

A. N. BAKH'S WORK IN CHEMISTRY, AND HIS ROLE IN
THE DEVELOPMENT OF SOVIET PHYSICAL CHEMISTRY

A. N. Frumkin

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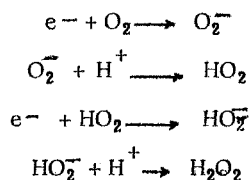
The subject matter of my paper is somewhat more restricted than its title would suggest. My main object is to trace the influence of A. N. Bakh's concepts of the mechanism of oxidation processes on the development of physicochemical investigations in this field and to compare his views with the results obtained more recently.

Bakh's first main postulate – which he stated sixty years ago [1] simultaneously with the German chemist Engler – was that an oxygen molecule O_2 does not immediately split into atoms when it enters into a chemical reaction. In the initial stages of its transformation these atoms remain linked though a single valence. It follows that the primary oxidation products should be peroxides. This conclusion, however, is still inadequate for the explanation of the phenomena observed. The formation of peroxides in oxidation reactions is often accompanied by the oxidation of other substances, which would not themselves react with oxygen under the given conditions. For example, according to Hoppe–Seyler [2], oxidation of the hydrogen of "palladium hydride" by molecular oxygen may be accompanied by vigorous oxidation reactions, indigo being converted into isatin, benzene into phenol, etc. These phenomena cannot be explained by the action of hydrogen peroxide – the final product of the oxidation of the atomic hydrogen present in the palladium – because hydrogen peroxide is not a sufficiently powerful oxidizing agent and does not undergo the reactions described. Bakh therefore proposed that, when oxidized, "atomic hydrogen can give not only hydrogen peroxide, but also still higher peroxides". This quotation from Bakh's classical paper is almost verbatim, but the terminology has been somewhat modernized: Bakh speaks not of atomic hydrogen, but of "hydrogen at the moment of its liberation", and he refers to H_2O_2 as "hydrogen dioxide", which is no longer in accord with usage.

Bakh's concepts, therefore, can be summed up in two main theses: 1) in the attachment of an oxygen molecule to a molecule of the substance undergoing oxidation, a linkage between the O atoms is preserved; and 2) the primary oxidation product is a "higher" peroxide, which differs from the usual stable peroxides. Bakh considered that the higher peroxide of hydrogen was H_2O_4 , consisting of a chain of four oxygen atoms with a hydrogen atom at each end. I shall return later to the question of the structure of the higher peroxide of hydrogen; at the moment I wish to indicate how the two main theses of A. N. Bakh became modified in the subsequent period.

Among the autoxidation processes examined closely by Bakh in his early investigations, the oxidation of metals, e.g., zinc or lead, by atmospheric oxygen in presence of water with simultaneous formation of hydrogen peroxide was of great importance from the point of view of reaction mechanism. We now know that in these reactions the principal role of the metal is that of electron donor: metal atoms, by losing electrons which attach themselves to oxygen, are transformed into the corresponding ions. The reaction addition of electrons to O_2 can be effected in a more direct way if conditions are created under which the whole process is limited to what we may call "the oxidation of an electron". This is realized in the electroreduction of oxygen at a metal cathode; for reasons that we shall not consider here, it is best to use a mercury cathode for this purpose. As a result of numerous investigations – particularly those of Soviet electrochemists, among which V. S. Bagotsky deserves special mention – the mechanism of the electroreduction of oxygen at a mercury cathode

can be considered to be completely elucidated; the process can be broken down into the following stages (e^- denotes an electron):



It will be seen that the primary reaction product is the species O_2^- . This combines with a hydrogen ion to give HO_2 , i.e., into an unstable intermediate compound, the monomer of the higher peroxide of hydrogen discussed by A. N. Bakh. By accepting a second electron, HO_2 passes into the HO_2^- anion of hydrogen peroxide, which passes further into a hydrogen peroxide molecule H_2O_2 , i.e., stable products in which, however, the bond between the two oxygen atoms is preserved. At other cathodes, e.g., platinum, the electron and hydrogen ion do not appear to add to different species, but first combine to give H atoms, which give HO_2 with O_2 ; this is still near to A. N. Bakh's concepts. Rupture of the bond between the O atoms, which results in the conversion of hydrogen peroxide into water, occurs only under much more vigorous conditions, and in the electrochemical reaction is possible only when the potential of the cathode is displaced to more negative values. Hence, this simple low-temperature reaction in which an oxygen molecule takes part is precisely in accord with the scheme proposed by A. N. Bakh.

Let us now examine the reaction of molecular oxygen in oxidation processes occurring at somewhat higher temperatures, e.g., the oxidation of hydrocarbons, in which oxygen acts on substances which, unlike an electron have no free valence. Clarity was introduced into these matters by the work of N. N. Semenov and his school. Even in 1934, in his monograph "Chain Reactions" N. N. Semenov wrote: "I wish to show that our chain theory of oxidation may be regarded as the logical development of classical theories of oxidation resulting from the consideration of . . . new facts that have emerged concerning the oxidation of gases and vapors."

I give here the scheme for the oxidation of the hydrocarbon RH in the form in which it is given by N. M. Emanuel and coworkers [3], omitting a few of the details and discussing only its main features. $R^\cdot$ here indicates a hydrocarbon residue, i.e. a free radical, and the dot denotes a free valence.



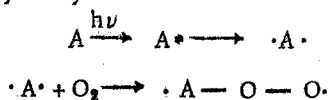
Our main interest lies in reactions (1) and (2). As a result of (1) the free radical $R^\cdot$ combines with O_2 molecule with formation of an $RO_2^\cdot$ radical - an analog of A. N. Bakh's higher peroxide. In the reaction (2) this higher peroxide passes into the relatively stable hydroperoxide ROOH. In these schemes something essentially new has appeared, thus vindicating Bakh's statement twenty years ago at a conference held on the occasion of the fortieth anniversary of the Bakh-Engler peroxide theory [4]: ". . . it is my hope that a new development in the peroxide theory will spring from chemical physics and provide an explanation for all the experimental facts . . .". We shall now see what this new development is. The above scheme indicates that the oxygen in reaction (1) does not add to the original hydrocarbon molecule RH, but to its scission product, the radical $R^\cdot$. For the reaction to go, it is essential that these active radicals should be formed in sufficient quantity. They are generated initially in the reaction (a), in which the original hydrocarbon is oxidized. This reaction, however, requires a considerable activation energy, and it rarely occurs; it is necessary only for the initiation of the chain. Subsequently, active species are provided by the chain process itself, as can be seen from reactions (2) - (5). Special significance for the kinetics of the process is to be found in stage (3), in which two active species are formed: branching of the chain occurs so that the whole process is autoaccelerating.

Here we give only the stages leading to the formation of the alcohols ROH by mechanism (4); the reaction actually goes further with formation of ketones and acids. N. M. Emanuel was able to confirm the proposed scheme with the aid of some shrewd experiments; in particular, it was found that the rate at which the final reaction products accumulated bore a simple relationship to the concentration of peroxides at each moment of the process. The important point for us is that in the interpretation not only of the mechanism, but also of the kinetics of oxidation reactions of hydrocarbons on the basis of Semenov's chain theory, all the essential principles underlying Bakh's views were preserved. This enabled the authors of the papers that I have cited to conclude that "A. N. Bakh's peroxide theory still, at this present time, is the operative theory for the explanation of the kinetics and chemistry of the oxidation of hydrocarbons."

Active species arising by the decomposition of a peroxide[reaction (3) in the scheme given above] ensure the continuation of the oxidation reaction. However, if a sufficiently unsaturated, e.g., dienic, hydrocarbon is oxidized, these active species may act as initiators also for polymerization reactions. As a result, there is a close relationship between oxidation and polymerization reactions, a relationship that has been elucidated as a result of many years of investigation by S. S. Medvedev and his coworkers and can be understood only when the part played by the intermediately formed peroxy compounds is taken into account.

Chain theory has greatly extended the scope of the possible application of A. N. Bakh's concepts in the interpretation of oxidation processes. However, as Bakh himself emphasized, the formation of unstable and stable peroxides can occur and have a decisive significance also in the case of oxidation processes which do not have a chain character. This occurs, for example, in the formation of triphenylmethyl peroxide, which was discussed frequently by Bakh and which probably proceeds by a scheme analogous to that cited at the beginning of this paper. As Frumkin and Burshtein [5] have shown, short-lived peroxide forms arise also in the simple process of absorption of oxygen on the surface of activated carbon.

Up to now we have considered the part played by peroxides in oxidation reactions in which the process is possible as a result of the utilization of the energy of an electric field or of the thermal motion of the molecules. An important group of oxidation processes is formed by processes proceeding under the action of light, the mechanism of which has been the subject of particularly profound study in our country by A. N. Terenin and his students. In this case also, the ideas of A. N. Bakh on the parts played by active peroxy compounds and the ways in which they may be formed were frequently applied and simultaneously acquired new formulations. By way of example I will refer to one of the numerous schemes of photooxidation reactions given in Terenin's book "Photochemistry of Dyes":



In absorbing a light quantum, the molecule of the aromatic compound A passes into the excited state A^* and further, by electronic rearrangement, into a diradical with two free valences $\cdot A \cdot$. This last species combines with an oxygen molecule and gives the unstable peroxide $\cdot A - O - O \cdot$, which by collision with another A molecule can give up its excess of energy and pass into the chemically isolable peroxide AO_2 or initiate a chain oxidation reaction.

The above discussion indicates the significance of the suggested existence of higher peroxy compounds for the interpretation of the mechanism of oxidation reactions on the basis of A. N. Bakh's theory. The simplest member of this class of compounds is the monomeric form of the higher peroxide of hydrogen HO_2 , which is formed as an intermediate product in solution or in the gas phase in various oxidation reactions. Special importance has recently been acquired by the theory of intermediate HO_2 formation in the interpretation of processes occurring in aqueous media under the action of ionizing radiations. The substance HO_2 has not yet been isolated in the individual state, and it probably cannot be isolated because of its instability. However, x-ray structure analysis has shown that the higher oxides — the so-called superoxides — of the alkali metals, which have the chemical composition of MO_2 and are quite stable in the solid crystalline state, contain O_2^- ions in their lattices, these being the ions that I have already mentioned in connection with the mechanism of the electroreduction of oxygen. These oxides, therefore, must be regarded as salts derived from the unstable peroxide HO_2 . For our information on this important and interesting group of compounds we are indebted mainly to I. A. Kazarnovsky, whose profound investigations (carried out in part in collaboration with J. D. Bernal) made a considerable contribution to the elucidation of the structures of crystalline

peroxides and superoxides. By synthesis under high pressure, I. A. Kazarnovsky and G. P. Nikolsky have obtained a new important member of this class – sodium superoxide NaO_2 – which has been found to be a valuable air-regeneration agent. More recently, I. A. Karnovsky has succeeded in obtaining even more highly oxidized products of the type of potassium ozonide KO_3 , whose interesting properties, however, I cannot discuss here.

As already stated, A. N. Bakh suggested that two unsaturated HO_2 radicals combine with formation of a molecule of hydrogen tetroxide H_2O_4 , and he attempted to confirm this suggestion by various experimental results. Thus, in the decomposition of KO_2 with dilute sulfuric acid with efficient cooling, Bakh obtained a solution which in permanganate titration yielded much more oxygen than would be expected for a solution of ordinary hydrogen peroxide. Bakh considered that this solution contained the hypothetical tetroxide H_2O_4 [6]. Various analogous suggestions were made also by later investigators, but no unequivocal proof of the existence of aqueous H_2O_4 solutions of appreciable concentration and stable at ordinary temperatures has yet been obtained. The nearest approach to the solution of the problem of the preparation of H_2O_4 is probably that of Kobozev, Nekrasov, and Eremin [7], whose work was published at the end of last year. Further information about the method was communicated quite recently in a paper by I. I. Skorokhodov read in the Chemistry Department of the Moscow State University. The authors bombarded a film of liquid ozone at -195° with atomic hydrogen. The blue color disappeared and a glassy substance was obtained which decomposed when heated to -55° with liberation of oxygen and formation of an aqueous solution of hydrogen peroxide. For each mole of H_2O_2 formed, one mole of oxygen was liberated, which indicates that the original substance was very probably of the composition H_2O_4 . In the author's opinion, under other conditions of formation of such "glassy substances", they may contain frozen monomer – the free radical HO_2 .

Oxidation reactions of organic compounds with atmospheric oxygen lie at the basis of processes for the preparation of synthetic fats, acetic anhydride, and other valuable products; they occur spontaneously in the fading of dyes. We meet these same reactions in the working of the gasoline engine of an automobile or aircraft. The correct understanding of the mechanism of oxidation processes, and in particular of the part played by peroxides in these processes, is therefore of great importance for the improvement of the conditions under which important technological processes occur, and it can result in the discovery of new ways of bringing these processes about, as is clear from N. M. Emanuel's recent work.* An interesting example of a technological process in which valuable products are obtained through the intermediate formation of a peroxide is the preparation of phenol and acetone by the decomposition of "cumene hydroperoxide", which is prepared by air-oxidation of cumene. In describing this method, B. D. Kruzhalov and P. G. Sergeev justifiably state that the process proceeds "in complete accord with the autoxidation theory advanced more than fifty years ago by A. N. Bakh" [9].

I have attempted to give a brief characterization of the development of ideas on the mechanism of reactions in which oxygen part – the essence of the peroxide theory of oxidation as applied in modern chemical kinetics, inorganic chemistry, and chemical technology. In so doing, without, I consider giving any unfair treatment, I have referred mainly to the work of Soviet investigators. Such concentration of these investigations in our country is not, of course, an accident, but a direct reflection of the enormous influence of A. N. Bakh on the development of Soviet chemistry.

Bakh's role as an initiator of physicochemical investigations was also very great. The L. Ya. Karpov Chemical Institute, which was originally the Central Chemical Laboratory of the Supreme Council of the National Economy and was founded jointly by A. N. Bakh and L. Ya. Karpov in 1918, is the largest (and for some years the only) center for physical chemistry in our country. The investigations of the Karpov Institute have made important contributions to such important branches of physical chemistry as the structure of matter, the physical chemistry of polymers, kinetics and catalysis, electrochemistry, theory of solutions, surface phenomena, radiation chemistry, and theory of the solid state, contributions of such significance that would be difficult to overestimate them. Various problems of great practical importance have been solved in the Karpov Institute, and this has helped greatly in the development of our chemical industry and in the strengthening of the defenses of our Fatherland.

A. N. Bakh possessed in high degree the ability to attract youth and to kindle and maintain its enthusiasm. From the very start of the activities of the Karpov Institute, he built up a group of young physical chemists who

* A review of the present position of the question of the structure and properties of organic peroxides has been given by A. Rieche [8].

later had considerable influence on various branches of this science. He very easily and rapidly oriented his ideas, even in branches of knowledge that were remote to him. With an approach that was just as kind as it was correct, he was able to appreciate the significance and future prospects of various lines of work, which enabled him to render friendly active assistance not only to the young scientists who had the good fortune to work with him in the Karpov Institute, but also to many others, now famous Soviet chemists.

In conclusion, in the name of the generation of Soviet physical chemists that stepped into the scientific arena shortly after the October Revolution and to which I myself belong, I should like to make a grateful tribute to this great man and great scientist.

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