Catalytic Activity of Phthalocyanines in the Autoxidation of Linseed Oil and Methyl Linoleate.

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Phthalocyanine and its related compounds have been in these ten years extensively studied by Linstead and his co-workers.(1) Among many remarkable results obtained concerning these compounds, their catalytic properties are of special interest. Polanyi and his co-workers(2) have found that metal-free phthalocyanine as well as copper phthalocyanine are capable to activate molecular hydrogen and to catalyse the conversion of para-hydrogen into normal hydrogen. Cook(3) has recently demonstrated that iron phthalocyanine and its related compounds have similar catalytic properties as haemin and other iron-containing compounds of porphyrin group, which are important from a biochemical point of view. They possess namely catalase and oxidase properties and are capable of catalysing the decomposition of hydrogen peroxide, the

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(1) R. P. Linstead, Phthalocyanine und verwandte Verbindungen, ein zusammenfassend. Vortrag., *Ber.* **72** (1939), A, 93.

(2) M. Polanyi, M. Calvin and E. G. Cockbain, *Trans. Faraday Soc.* **32** (1936), 1436, 1443.

(3) A. H. Cook, *J. Chem. Soc.* **1938**, 1761, 1768, 1774, 1845.

oxidations of hydrogen iodide, benzaldehyde and a number of olefinic compounds and the chemiluminescent reaction of luminol.

According to our own observations, a weak luminescence came out, when 0.05%-luminol solution in 5%-aqueous NaOH was treated with 3%-hydrogen peroxide in the presence of a small amount of chloriron phthalocyanine, while with copper- or magnesium phathalocyanine the reaction occurred so feebly that the emitted light was only just discernible. The catalase activities of these compounds were examined in aqueous solution of hydrogen peroxide in which a small amount of catalyst was suspended, the course of decomposition being normally followed by titration with potassium permanganate. The first order velocity constant thus determined at 20°C. are approximately 0.01 min.$^{-1}$ for chloriron phthalocyanine, 0.001 min.$^{-1}$ for magesium- and copper phthalocyanine, whereas the velocity constant of haemin is about 0.05 min.$^{-1}$ The catalase activity of chloriron phthalocyanine is therefore about 1/5 of that of haemin, which is in accordance with the fact that chloriron phthalocyanine is highly surpassed by haemin in the catalytic influence upon the luminescent oxidation of luminol.

Now, some of the compounds of phthalocyanine are used as colours. They are valuable because of their beauty of appearance, strong colouring power, unusual stability against light, heat, alkali, and acid and insolubility in ordinary solvents. Granted that they have more or less the oxidase activity, it is a matter of interest to examine whether they themselves act as driers, when they are used as colours in paints. Mr. Akiyama, who kindly afforded us metallic pathalocyanines(4) and other materials used in the present experiment, made some preliminary observations on this subject. Among the metallic phthalocyanines, chloriron phthalocyanine was found to be effective as a drier, though its efficiency was not so great as that of Co-Pb-naphthenate ("Soligen") of I. G., a well known drier.

We first determined the rate of drying of linseed oil at 50°C. in air, once with Co-Pb-naphthenate and then with metallic phthalocyanines, the oil being well mixed with a small quantity (0.05 g. per 1 c.c. oil) of catalyst. The linseed oil with Co-Pb-naphthenate dried in about 3 hours, while with chloriron phthalocyanine in about 7 hours and with copper or magnesium phthalocyanine in about 25 hours.

We then made some experiments concerning the catalytic action of metallic phthalocyanines as compared with that of Co-Pb-naphthenate of I. G. towards the autoxidation of methyl linoleate and linseed oil. Methyl linoleate has been prepared from cotton seed oil as follows:(5) 1 kg. cotton-seed oil is saponified and fatty acids thereby obtained are dissolved in 1500 c.c. ligroin, into which bromine is added under cooling until a red colour comes to stay. The bromination product is recrystallized from ligroin. The bromide together with methyl alcohol and zinc granules is then heated till the mixture boils, and into it is added methyl alcoholic

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(4) The method of preparation of metallic phthalocyanines adopted by Mr. Akiyama is principally the same as that of Linstead and his co-workers. Compare *J. Chem. Soc.*, **1934**, 1017–1031.

(5) Beilstein, Organische Chemie, Bd. II, 496.

hydrochloric acid: the mixture is again boiled for an hour. On cooling, the methyl ester of linoleic acid separates itself, which is extracted with petroleum ether and washed with water several times and dried by means of sodium sulphate: petroleum ether is then expelled by evaporation. The pure product is obtained by distillation in vacuo.

Linseed oil as well as methyl linoleate were dissolved in carbon tetrachloride with catalyst (0.015 g. catalyst in 50 c.c. solution) in a reaction vessel with upright cooling condenser, into this mixture air was gently passed through for 20–24 hours, during which time the reaction vessel was maintained at a constant temperature of 20°C. From time to time, a small portion of the solution was pipetted out, of which the iodine number was determined according to the method of Wijs and thus we compared the rate of autoxidation.

The results are given in the following tables, one for methyl linoleate and another for linseed oil, where chloriron phthalocyanine and Co-Pb-naphthenate are compared as to their catalytic activity.

Table 1. Autoxidation of Methyl Linoleate.

With chloriron phthalocyanine as catalyat		With Co-Pb-naphthenate as catalyat	
Time (hours)	Iodine number	Time (hours)	Iodine number
0	174	0	174
3	130	3	104
10	92	10	85
20	75	20	70

Table 2. Autoxidaton of Linseed Oil.

With chloriron phthalocyanine as catalyst		With Co-Pb-naphthenate as catalyst	
Time (hours)	Iodine number	Time (hours)	Iodine number
0	175	0	175
3	140	2.5	136
10	91	10	90
24	62	24	61

The accuracy of the determination of iodine number was not the same in all cases and allowance should be made for errors due to the variation of concentration of the reacting mixture in the course of the reaction time. The general features of the matter are nevertheless evident. Chloriron phthalocyanine has, as is shown above, really a marked catalytic activity towards the autoxidation of methyl linoleate as well as of linseed oil; its activity is almost as powerful as that of Co-Pb-naphthenate, although the latter always excels the former.

Out of other metallic phthalocyanines copper phthalocyanine was chosen and examined, whose activity was, however, found to be much weaker than that of chloriron phthalocyanine, the iodine number of methyl linoleate decreasing from 174 to 110 in 20 hours while that of linseed oil from 175 to 120 in the same time.

Summary.

The catalytic action of metallic phthalocyanines towards the autoxidation of linseed oil and methyl linoleate is demonstrated. Chloriron phthalocyanine is remarkably effective as catalyst, whereas copper- and magnesium phthalocyanine are slightly effective.

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