

Peroxides, Superoxides, and Ozonides of Alkali and Alkaline Earth Metals

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PLENUM PRESS • NEW YORK • 1966

Born in 1913, Il'ya Ivanovich Vol'nov is head of the laboratory of peroxide chemistry of the N. S. Kurnakov Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR in Moscow. He joined the Institute in 1939 and since 1949 he has authored more than 50 articles dealing with the chemistry of the inorganic peroxides, superoxides, and ozonides. Vol'nov served as editor for the proceedings of the 2nd All-Union Conference on the Chemistry of Peroxide Compounds, published by the Academy of Sciences in 1963. He was also editor of T. A. Dobrynina's monograph on *Lithium Peroxide*, published in 1964, and edited a bibliographical index covering the world-wide literature for the period 1956 to 1962 on the chemistry of peroxide compounds (other than hydrogen peroxide) published under the auspices of the library of the Academy of Sciences of the USSR.

ISBN 978-1-4684-8254-6

ISBN 978-1-4684-8252-2 (eBook)

DOI 10.1007/978-1-4684-8252-2

Library of Congress Catalog Card Number 66-22125

The original Russian text, first published for the N. S. Kurnakov Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR by Nauka Press in Moscow in 1964, has been corrected by the author for the English edition.

Илья Иванович Вольнов

**Перекиси, надперекиси и озониды
щелочных и щелочноземельных металлов**

**PEREKISI, NADPEREKISI I OZONIDY SHCHELOCHNYKH
I SHCHELOCHNOZEMEL'NYKH METALLOV**

**PEROXIDES, SUPEROXIDES, AND OZONIDES OF ALKALI
AND ALKALINE EARTH METALS**

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Softcover reprint of the hardcover 1st edition 1966

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Editor's Preface

Since the early 1930's, Soviet chemists have played a leading role in the study of unfamiliar oxidation state compounds of the peroxide, superoxide, and ozonide types. Interest in the alkali and alkaline earth metal derivatives is now widespread and diverse, and numerous practical applications of these compounds have evolved, ranging from their use as air revitalization materials in space cabins to their use in compounding semiconductor materials.

Professor Vol'nov is eminently qualified to write this monograph since for many years he has been a leading investigator and prolific writer in the field of peroxide, superoxide, and ozonide chemistry. He has succeeded in presenting a lucid and detailed discussion of past work, the present state, and the future potential of this area of unfamiliar oxidation state chemistry.

Of particular interest is Professor Vol'nov's extensive compilation of available thermodynamic, kinetic, and structural data for the alkali and alkaline earth peroxides, superoxides, and ozonides. In addition, he has reviewed the known methods of synthesis, as well as the practical applications for which these compounds are suited.

This monograph will be of interest and value to chemists, not only for the information it imparts, but equally for the information it does not impart, thereby illuminating the research paths and investigation which must be undertaken in order to increase our knowledge concerning the chemistry of this important class of chemical compounds.

Chemists studying inorganic free radical mechanisms will find much of significance in this work since nearly all the important free radical and ionic species of oxygen, namely OH, HO₂, HO₃, O₃⁻, O₂⁻, and O₂⁼, enter into mechanisms postulated for various reactions of these compounds. In Chapter IV, Professor Vol'nov has presented a concise and excellent compilation of the information available on the hydroperoxyl radical, HO₂.

The reader should keep in mind that the author has reported data as he has found them in the literature, and on the whole has limited critical discussion of reported data to information of which he or his colleagues have first-hand knowledge as a result of direct experimentation.

I express my thanks to Professor Vol'nov for his kind cooperation in the preparation of this English-language edition, and also thank Dr. J. Marriott, Mr. R. Uno, and Dr. A. Capotosto, Jr., for their valuable suggestions and critical review of the edited translation, and to Mrs. R. Hill who typed the manuscript of the English-language translation.

A. W. Petrocelli

Westerly, Rhode Island
July, 1966

Foreword

In recent years, a large number of articles and patents have been published dealing with improved methods for the synthesis and stabilization of hydrogen peroxide and its derivatives. The discovery of new inorganic and organic peroxide compounds has also been reported. The practical application of these compounds is continuously increasing and they are important in widely diversified areas of the national economy.

Much of the experimental material that has been published in various journals and in different languages has been summarized in monographs. Since 1951, several such monographs and reviews dealing mainly with hydrogen peroxide have been published abroad. However, much of the information accumulated in the last decade on production methods; properties and application of metal peroxides, superoxides, and ozonides; peroxides and their salts; peroxide complexes; and peroxyhydrates is not adequately discussed in these works.

A brief monograph by W. Wood,¹ published in 1954, gives only a summary description of the production methods, properties, and applications of hydrogen peroxide.

A monograph by W. Machu,² the first edition of which has been translated into Russian, was the most complete review available of the production methods, properties, and uses of hydrogen peroxide and its derivatives until the publication of

¹W.S. Wood, Hydrogen Peroxide, The Royal Institute of Chemistry, lectures, monographs, and reports, London (1954).

²W. Machu, Das Wasserstoffperoxyd und die Perverbindungen, 2nd edition, Springer Verlag, Vienna (1951).

a book written by W. Schumb, C. Satterfield, and R. Wentworth.³ The Machu monograph was a supplement to a previously published monograph by O. Kausch,⁴ which was more of a bibliography than a review. In his monograph, W. Machu was concerned mainly with hydrogen peroxide. Out of 400 pages, only approximately 100 pages are devoted to peroxide compounds other than hydrogen peroxide. Moreover, many of the data are obsolete. One of the main shortcomings of the monographs written by Machu and Kausch is that the authors are not specialists on peroxide compounds. For this reason they did not present a critical evaluation of the data, nor did they present a creative approach in explaining the theoretical foundations underlining the developments in our knowledge of the chemistry of peroxide compounds.

A discussion of oxygen, ozone, and hydrogen peroxide by P. Pascal is found in the 13th volume of a handbook of inorganic chemistry published in 1960.⁵ All aspects of the chemical and physical methods concerning qualitative and quantitative analysis of these substances are thoroughly reviewed in the 6th volume of a handbook of analytical chemistry published in 1953.⁶ A review concerning inorganic peroxides has been recently published by N. Vannerberg in which the structure of these compounds is stressed.⁷

The aforementioned monograph by W. Schumb et al., the Russian translation of which appeared in 1958, covers more than 2500 literature sources published up to mid-1954. However, it is almost completely dedicated to hydrogen peroxide. Other inorganic peroxides, the industrial significance of which is just as important and which are of considerable scientific interest, are treated in a brief space of approximately 30 pages, and the discussion of these compounds is limited to information drawn from only 123 literature sources, nine of which appeared in 1953.

³W. Schumb, C.N. Satterfield, and R.L. Wentworth, *Hydrogen Peroxide*, Reinhold, New York (1955).

⁴O. Kausch, *Das Wasserstoffsperoxyd*, Knapp Verlag (1938).

⁵P. Pascal, *Nouveau Traité de Chimie Minérale*, Vol. XIII, Paris (1960).

⁶*Handbuch der analytischen Chemie*, Vol. VI, Springer, Berlin (1953).

⁷N.G. Vannerberg, *Progress in Inorganic Chemistry*, Vol. 4, Interscience, New York (1962).

To fill the gap, the author of this monograph has systematized and summarized information from Soviet and foreign chemical journals and patents published from 1950 through 1962. This monograph is devoted to one of the most important branches in the chemistry of inorganic peroxide compounds, namely, the synthesis and properties of peroxides, superoxides, and ozonides of alkali and alkaline earth metals. The alkali and alkaline earth peroxides and superoxides are already economically important compounds which are widely used in various branches of our national economy, as well as that of foreign countries. The alkali and alkaline earth ozonides have only recently been produced in the USSR and they are undergoing detailed and extensive studies.

Because of the difference in the structure and properties of the many types of inorganic peroxide compounds, it is difficult to establish specific regularities describing the formation of peroxide compounds by all of the elements of the periodic table until the available information concerning the separate groups is systematized. For this reason, I have decided to cover in this monograph only peroxide compounds formed by alkali and alkaline earth metals, i.e., simple peroxide compounds. A presentation of the information that has been uncovered in the last decade on the synthesis and properties of peroxides, superoxides, and ozonides of the alkali and alkaline earth metals will serve to establish for the reader a good picture of our present state of knowledge concerning peroxide compounds. Complex peroxide compounds will be discussed in a separate study which is being prepared by the author. A significant part of this review is dedicated to research completed in the Laboratory of Peroxide Compounds of the N.S. Kurnakov Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR. Extensive use has also been made of the bibliographical index⁸ published by the author.

I. I. Vol'nov

⁸Chemistry of Peroxide Compounds (Except Hydrogen Peroxide), Bibliographical Index of Domestic and Foreign Literature, 1956 — 1962, Library of the Academy of Sciences of the USSR (1963).

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