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Thomas Bayley Assoc. R.C.Sc.I.

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XVIII. *On Catalysis, and the Nomenclature of Oxides.* By THOMAS BAYLEY, Assoc. R.C.Sc.I., Demonstrator of Practical Chemistry, Analysis, and Assaying in the Mining School, Bristol*.

AMONG the most remarkable, and at first sight the most inexplicable, of the heterogeneous class of reactions known as catalyses are the decompositions undergone by hydrogen peroxide in contact with certain substances. But on further examination these phenomena afford us the means of explaining and differentiating a considerable number of similar reactions and of effecting a classification of them. As is well known, hydrogen peroxide, although one of the least stable of well-defined compounds when in the concentrated form, becomes when diluted, especially in the presence of acids, much less subject to decomposition.

A solution of peroxide of hydrogen, sufficiently dilute to remain unaffected for a considerable time when mixed with dilute solution of sodic hydrate, may be used effectively in the preparation of the peroxides of several metals. If to a solution of a cobalt salt, sodic hydrate and then hydrogen peroxide be added in the cold, the hydrate of cobalt at first precipitated becomes rapidly blackened, and a hydrated peroxide of variable composition is produced. Almost immediately a rapid evolution of oxygen takes place; and before long the whole of the excess of peroxide of hydrogen is decomposed, the cobalt peroxide, however, remaining unchanged. Under similar circumstances salts of lead and manganese give the same reaction, namely the formation of a dark-coloured peroxide and the decomposition of the excess of hydrogen peroxide. With copper the effects are somewhat different: on the addition of the hydroxyl the suspended blue hydrate of copper assumes a transient yellowish-red colour, but almost immediately resumes its original appearance, while the evolution of oxygen proceeds as in the former cases. Nickel, although possessing properties remarkably resembling those of cobalt, under the influence of the mixture of soda and hydroxyl is not peroxidized; the suspended green hydrate is permanent, and the liquid retains for a long time the properties of a solution of hydrogen peroxide. But although the latter has not the power of peroxidizing nickel salts, the hydrated peroxide of nickel, formed by other means, effects almost as readily as does the corresponding cobalt compound the destruction of hydroxyl. It is this difference between the behaviour of nickel and cobalt that affords the key to these remarkable phenomena. It is evident, and it

* Communicated by the Author.

is proved by experiment, that a small quantity of cobalt peroxide can effect the decomposition of an unlimited amount of hydroxyl, time being, of course, an important factor. On the other hand, the amount of hydroxyl destroyed by the nickel compound is simply that required for its own decomposition.

The causes of the resolution of hydrogen peroxide into water and oxygen by contact with these peroxides may be due, not to any opposite polarity of the two oxygen atoms, contained one in the metallic oxide and the other in the hydroxyl, which coalesce to yield a molecule of oxygen, but simply to the presence of a *strain* in the two reacting molecules. These *oxides*, water and cobalt or nickel oxide, are compounds in which the attractions are, as it were, evenly balanced, the attraction of the metal, or hydrogen, being satisfied by the counteracting atom of oxygen; and the fact that special means, such as the employment of powerful oxidizers, must be taken to introduce additional oxygen into the molecule, justifies the view that the latter is held there by a comparatively weak affinity—and that the condition of this extra oxygen is such, that when in the presence of a foreign body similarly constituted, for example hydroxyl, there results an effective outward strain. The affinity between the extra atoms of oxygen in the two compounds being greatest, they coalesce to form oxygen, leaving the metallic oxide and water. Cobalt, however, has a greater affinity for oxygen than has nickel; and while the cobalt oxide thus formed becomes immediately reoxidized by the excess of hydroxyl, nickel once reduced is not further acted upon. This difference in the deportment of the two metals confirms the view that catalysis is due to a series of molecular decompositions and reformations of the catalyzing body.

The mutual decomposition of hydroxyl and silver oxide closely resembles that between nickel peroxide and the same body. For although the silver compound is not a *peroxide* in the ordinary sense, the ease with which it is reduced by heat and by comparatively weak reducing agents shows that its oxygen is held by a weak attraction; and when it is in contact with hydroxyl, there is a tendency for the oxygen in the silver oxide and the second loosely combined oxygen atom in the hydroxyl to unite. The metallic silver thus produced is not reoxidized; and the action is therefore not continuous. When hydroxyl acts upon suspended copper hydrate, the first product is a yellowish-red substance, probably a peroxide, of transient existence, which disappears as soon as the catalysis commences, and is never afterwards visible. The action, although differing from that of cobalt in that there is no final production of a peroxide, resembles it in the essential fact of

consisting of a series of decompositions and reformations. It is therefore a catalysis. Hydrated sesquioxide of iron and hydrate of zinc have no action upon dilute hydrogen peroxide. We may therefore argue from this, as from its other properties, that sesquioxide of iron is not a *peroxide* in the sense in which the term is used in this paper, namely as denoting an oxide in which one or more of the atoms of oxygen are held in such a way as to have an outward strain in presence of hydroxyl or a similar body. This definition being accepted, the sesquioxide of iron must be regarded as the *oxide* of iron, the term protoxide being reserved for the lower compound. In the same way we should speak of Ni_3O_5 as a *peroxide* of nickel, of NiO as the oxide, and of some lower, at present unknown, compound as the protoxide. Our view of catalysis being as above stated, it is easy to explain the action of nickel or cobalt upon hypochlorites. These are capable of peroxidizing nickel; and this constitutes the difference between the action of the latter with them and with hydroxyl. The cycle of operations can be performed and catalysis established. A further explanation of the difference between the action of copper and of cobalt with hydroxyl suggests itself. The change constituting the cycle in the case of copper is from hydrated oxide to an unknown peroxide and back again; and since the final moment of catalysis, that in which the last hydroxyl disappears, must consist in the reduction of the copper to the lower of the two limits between which the action alternates, we find oxide of copper and water as the final products. In the catalysis of hypochlorites by cobalt, the two limits are probably tricobaltic pentoxide (Co_3O_5) on one side, and cobaltic dioxide (CoO_2) on the other; since (Co_3O_5) has been shown to be the result of the reaction.

The decompositions of dilute hydroxyl are very distinct from those which occur to the concentrated compound on contact with finely divided silver, gold, or platinum, with various oxides (as, for instance, with nickel oxide), and with many other bodies. We cannot suppose that finely divided gold or platinum is acted upon by hydroxyl; the action is probably connected with some power possessed by the surface, and especially by edges and by fine particles, of these metals to attract oxygen. In concentrated hydroxyl at ordinary temperatures the oxygen is quivering on the verge of liberation, and such a surface action is sufficient to induce decomposition.

The phenomena of catalysis thus group themselves into physical and chemical. Physical catalyses are those in which the catalyzing body, often an inert substance chemically, remains unchanged and exerts a surface action purely phy-

sical. Chemical catalyses are those which consist of a true chemical action; and are distinct from ordinary chemical actions only in this, that one of the bodies remains in the same state after the action as it was before it.

According to this view of catalysis and of the constitution of oxides, we retain the old terms *protoxide*, *oxide*, and *peroxide* (distinct from acid anhydride) with somewhat different meanings. Oxide of copper (CuO) is no longer the protoxide but the oxide; the unknown yellow body is the hydrated peroxide, while Cu_2O is the protoxide. In like manner the oxygen atoms which in peroxides are held with the least affinity may be called the *peroxygen* atoms, and those which are the last to leave the compound may be called the *protoxygen* atoms. This nomenclature is distinct from the ordinary one founded upon the use of the suffixes "ic" and "ous," and of numerical prefixes, and need in no way interfere with it. Being founded strictly upon the chemical behaviour of the compounds and not upon the constitution of their molecules, it possesses evident advantages; but the other terms have important uses, and might with advantage be retained in the majority of instances.

XIX. *Crystallography of the Nitrosoterpenes of Dr. Tilden.*

By N. S. MASKELYNE, F.R.S.*

[Plate VII. figs. 1-6.]

THE varieties of nitrosoterpenes obtained in crystals by Dr. Tilden belong to two crystalline types. The first includes the substances formed (a) from ordinary turpentine, (b) from French turpentine, (c) from juniper turpentine. To the second type belong the substances obtained from the oils of orange, of bergamot, and of caraway.

I. *First group.*—The crystals of nitrosoterpene produced in different ways from the American oil of turpentine have already been described in connexion with Dr. Tilden's notice of the substances in the Journal of the Chemical Society, June 1875. They were of two kinds, differing in habit—the one being twinned on the plane 001, and the other not evincing any twin habit. The crystals obtained from French oil of turpentine and from juniper oil are very dissimilar in appearance to those made from the American oil; but a goniometrical study of them proves that they belong to the same crystalline type with those previously investigated. The crystals of the latter kinds furnished me by Dr. Tilden presented considerable difficulty under measurement, since certain of the faces are rounded; and from their being very minute and in-

* Communicated by the Crystallogological Society.