedinenii" (A Proposed Nomenclature of Inorganic Compounds), Izd. Vses. Khim. Obshch. im Mendeleeva, Moscow, 1962, p. 12.
55. I.A. Kazarnovskii, "Nauchnaya Sessiya Uchenogo Soveta Fiziko-khimicheskogo Instituta im. L. Ya. Karpova, Posvyashchaetsya 40-Letiyu Velikoi Oktyabr'skoi Sotsialisticheskoi Revolyutsii, Tezisy Dokladov" (Scientific Session of the Scientific Council of the Karpov Physicochemical Institute Commemorating the Fortieth Anniversary of the Great October Socialist Revolution. Abstracts of Reports), Izd. MKhP SSSR, Moscow, 1957, p. 17.
56. VIII Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii. Proekt Nomenklatury Neorganicheskikh Soedinenii" (The Eighth Mendeleev Congress of General and Applied Chemistry. A Proposal for the Nomenclature of Inorganic Compounds), Izd. Akad. Nauk, SSSR, Moscow, 1959, p. 14.
57. I.A. Kazarnovskii, Dokl. Akad. Nauk SSSR, 64, 69 (1949).
58. IUPAC, "Comptes Rendus de la 22-me Conference", London, 5–9 July, 1963.
59. P.G. Melikov and L.V. Pisarzhevskii, "Issledovaniya nad Perekisyami" (Studies on Peroxides), Zap. Akad. Nauk Fiz. Mat. Otd., Ser. 9, No. 8, 53 (1900).
60. F. Einstein and B. Penfold, Acta cryst., 17, 1127 (1964).
61. R. Stomberg, Acta Chem. Scand., 22, 1076 (1968).
62. D. Schwarzenbach, Inorg. Chem., 9, 2391 (1970).
63. J. Fergusson, J. Chem. Soc., 2137 (1962).
64. W. Griffith, J. Chem. Soc,, 3948 (1962).
65. R. Stomberg, Arkiv Kemi, 24, 283 (1965).
66. W.H. Zachariasen and R.L. Moohey, Z. Kryst., 88, 63 (1933).
67. A. Hansson, Acta Chem. Scand., 15, 934 (1961).
68. N.G. Vannerberg, Acta Cryst., 16, 247 (1963).
69. L. Vaska, Science, 140, 809 (1963).
70. J.A. Ibers and S.J. La Placa, Science, 145, 920 (1964).

71. S. J. La Placa, J. Amer. Chem. Soc., 87, 2481 (1965).
72. J. P. Franck et al., Rev. Inst. Franc. Pétrole, 24, 710 (1969).
73. J. P. Collman, Accounts of Chem. Res., 1, 142 (1968).
74. N. G. Vannerberg, see Ref. 13, p. 166.
75. D. I. Mendeleev, Zhur. Russ. Fiz.-khim. Obshch., No. 6, Section I, 561 (1881).
76. S. M. Gussein-zade, Azerb. Khim. Zhur., 2, 126 (1959).
77. G. Rietz, Wissen. Ztschr. Tech. Hochschule Chem. "C. Schorlemmer", 12, 125 (1970).
78. R. Bruce, J. Amer. Chem. Soc., 87, 2057 (1965).
79. G. Rietz, Z. Chem., 8, 278 (1968).
80. S. Z. Makarov and V. N. Chamova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 126 (1951).
81. W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, "Hydrogen Peroxide" (Translated into Russian), Inostr. Lit., Moscow, 1958, p. 26.
82. T. G. Brilkina and V. A. Shushunov, Trudy Khim. i Khim. Tekhnol. Nauch.-Issled. Inst. Khim. Gor'kovsk. Gos. Univ., 3, 505 (1960).
83. I. I. Vol'nov, Soobshch. Nauch Rabot. Chlenov Vses. Khim. Obshch. im Mendeleeva, No. 1, 52 (1955).
84. I. I. Vol'nov, Symposium, "Khimiya Perekisnykh Soedinenii" (The Chemistry of Peroxy-compounds), Izd. Akad. Nauk SSSR, Moscow, 1963, p. 15.
85. I. I. Vol'nov, in "Kratkaya Khimicheskaya Entsiklopediya" (A Short Chemical Encyclopaedia), Izd. Sovetskaya Entsiklopediya, Moscow, 1964, Vol. 3, p. 931.
86. I. I. Vol'nov, "Perekisi, Nadperekisi i Ozonidy Shchelochnykh i Shchelochnozemel'nykh Metallov" (Alkali and Alkaline Earth Metal Peroxides, Superoxides, and Ozonides), Izd. Nauka, Moscow, 1964, p. 21.
87. I. I. Vol'nov, Doctoral Thesis, Institute of General and Inorganic Chemistry of the USSR Academy of Sciences, Moscow, 1967, p. 4.
88. A. Jackson, J. Chem. Soc., 4585 (1962).
89. J. W. Linnet, J. Chem. Soc., 4663 (1963).
90. A. G. Streng, Chem. Rev., 63, 607 (1963).
91. N. Batler and W. Lehman, Proc. Chem. Soc., 115 (1962).
92. I. J. Solomon, R. I. Brabets, R. K. Uenishi, J. N. Keith, and J. M. McDonough, Inorg. Chem., 3, 457 (1964).
93. H. B. Gray, "Electrons and Chemical Bonding" (Translated into Russian), Izd. Mir, Moscow, 1967, p. 72.

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