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CHEMISTRY OF PEROXIDE COMPOUNDS

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This survey discusses Russian research on peroxide compounds from 1866 to 1967. In the Soviet era, this research has dealt mainly with peroxide kinetics, reactivity and characteristics and with peroxide production processes and, more recently, with superoxides and ozonides, with continued emphasis on the higher oxides of group I and II elements. Solid state fluidized bed synthesis and production of high purity products based on the relative solubilities of the initial, intermediate and final compounds and elements in liquid ammonia are discussed.
CHEMISTRY OF PEROXIDE COMPOUNDS
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The chemistry of inorganic peroxides has famous traditions in Russia. Russian scientists began to be interested in these compounds in the second half of the nineteenth century, and the first experimental work in this field, performed by professor E.B. Shyene, of the Petrovskaya (now the Agricultural im. K.A. Timiryazayev) Academy, were in 1866. They dealt with the synthesis of hydrates of alkaline earth metal peroxides. The founders of the chemistry of peroxide compounds in Russia are D.I. Mendeleyev (1834-1907), his contemporary E.B. Shyene (1834-1896), P.G. Melikov (Melikishvili) (1850-1927) and A.N. Bakh (1857-1946).

D.I. Mendeleyev did not conduct experimental studies in the field of peroxides. His interest in this class of compounds was dictated by the apparent contradictions between the chemical composition of peroxides and the regularity of the periodic properties of the elements in the formation of oxides. In all editions of Osnov khimii [Foundations of Chemistry] and in individual articles, D.I. Mendeleyev emphasized the difference of peroxides from oxides which have a similar empirical composition, and he expressed many interesting thoughts which were the key to a deeper understanding of the nature of these compounds, which were confirmed experimentally later in the work of other Russian and foreign scientists.

E.B. Shyene is a pioneer in the field of experimental study of inorganic peroxides in Russia. He generalized his studies of hydrates and peroxyhydrates of peroxides from hydrogen peroxide to ozone, chlorine, manganese and lead dioxides, potassium iodide and other halides in the monograph Opytnye issledovaniya nad perekis'yu vodoroda [Experimental Studies of Hydrogen Peroxide], published in 1875. This

*Numbers in the margin indicate pagination in the foreign text.
monograph on peroxides still is important today.

At the end of the last century, in Novorossiysk (Odessa) University, P.G. Melikov and S.M. Tanatar founded the first school for the study of peroxides and, together with their students, L.V. Pisarzhevskiy, N.I. Petrenko, B.V. Klimenko, I.P. Kazanetskiy, A.S. Komarovskiy and others, they made a considerable contribution to the development of this field of inorganic chemistry. The starting point for the studies of P.G. Melikov and L.V. Pisarzhevskiy was the statements of D.I. Mendeleyev on the nature of peroxy acids. After study of the properties of a number of salts of peruranic, permolybdic, pertungstic, pervanadic, perniobic, pertantalic and pertitanic acids, P.G. Melikov and L.V. Pisarzhevskiy formulated a series of regularities of their formation which, in the words of D.I. Mendeleyev, contributed to strengthening of the periodic system. However, it should be noted that, at the present level of our knowledge and with deeper study of the properties of these compounds, some conclusions offered by P.G. Melikov and L.V. Pisarzhevskiy obviously will be reexamined.

S.M. Tanatar has the credit for discovery of a number of molecular compounds of hydrogen peroxide with salts and organic bases. Among them are sodium monoperoxyhydrate trihydrate metaborate and urea peroxyhydrate, which now are produced on the multiton scale under the names "perborate" and "perhydrate," and are used as mild oxidizers in bleaching and dyeing both natural and synthetic fibers and also as initiators of some polymerization processes.

A special place is occupied by the work of A.N. Bakh, one of the founders of the peroxide theory of slow oxidation, which represents oxidation as a process, the first stage of which is the addition of molecular oxygen to the active molecule of the compound being oxidized, with the formation of an intermediate peroxide. Today, this theory is the basis of our concepts of biological oxidation processes.

P.G. Melikov, L.V. Pisarzhevskiy and A.N. Bakh, who worked during the Soviet era after the Great October Revolution maintained creative
groups in the institutes they directed, Georgian Institute of Chemistry, Ukrainian Institute of Physical Chemistry, Physical Chemistry Institute im. L.Ya. Karpov, which contributed to the further development of the chemistry of peroxide compounds. First and foremost, the studies of A.I. Brodskiy (student of L.V. Pisarzhevskiy) should be mentioned. He was the first to use the heavy isotope of oxygen to explain the mechanism of formation and decomposition of peroxide compounds. At the Physical Chemistry Institute im. L.Ya. Karpov, the school of I.A. Kazarnovskiy developed, the research of which dealt with the structure of a number of peroxide compounds of groups I and II of the periodic system.

The development of the chemistry of peroxide compounds was stimulated by both defense needs and the requirements of the national economy. The World War II German use of concentrated hydrogen peroxide to launch the Fau-2 rocket shells and as an oxidizer in the engines of the submarine fleet, and the later use by England and the USA in liquid rocket engines, the necessity of providing oxygen to people who had to be in air tight places isolated from the outside environment, for example, in submarines, the use of some peroxide compounds in portable oxygen generators and in pyrotechnics, the use of peroxides to extract uranium from ore concentrates and the necessity of explaining the role of the peroxides formed as a result of radiolysis on processes occurring in homogeneous nuclear reactors, the use of peroxides for production of some semiconductor materials, all advanced to the foreground the question of the need for more thorough study of inorganic peroxide compounds, first and foremost, hydrogen peroxide and peroxides of group I and II elements. Together with these problems of primary importance, problems arose in connection with the use of peroxides for the improvement of working and living conditions: the use of peroxides in personal mining safety equipment, in bleaching pulp, cellulose, soap, fats, oils, furs, cloth and synthetic fibers, for the production of foam plastic and porous concrete, for the preservation of foodstuffs and in baking, in the cosmetic industry, for the production of laundry powders, in medicine.
In the 1940s in our country, the scientific research and technological development front in the field of peroxides expanded, and considerable progress was achieved in both the theoretical and applied fields. This led to the creation of a quite powerful base for the production of hydrogen peroxide of any concentration, while it was previously produced almost exclusively in the form of a 3% water solution and was used only for medical purposes. This not only eliminated the lag in the field of industrial production of potassium superoxide, the basic component of means of air regeneration which was obtained by lend lease from the USA during the war, but a new compound was discovered, sodium superoxide (I.A. Kazarnovskiy), and its industrial production was developed.

The production of potassium and sodium superoxide raised a series of problems associated with a search for the best conditions of their utilization and the development of both a formula for regenerative means based on them and equipment for their more efficient use. In 1943, pioneered by S.Z. Makarov, the Laboratory of Peroxide Compounds was established at the Institute of General and Inorganic Chemistry. The basic problem of the Laboratory was to develop the scientific foundations of the regeneration of exhaled human air with peroxides. The Laboratory made a significant contribution to the solution of this problem: the optimum conditions of water vapor feed, which assist in the regenerative formation of superoxides, were established; the role of the intermediate products formed by the reaction of superoxides with wet carbon dioxide was explained; the reactivity of superoxides with other gaseous products of the vital activities of the human body (ammonia, hydrogen sulfide, carbon monoxide, methane, ethane) was studied; a new formula for means of regeneration was recommended.

However, the subject matter of the Laboratory of Peroxide Compounds was not limited to this field of study. Published in 1951-1952, i.e., 8 years after its founding, the first papers of the Laboratory [1-4] indicate that, together with study of the process of air regeneration with peroxides, the primary scientific area was based on the application of the learning of N.S. Kurnakov to the study of the solubility and fusibility of systems in mixed \( \text{H}_2\text{O}_2-\text{H}_2\text{O} \) solvent and characteriza-
tion of the solid phases formed by thermography. S.Z. Makarov and colleagues studied 11 systems of water solutions of hydrogen peroxide with the hydroxides of group I and II elements, with sodium and potassium carbonates and with urea, by the isothermal solubility method, with determination of the solid phase compositions by the "residues" method. The limits of thermal stability of the solid phases of these systems were determined by differential thermal analysis. All this permitted the development of efficient methods of synthesis of the peroxides of lithium, calcium, strontium, barium and zinc and sodium and potassium carbonate peroxyhydrates [5], which were produced as custom made reagents by individual inorganic peroxide production plants.

The individual isotherms of systems of water solutions of hydrogen peroxide with beryllium and magnesium hydroxides, sodium sulfate and sodium metasilicate were studied by I.I. Vol'nov, and those with cadmium, lanthanum, cerium and some rare earth element hydroxides, by S.Z. Markarov and L.V. Ladeynova. Since only the "residues" method was used for determination of the solid phase compositions, without involving other physical chemistry methods, the data obtained should be considered preliminary. This is particularly true with respect to the composition of rare earth element peroxide compounds.

K.Ye. Mironov [6] studied the phase diagrams of the binary systems \( \text{H}_2\text{O}_2-\text{H}_2\text{O} \) and \( \text{H}_2\text{O}_2-\text{C}_4\text{H}_10\text{O} \) (diethyl ether) and the ternary systems \( \text{H}_2\text{O}_2-\text{NaClO}_4-\text{H}_2\text{O} \) and \( \text{H}_2\text{O}_2-\text{LiClO}_4-\text{H}_2\text{O} \). It should be noted that the concept of the existence of the solid solutions \( \text{H}_2\text{O}_8-\text{H}_2\text{O}_2 \) and \( \text{H}_2\text{O}_2-\text{H}_2\text{O}_2.2\text{H}_2\text{O} \) was refuted by these investigations. This was extremely important for a decision on the possibility of storage of concentrated hydrogen peroxide solutions at below zero temperatures. At present, the area of study of the solubility and fusibility diagrams of systems with hydrogen peroxide is being successfully developed by T.A. Dobrynina et al [7]. In study of the systems \( \text{Rb}_2\text{CO}_3-\text{H}_2\text{O}_2-\text{H}_2\text{O} \), \( \text{Cs}_2\text{CO}_3-\text{H}_2\text{O}_2-\text{H}_2\text{O} \), \( \text{KOH}-\text{H}_2\text{O}_2-\text{H}_2\text{O} \), \( \text{RbOH}-\text{H}_2\text{O}_2-\text{H}_2\text{O} \) and \( \text{CsOH}-\text{H}_2\text{O}_2-\text{H}_2\text{O} \), a series of new compounds was discovered, which are the primary result of the molecular addition of \( \text{H}_2\text{O}_2 \) and are of well known interest to the explanation of the regularities of the substitution of water by hydrogen peroxide in crystal hydrates. The method of synthesis of lithium peroxide, de-
veloped earlier by T.A. Dobrynina, has been introduced into industry. Hydrogen peroxide solutions also were used by N.K. Grigor'yeva and K.I. Selezneva, as a medium for synthesis of some peroxo compounds of vanadium, niobium and tantalum. The method obtaining sodium and potassium orthoniobates and lithium metaniobate through the peroxyniobates, developed by K.I. Selezneva, is of interest.

Among the studies of the Laboratory of Peroxide Compounds, study of the reaction of nitrogen oxides with ozone, performed by T.I. Arnold under the direction of S.Z. Makarov, in order to find ways of synthesis of the higher oxides of nitrogen, occupies a somewhat special place. This area has not been properly developed and, evidently, more reliable methods of identification of the final reaction products should be involved here. For the majority of solid phases formed in the system mentioned above or synthesized preparatively, the limits of thermal stability were determined by differential thermal analysis. A substantial contribution to study of the thermal properties of alkali metal superoxides by this method was made by T.V. Rode [8]. All these data were correlated by I.I. Vol'nov [9], which permitted some conclusions to be stated as to the regularities of thermal decomposition of inorganic peroxide compounds, in their use as sources of chemically bound oxygen as a function of the nature of the bonds between the atoms of the elements which form peroxide compounds and various forms of molecular ions of oxygen or peroxy ligands. However, insufficient attention has been given to the thermochemical study of these compounds. Actually, only one study has been performed in the field of thermochemistry, by Yu.M. Kessler, which dealt with the heats of dilution of solutions of alkali metal chlorides and highly concentrated hydrogen peroxide at 0°C.

Study of the reactivity of alkali metal superoxides with wet carbon dioxide, in connection with the problem of air regeneration, was developed in the work of A.Kh. Mel'nikov and T.P. Firsova [10] and then by T.P. Firsova et al [11]. The reactions of sodium and potassium superoxides with water vapor at reduced temperatures, with carbon dioxide in the presence of water vapor over a wide temperature interval, as
well as of carbon dioxide with alkaline solutions of hydrogen peroxide were studied. A number of intermediate products of the reactions (peroxide hydrates and peroxocarbonates) were isolated, and some of their properties were determined. New methods of synthesis of sodium and potassium peroxodicarbonates and the acid salt of potassium peroxomonocarbonate were developed, and two patents \[11a\] were obtained for the method of production of alkali metal peroxocarbonates.

At the end of 1961, the Institute of General and Inorganic Chemistry convened the Second All-Union Conference on the Chemistry of Peroxide Compounds, in which approximately 300 representatives of a number of organizations participated. At this conference, which contributed to the coordination of research to a certain extent, 80 papers were given and published in a separate collection \[12\]. Based on the decisions of the conference, the subject matter of the Laboratory of Peroxide Compounds, Institute of General and Inorganic Chemistry, was expanded. Beginning in 1962, exploratory studies on the synthesis of new superoxides and ozonides and the development of new methods of synthesis of known compounds of this type were carried out on a broad front. Research on the kinetics of decomposition of a number of peroxide compounds and on the reactions of peroxides with hydroxides and salts in the solid state began to develop. There was some development of X-ray studies and, for study of a number of peroxide compounds, the use of such methods of study began as, for example, the isotope method, electron paramagnetic resonance and the crystal optic method.

Exploratory studies of new methods of synthesis of superoxides were carried out primarily in three areas: 1. study of the reaction of atomic hydrogen generated in a glow discharge with alkali and alkaline earth metal hydroxides; 2. study of the intramolecular oxidation-reduction reactions of molecular peroxide compounds with hydrogen peroxide; 3. study of the nature of the reaction products of peroxides with solutions of ozone in freons. In study of the reaction of atomic hydrogen with hydroxides, the possibility of the formation of KO₂, mixtures of sodium peroxide and superoxide and calcium and strontium peroxides was shown. Studies of the intramolecular oxidation-reduction
reactions of peroxide peroxyhydrates indicated the possibility of the formation of mixtures of sodium, calcium, strontium and barium peroxides and superoxides [13]. In studies of the reactions of lithium and magnesium peroxides and beryllium hydroxide suspended in freon-12 with dissolved ozone, the possibility of the formation of lithium and magnesium superoxides and beryllium peroxide, stable down to -35°C, was shown [14]. A sprayer method of laboratory production of cesium and rubidium superoxides also was developed [15].

A search for new methods of ozonide synthesis was carried out primarily by study of the reactions of ozone-oxygen mixtures with superoxides in a fluidized bed, and the reactions of 100% ozone with superoxide suspensions in freons.

As is known, in study of the reactions of ozone with solid anhydrous alkalis in a fixed bed at below zero temperatures, I.A. Kazarnovskiy et al determined that the red products formed are representatives of a new class of compounds, ozonides. The ability to form ozonides is characteristic of sodium, potassium, rubidium, cesium and ammonia. Because of the ability of inorganic ozonides to dissolve in liquid ammonia and because KOH and NaOH have extremely low solubility in this solvent, there is the possibility of extraction of nearly pure KO₃ and NaO₃ from ozonated alkalis. S.Z. Makarov and Ye.I. Sokovnin [16] showed that potassium ozonide can be produced by the reaction of an ozone-oxygen mixture with solid KOH, not only at below zero but at above zero temperatures. As a consequence of this, an efficient method was developed for the ozonation of solid powdered alkalis at 40°C in a fluidized bed produced by the flow of the ozone-oxygen mixture. The optimum conditions of extraction of the ozonide and its crystallization from an ammonia solution were determined by study of solubility in the KO₃-NH₃ system. S.A. Tokareva [17] studied the synthesis of sodium ozonide in greater detail, and she determined some of its properties.

T.I. Vol'nov, Ye.I. Sokovnin, S.A. Tokareva, V.V. Matveyev and M.S. Dobrolyubova [18] established the possibility of the production of alkali metal ozonides by the direct reaction of ozone with super-
oxides. This reaction proved to be extremely efficient in the synthesis of cesium and rubidium ozonides, which were obtained with a 95% content of the basic compound. Starting with the hydroxides, the preparations contain only 67% ozonide. This is because, in extraction of the ozonides from the ozonated hydroxide with liquid ammonia, the unreacted portion of cesium and rubidium hydroxides go into solution. The superoxides are practically insoluble in liquid ammonia. Jointly with S.A. Tokareva, a method of synthesis of potassium ozonide from potassium superoxide, which bypassed liquid ammonia extraction, was developed for the first time. For this purpose, the reaction was carried out in a freon-12 medium. The possibility of the formation of alkaline earth metal ozonides by the reaction of the powdered hydroxides at below zero temperatures, in a fluidized bed produced by the flow of the ozone-oxygen mixture or by the reaction of the peroxides of these elements with ozone in a freon-12 medium, also was demonstrated for the first time.

Some properties of alkali metal ozonides were studied in greater detail, and lithium and magnesium superoxides were synthesized for the first time. V.M. Bakulina [19] determined the crystal lattice parameters of sodium and cesium ozonides and lithium, magnesium, and tetramethylammonium superoxides. V.N. Belevskiy obtained electron paramagnetic resonance spectra of lithium, magnesium, calcium, and tetramethylammonium superoxides and the alkaline earth metal ozonides, and he determined the values of the g factor. V.I. Sokol determined the density and index of refraction of sodium, potassium, rubidium, and cesium ozonides, and he provided their refractometric characteristics. T.P. Firsova studied the reaction of potassium ozonide with water vapor and carbon dioxide.

In the fields of kinetics and reactivity of peroxides, the work performed by A.B. Tsentsiper et al [20], on the identification of the products formed at low temperature from \( \text{H}_2\text{O} \) and \( \text{H}_2\text{O}_2 \) vapors dissociated in a glow discharge, as well as work which dealt with the formation and decomposition of the peroxide compounds of calcium, strontium, and barium, thermal decomposition of lithium peroxide and the solid state reactions
between KO$_2$ and LiCl, KO$_2$ and K$_2$CO$_3$, and KO$_2$ and KOH should be noted. For study of some questions of the formation and decomposition of peroxide compounds, the isotope method was used, with the application of hydrogen peroxide synthesized from oxygen labeled water vapor dissociated in a glow discharge. $^{18}O$ enriched KOH and oxygen also were used.

The colleagues of the Laboratory of Peroxide Compounds, Institute of General and Inorganic Chemistry, have published 225 articles in 25 years. Together with the translation of the monograph of U. Shamba on hydrogen peroxide, edited by A.I. Gorbanev and K.Ye. Mironov, the publication of the collected proceedings of the Second Conference on the Chemistry of Peroxide Compounds [12] and two bibliographic indices [21, 22], the monographs of T.A. Dobrynina on lithium peroxide [23] and I.I. Vol'nov on peroxides, superoxides and ozonides of alkali and alkaline earth metals [24] were published.

In conclusion, we point out the necessity for the development of more modern methods of study of the nature of peroxide compounds of other elements, i.e., elements, the peroxide compounds of which are not of the ionic type. This obviously should be a basic area of study of the Laboratory in the next few years.
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