CLXVIII. THE FORMATION OF HYDROGEN PEROXIDE IN CATALYTIC DEHYDROGENATION.

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ACCORDING to Wieland's dehydrogenation theory [1922, 1, 2; 1932] enzymic oxidation is effected by removal of hydrogen, the function of the enzyme being to activate certain hydrogen atoms of the substrate molecule and thus render them capable of removal by a hydrogen acceptor (oxygen, methylene blue, quinones and other substances). This theory is strongly supported by experimental evidence, perhaps the most important being the fact that the dehydrogenating enzymes exhibit marked specificity towards substrates but no specificity towards hydrogen acceptors. According to Wieland, catalytic dehydrogenation, such as that effected by the metals of the platinum group, is strictly analogous to enzymic dehydrogenation and is dependent on the activation of certain hydrogen atoms in the molecules by the catalysts and the subsequent removal of these hydrogen atoms by a hydrogen acceptor. It has been postulated that the hydrogen activations brought about by the dehydrases and the metallic catalysts are effected by the enzyme or catalyst forming a molecular complex with the substrate molecule resulting in the weakening of the bonds holding certain of the hydrogen atoms. The combination of hydrogen and oxygen, catalysed by the metals of the platinum group, is effected in a similar manner; a catalyst-hydrogen complex is first formed resulting in the activation of the hydrogen, followed by its subsequent removal from the complex by the oxygen.

In aerobic dehydrogenations with both enzymes and catalysts the formation of hydrogen peroxide is demanded, the first step being the addition of the activated hydrogen atoms to the double bond of the oxygen molecule

In the aerobic dehydrogenations of xanthine and aldehydes in presence of their respective dehydrases it has been proved that hydrogen peroxide is formed [Wieland and Rosenfeld, 1929; Wieland and Macrae, 1930], and it is therefore probable that it is formed in all enzymic aerobic dehydrogenations; hydrogen peroxide is also an intermediate in the catalytic combination of hydrogen and oxygen [Hofmann, 1922]. The aim of this investigation was to establish that hydrogen peroxide is formed in catalytic dehydrogenation, as is demanded by the dehydrogenation theory. The catalytic dehydrogenation of alcohols to aldehydes [compare Wieland, 1912], which in itself is perhaps the most important dehydrogenation, has been investigated.

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Difficulties in proving the intermediate formation of hydrogen peroxide in the aerobic dehydrogenation of alcohols were to be expected for the following reasons. Palladium black and the other catalysts of the platinum group decompose hydrogen peroxide very rapidly into water and oxygen [Wieland, 1921]. It is very probable that hydrogen peroxide might compete successfully with oxygen as hydrogen acceptor in the dehydrogenation of further quantities of alcohol. Finally hydrogen peroxide is capable of combining with aldehydes [Wieland and Wingler, 1923]. In recent years, however, cerous hydroxide has proved a valuable reagent for the detection of small quantities of hydrogen peroxide [Wieland and Rosenfeld, 1929; Wieland and Macrae, 1930; Macrae, 1931], and it seemed possible that it might be successfully employed in this investigation. When a suspension of cerous hydroxide is treated with hydrogen peroxide the suspension changes from white to a deep yellow-orange due to the formation of the very sparingly soluble ceric hydroperoxide

The ceric hydroperoxide may be centrifuged down and estimated iodimetrically; after some experience it is possible to estimate the amount of ceric hydroperoxide from the depth of the yellow coloration. Using cerous hydroxide $10^{-6} M$ or even less of hydrogen peroxide may be detected and $10^{-5} M$ may be determined with considerable accuracy.

Preliminary experiments on the catalytic combination of hydrogen and oxygen in presence of cerous hydroxide were carried out. Ceric hydroperoxide was formed and the observations of Hofmann [1922] have thus been verified. As was to be expected the ceric hydroperoxide formed represented only a very small percentage of that demanded by theory, the greater part of the hydrogen peroxide being decomposed or reduced to water before it could combine with the cerous hydroxide.

When aqueous solutions of ethyl alcohol and methyl alcohol containing cerous hydroxide in suspension were shaken with air in presence of a specially prepared palladium black, a small yield of ceric hydroperoxide was produced, thus demonstrating that hydrogen peroxide is formed in the aerobic catalytic dehydrogenation of these alcohols to the corresponding aldehydes. The reaction therefore proceeds according to the equation:

This provides substantiation of the Wieland dehydrogenation theory. The catalytic dehydrogenation of other compounds will be investigated.

EXPERIMENTAL.

Preparation of the catalyst. Palladium black has been used throughout this investigation. The method of preparation employed was that of Willstätter and Waldschmidt-Leitz [1921]. It was found that immediately after preparation the catalyst was quite unsuitable for this work, being much too active. The palladium was therefore stored in a desiccator over potassium hydroxide and sulphuric acid for about 2 months; after that time the activity of the catalyst had fallen very considerably, but it still retained the power of catalysing the combination of hydrogen and oxygen and it also slowly effected the aerobic dehydrogenation of methyl alcohol and ethyl alcohol. Different preparations varied greatly in their suitability for this investigation.

Determination of ceric hydroperoxide. Ceric hydroperoxide may be estimated with considerable accuracy by colorimetric comparison with standard sus-

pensions, but confirmation by a titration method was thought desirable. The method described for the determination of ceric hydroperoxide by Wieland and Macrae [1930] requires catalase and therefore is not convenient. It was found, however, that this compound may be directly titrated iodimetrically, and although absolute accuracy is not obtained by this method, it was considered sufficiently accurate for these experiments.

When ceric hydroperoxide is decomposed by mineral acids it is converted into ceric salt and hydrogen peroxide (equation i). Iodimetric determination of the ceric salt and hydrogen peroxide is unfortunately impossible because a rapid interaction occurs between the ceric salt and the hydrogen peroxide resulting in the liberation of oxygen (equation ii).

When, however, the ceric hydroperoxide is decomposed by very dilute acetic acid in presence of potassium iodide, the liberation of oxygen is almost completely suppressed, and if the liberated iodine is immediately titrated with sodium thiosulphate fairly consistent results are obtained. Under these conditions it is only the ceric salt which liberates iodine; the liberation of iodine by hydrogen peroxide is very slow and may be ignored. 0.02 *M* cerous sulphate (2 cc.) was treated with 0.16 *M* sodium borate (2 cc.) and to the resulting suspension of cerous hydroxide 0.0079 *M* hydrogen peroxide (1 cc.) was added. After 10 minutes the yellow coloured mixture of cerous hydroxide and ceric hydroperoxide was centrifuged down, washed once with water and suspended in water (2 cc.) containing a few drops of *M* potassium iodide. *M* acetic acid (0.5 cc.) and two drops of a starch indicator solution were added, and the mixture was stirred. The suspension dissolved, and after 30 seconds the solution was titrated with 0.01 *N* sodium thiosulphate. In 6 experiments the titrations were 0.52, 0.50, 0.58, 0.56, 0.48 and 0.52 cc. of 0.01 *N* sodium thiosulphate—the theoretical value being 0.53 cc.

The catalytic combination of hydrogen and oxygen. 0.02 *M* cerous sulphate (2 cc.) was added to several aggregates of palladium black (about 50 mg.) in the vessel (100 cc.) of a shaking apparatus. After about 1 minute 0.16 *M* sodium borate (2 cc.) was added, which precipitated cerous hydroxide. The vessel was filled with a mixture of equal parts of hydrogen and air and was connected to a gasometer. The mixture was then shaken gently so that only a swirling motion was obtained, and the aggregates of palladium remained at the bottom of the vessel whilst the cerous hydroxide remained in suspension. There was a gradual absorption of gas, and after about 2 hours 15 cc. had been absorbed, and meantime there had been a gradual development of a yellow coloration due to the formation of ceric hydroperoxide. The cerous hydroxide-ceric hydroperoxide suspension was decanted from the palladium and estimated by the methods described above. This experiment was repeated several times (Table I). Other experiments were carried out using finely divided preparations of a more active catalyst. A more rapid absorption of gas was thus obtained, but no development of a yellow coloration was noted, partly because of the masking effect of the palladium black which formed a fine suspension. In these experiments only a very slight liberation of iodine resulted on centrifuging, washing and dissolving the cerous hydroxide in acetic acid in presence of potassium iodide; it is probable that the palladium effected almost complete decomposition of the hydrogen peroxide before it could combine with the cerous hydroxide.

Table I.

Palladium black mg.	0.02 <i>M</i> cerous sulphate cc.	0.16 <i>M</i> sodium borate cc.	Time hours	Gas absorbed cc.	Mols. of hydrogen peroxide estimated colori- metrically $\times 10^{-5}$	Mols. of hydrogen peroxide estimated iodi- metrically $\times 10^{-5}$
50 (feebly active)	2.0	2.0	2	21	0.45	0.43
50 "	2.0	2.0	2	16	0.45	0.37
50 "	2.0	2.0	1	10	0.30	0.28
50 "	2.0	2.0	2	15	0.45	0.49
50 (active)	2.0	2.0	0.5	30	—	<0.05
50 "	2.0	2.0	0.5	28	—	<0.05
—	2.0	2.0	4	0	0	0
—	2.0	2.0	4	0	0	0

Control experiments were carried out in the absence of palladium. Here there was no measurable absorption of gas and the cerous hydroxide suspension remained white; on subsequent treatment as above with acetic acid and potassium iodide it gave no liberation of iodine.

The amount of hydrogen peroxide obtained as ceric hydroperoxide represents only a very small percentage of the theory (about 1 %), but there is little doubt that the first step in the combination of hydrogen and oxygen results in the formation of hydrogen peroxide.

The catalytic dehydrogenation of methyl alcohol. 0.02 *M* cerous sulphate (2 cc.) was added to aggregates of palladium black (50 mg.) in the vessel of a shaking apparatus. After 1 minute 0.16 *M* sodium borate (2 cc.) was added and then pure methyl alcohol (0.5 cc.). As in the previous experiments the contents of the vessel were then gently shaken with air so that a swirling motion was obtained and the palladium remained at the bottom of the vessel whilst the cerous hydroxide remained in suspension. There was a slow absorption of gas and after several minutes the characteristic yellow colour of ceric hydroperoxide appeared and became more intense as the shaking continued. After about 5 hours 5 cc. of oxygen had been absorbed. The cerous hydroxide-ceric hydroperoxide

Table II.

Palladium black mg.	0.02 <i>M</i> cerous sulphate cc.	0.16 <i>M</i> sodium borate cc.	Methyl alcohol cc.	Time hours	Oxygen absorbed cc.	Mols. of hydrogen peroxide estimated colori- metrically $\times 10^{-5}$	Mols. of hydrogen peroxide estimated iodi- metrically $\times 10^{-5}$
50 (feebly active)	2.0	2.0	0.5	3	3.5	0.45	0.39
50 "	2.0	2.0	0.5	5	5.0	0.52	0.51
50 "	2.0	2.0	0.5	5	6.0	0.60	0.63
50 "	2.0	2.0	0.5	5	6.2	0.75	0.72
50 (active)	2.0	2.0	0.5	2	9.5	—	0.05
50 "	2.0	2.0	0.5	2	10.0	—	0.06
50 (feebly active)	2.0	2.0	—	5	0	0	0
50 "	2.0	2.0	—	5	0	0	0
—	2.0	2.0	0.5	5	0	0	0
—	2.0	2.0	0.5	5	0	0	0

suspension was decanted from the palladium and the characteristic odour of formaldehyde was perceptible. The ceric hydroperoxide was determined colorimetrically and iodimetrically as in the previous experiments. The experiment was repeated several times (Table II). Experiments using a more active finely divided catalyst were less successful. The following control experiments were carried out: cerous hydroxide and palladium black were shaken for 5 hours with

air; cerous hydroxide and methyl alcohol were shaken for 5 hours with air in the absence of palladium black. In both these experiments no oxygen was absorbed, no yellow coloration developed and no iodine was liberated in the iodimetric estimation.

The yield of ceric hydroperoxide represents about 1 % of the theory.

The catalytic dehydrogenation of ethyl alcohol. The procedure was the same as in the experiments with methyl alcohol. Pure ethyl alcohol was used and a slow absorption of oxygen accompanied by the development of the characteristic yellow colour of ceric hydroperoxide resulted. At the end of the experiment the

Table III.

Palladium black mg.	0.02 <i>M</i> cerous sulphate cc.	0.16 <i>M</i> sodium borate cc.	Ethyl alcohol cc.	Time hours	Oxygen absorbed cc.	Mols. of hydrogen peroxide estimated colori- metrically $\times 10^{-5}$	Mols. of hydrogen peroxide estimated iodi- metrically $\times 10^{-5}$
50 (feebly active)	2.0	2.0	0.5	5	5.8	0.67	0.66
50 "	2.0	2.0	0.5	4	5.0	0.60	0.53
50 "	2.0	2.0	0.5	4	4.8	0.60	0.57
50 "	2.0	2.0	0.5	3	4.0	0.45	0.46
50 (active)	2.0	2.0	0.5	2	11.0	—	0.04
50 "	2.0	2.0	0.5	1.5	8.5	—	0.06
—	2.0	2.0	0.5	5	0	0	0
—	2.0	2.0	0.5	5	0	0	0

odour of acetaldehyde was perceptible. The ceric hydroperoxide was estimated as in the experiments with methyl alcohol (Table III). As before an active finely divided catalyst was less suitable. A control experiment without palladium gave no gas absorption, no yellow coloration and no iodine liberation in the iodimetric determination.

SUMMARY.

1. It has been verified that hydrogen peroxide is formed intermediately in the catalytic combination of hydrogen and oxygen.

2. Hydrogen peroxide has been detected in the catalytic aerobic dehydrogenation of methyl alcohol and ethyl alcohol. The Wieland theory of dehydrogenation is thus substantiated.

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