325. *Catalytic Properties of the Phthalocyanines. Part I. Catalase Properties.*

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The ability of pigments of the metal phthalocyanine class to catalyse the decomposition of hydrogen peroxide has been investigated. Iron pigments were shown to be outstanding in this respect, the effect having been studied quantitatively in 75% pyridine solution and in aqueous suspensions of the pigments deposited on carriers. The influence of physical variables (p_H, poisons, etc.) was examined, and the results compared with iron-porphyrin catalyses and others of biochemical interest.

Although catalysed reactions in organic chemistry are frequently encountered, organic catalysts of known and easily varied constitution are, with the exception of organic bases,

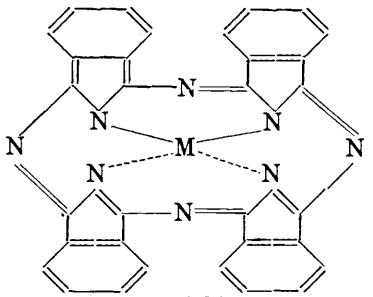
* The curve for R in the triethylamine–chloroform system does not cut the polarisation axis at 0 for zero concentration. This is probably due to the fact that the chloroform contained a very slight amount of hydrogen chloride which would give a highly polar ion-pair when mixed with triethylamine, so that all the polarisation values obtained for the mixture will be higher by a roughly constant amount than the calculated values, apart from any compound formation.

comparatively rare. The phthalocyanines and related compounds provide a series of pigments combining organic character with the stability of inorganic compounds, and it appeared of interest to investigate how far typical metal-ion catalysts preserve or modify their catalytic properties on entering the phthalocyanine nucleus, and how far the peculiarly stable organic superstructure can contribute activity of its own. In particular, the formal structural relationship between phthalocyanines and porphyrins made it desirable, in view of the known catalytic properties of iron-porphyrins as exemplified in some enzymes such as catalase, etc., to establish the presence or absence of phthalocyanine parallels to the biological oxidations, oxidation–reductions, etc.

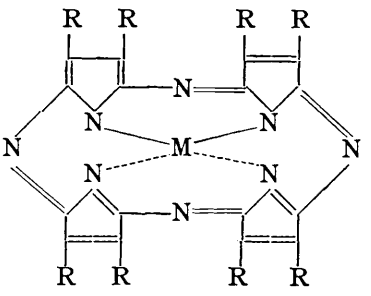
The present paper deals therefore with the catalase activity of phthalocyanines and related compounds.

The ability to catalyse the decomposition of hydrogen peroxide is possessed to varying but generally very small extents by many metallic compounds, *e.g.*, simple salts of copper, tungsten, complex salts (K. and Y. Shibata, " Katalytische Wirkungen der Metallkomplex-verbindungen," Tokio, 1936, 32). The outstanding, but still quite small, activity of many simply constituted iron compounds, well known through the work of Warburg, Kuhn, Krause, and others, is surpassed by that of certain organic complexes of iron such as those of αα′-dipyridyl and *o*-phenanthroline (Kuhn and Wassermann, *Annalen*, 1933, **503**, 203), and particularly those of hæmin and its complexes (Stern, *Z. physiol. Chem.*, 1933, **215**, 35) and other iron compounds of the porphyrin group (Kuhn and co-workers, *Ber.*, 1926, **59**, 2370; 1927, **60**, 1151).

Although the slight solubility of the phthalocyanines has precluded a complete survey of the catalatic activities of all known metallic phthalocyanines in homogeneous solution, it has been possible to establish the very considerable activity of the bi- and ter-valent iron phthalocyanines (I and II) in 75% pyridine solution, (II) being somewhat less active.



(I, M = Fe; II, M = FeCl.)



(III, M = Fe; R = Ph.)

In view of the marked solubility in organic solvents of the octaphenyltetrazaporphins (octaphenylporphyrazines) recently synthesised in these laboratories (Cook and Linstead, J., 1937, 929), the bivalent iron representative of the series (III) was prepared in the expectation that it would prove sufficiently soluble to enable its catalytic properties in dilute aqueous organic solvents to be studied. The new compound, however, had no advantage in this respect over the phthalocyanines, although possessing comparable catalytic activity. (Ferrous octaphenyltetrazaporphin is a compound of unusual interest in other ways and will form the subject of a separate paper.) Ability to catalyse the decomposition of hydrogen peroxide under similar conditions was not detectable (*i.e.*, any activity was certainly less than 1% of that of the iron compounds) in those cases where sufficient solubility made examination possible (magnesium, beryllium, zinc, chloro-aluminium, and metal-free phthalocyanines; magnesium, copper, copper chloro- and metal-free octaphenyltetrazaporphins; magnesium octanitrophenyltetrazaporphin; α- and β-magnesium naphthalocyanine, and magnesium thionaphthalocyanine). Only with cobalt and chromium phthalocyanines was feeble activity apparent, and in these cases the slow decomposition was accompanied by slow degradation of the pigment.

The catalytic activity discussed here, therefore, has its ultimate origin in the central metal atom (iron) and not in the organic superstructure, and thus has no connection with

the hydrogen-activating properties of the phthalocyanine ring system discovered by Polanyi and his co-workers (*Trans. Faraday Soc.*, 1936, **32**, 1436).

Although completely insoluble in water, the iron compounds had an activity in absence of organic solvents, as was demonstrated by supporting them on inactive or only slightly active materials. For instance, deposits of 1% of iron phthalocyanine on barium sulphate were quantitatively equivalent to an equal quantity of iron complex in 75% pyridine solution under similar temperature conditions, whilst the activity on silica gel was somewhat less; possibly the physical nature of this support prevents utilisation of that part of the catalyst embedded in the granules, but it is equally likely that the effect is due to a specific action of the silica gel.

When the catalyst was supported on a wood charcoal of low catalatic activity, its activity—always calculated for comparative purposes on the basis of the iron-complex content—was increased 8—10 fold under similar physical conditions. This phenomenon was exhibited by iron octaphenyltetrazaporphin also. Supernorite was unsuitable for these experiments as it possessed considerable catalatic activity before treatment with pigment. For instance, whereas 400 mg. of wood charcoal decomposed only 6·5% of the hydrogen peroxide in 50 c.c. of N/40-solution during 120 mins., a similar quantity of supernorite decomposed 30% of a like quantity of hydrogen peroxide in 30 mins. When 4 mg. of iron phthalocyanine or an equivalent quantity of iron octaphenyltetrazaporphin were deposited on the supernorite or charcoal, the hydrogen peroxide suffered over 95% decomposition within 5 mins.

The pigments were generally deposited on the carriers by precipitation with ice-water of solutions in concentrated sulphuric acid. This treatment is attended by little danger of decomposition in the case of the iron compounds, for these are particularly stable to acids—iron phthalocyanine has so far resisted all attempts to remove the metal whilst leaving the superstructure intact. The primary product of such treatment is a pigment–sulphuric acid compound recognisable by a green or red colour in the cases of iron phthalocyanine or octaphenyltetrazaporphin, respectively, and possessing considerable stability even to hot water. The catalatic activity of such deposits was, however, quite independent of this combined acid, and altered only very slightly when the deposit was converted into one of the free pigment by treatment with alkali.

Catalysts of an order of activity comparable with the sulphuric acid deposits on charcoal were prepared by dissolving iron phthalocyanine in quinoline containing charcoal in suspension, and then removing the base by distillation in steam. This procedure was not, however, generally adopted, for the pigments tended to separate as a scum rather than as a uniform deposit. Among other phthalocyanines possessed of sufficient stability towards sulphuric acid to allow deposition on charcoal by the above method, none was found to have any marked activity, although the deposits were always more active than either charcoal or the pigments alone—400 mg. of charcoal deposits containing 4 mg. of pigments (zinc, platinum, nickel, copper, vanadium phthalocyanines) decomposed 12—15% of 50 c.c. of N/40-hydrogen peroxide during 120 mins.

Finally, the catalatic activity of a water-soluble monosulphonated iron phthalocyanine was examined. Although apparently possessing considerable "potential" activity, its decomposition of hydrogen peroxide quickly ceased owing to oxidation of the catalyst itself.

When iron phthalocyanine is brought into 75% pyridine solution with hydrogen peroxide, the decomposition of the latter is accompanied by slow oxidation of the pigment, the solution passing through an intermediate green phase and becoming ultimately colourless. The same is true of chloro-iron phthalocyanine and iron octaphenyltetrazaporphin, but it is remarkable that slightly active pigments (*e.g.*, of chromium) are only slowly decomposed, whilst catalatically inactive pigments are indefinitely stable towards hydrogen peroxide. In homogeneous solution, only when hydrogen peroxide is being decomposed is the pigment destroyed, this generalisation holding also for the sulphonated iron phthalocyanine, although here sulphonation has resulted in a shortening of the catalytic "working life." Attention may be directed to the similar behaviour of hæmin (Haurowitz, *Enzymologia*, 1937, **2**, 9; **4**, 139). There appears to be no invariable stoicheiometric relation between the amounts of hydrogen peroxide decomposed and of phthalocyanine

oxidised, and indeed no decomposition of iron phthalocyanine deposited on charcoal was observed, the pigment being extracted in apparently undiminished quantity by organic solvents even after prolonged contact with decomposing hydrogen peroxide solutions.

There is strong evidence that a major part of the decomposition is effected by the phthalocyanine itself, or by a peroxide or oxygen addition product, and not merely by a simple oxidation product such as colloidal iron oxide. Although it is true that, as with the iron porphyrins and most enzymes, the active catalyst slowly disappears during reaction, yet the brown solution obtained by treating the blue iron phthalocyanine under mild conditions with hydrogen peroxide in relatively concentrated pyridine solution, which contains no unchanged phthalocyanine, returns to the blue colour of the pigment and again exhibits the spectrum of iron phthalocyanine on addition of reducing agents (aqueous sodium hyposulphite, hydrazine, etc.) (excess of reducing agent must be avoided, as the pigment itself is further reduced to a leuco-compound). When reaction with hydrogen peroxide is allowed to proceed with vigour, the phthalocyanine is irreversibly oxidised and catalatic activity practically disappears. The products are iron oxide, phthalimide, and an ill-defined complex of iron with organic material. The formation of oxygen or peroxide addition products, catalytic decomposition of hydrogen peroxide, and peroxydatic destruction of the pigment itself are thus features of the phthalocyanine reaction parallel with that of hæmin (Haurowitz, *loc. cit.*; cf. also Keilin and Hartree, *Proc. Roy. Soc.*, 1938, *B*, **124**, 397).

The action of all the above catalysts is subject to a number of influences. There was approximate proportionality between decomposition and quantity of any one catalyst preparation when compared under standard conditions, this statement applying both to homogeneous reactions in 75% pyridine and to heterogeneous reactions using deposits of the pigments on carriers. A given weight of iron phthalocyanine, however, when deposited on charcoal, exhibited increasing activity as the ratio charcoal : pigment increased from 66 : 1 to 200 : 1, the activity then decreasing with further "dilution" of pigment. These deposited charcoal catalysts slowly lost their enhanced activity on keeping in air; *e.g.*, although there was no noticeable deterioration over a few days, the activity of a 1 : 100 deposit of iron phthalocyanine fell to 35—40% of its original value after 8 weeks. Moderate changes of temperature had but a small effect on the activity of the catalysts; *e.g.*, over the range 0—20° the % decomposition of 100 c.c. of N/80-hydrogen peroxide by 2 mg. of iron phthalocyanine deposited on 198 mg. of wood charcoal was practically unchanged over a moderate period, although there was a marked effect on the decomposition–time curve in the sense that an initial short period of great activity was less pronounced at the higher temperature. All of the iron catalysts are very sensitive to cyanide ions, as shown by two series of experiments :

(*a*) 50 C.c. of N/40-hydrogen peroxide in pyridine + 4 mg. of iron phthalocyanine in 10 c.c. of pyridine + potassium cyanide added in 1 c.c. of water, at 17·5° :

KCN, 1·26M ×	0	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}
Decompn., %, in 60 mins.	51	59	67	62	13	10

(*b*) 100 C.c. of N/80-hydrogen peroxide in water + 200 mg. of iron phthalocyanine–wood charcoal deposit (1 : 100) + potassium cyanide in 5 c.c. of water, at 0° :

KCN, 7·3M ×	0	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}
Decompn., %, in 60 mins.	73	71	66	39	32	29

Although cyanide exerts a steadily increasing inhibiting effect on the charcoal deposits, very small amounts have a stimulating action on the homogeneous catalyses in pyridine solution, but larger amounts have an inhibiting action. The above experiments indicate that the stimulating action is greatest at a cyanide concentration corresponding to approximately one CN radical for each atom of iron (pigment concentration 7×10^{-5}M). The increased activity in presence of minimal quantities of catalyst poison has been noticed in other cases (Part II), and is not uncommon among catalyses of this type; *e.g.*, increasing quantities of mercury vapour have a similar effect on the catalytic activity of yeast (Floresco, *Chem. Zentr.*, 1936, i, 2959). In other respects the sensitivity of the iron

phthalocyanine preparations is broadly comparable with that of iron porphyrins and related enzymes :

Catalyst.	Concn. (M) of CN required to reduce activity by 50%.
Iron phthalocyanine in pyridine	5×10^{-3}
Iron phthalocyanine on charcoal (1 : 100)	1×10^{-5}
Hæmatin [1]	1×10^{-3}
Catalase [2]	8×10^{-7}
Oxygenase [3]	10^{-3}—10^{-4}
Peroxidase [4]	5×10^{-6}

[1] Krebs, *Biochem. Z.*, 1929, **204**, 322; [2] Zeile and Hellstrom, *Z. physiol. Chem.*, 1930, **192**, 171; [3] Warburg, *Ber.*, 1925, **58**, 1001; [4] Wieland and Sutter, *Ber.*, 1928, **61**, 1066.

As iron octaphenyltetrazaporphin yields a well-defined complex with pyridine, it is probable, in view of the unusual solubility of iron phthalocyanine in this solvent, that a similar complex is present in solution in this instance also, and that the true catalyst in the above partly poisoned catalysts in pyridine solution is a pyridine–cyanide complex analogous to the pyridine–cyanide hæmochromogens of the blood-pigment series.

The rate of decomposition is markedly affected by moderate changes in p_H :

50 C.c. of N/40-hydrogen peroxide in water + 55 c.c. of water containing a measured quantity of acid or alkali were treated with 200 mg. of iron phthalocyanine deposited on charcoal (1 : 100) at 0° :

	H_2SO_4, mols.				NaOH, mols.		
Addition	0·05	0·005	0·0005	0	0·001	0·01	0·1
Decompn., %, in 10 mins.	94	74	55	33	87	87	65

Bredig and v. Berneck (*Z. physikal. Chem.*, 1899, **31**, 258) observed that addition of increasing quantities of sodium hydroxide to colloidal platinum decomposing hydrogen peroxide first raised then lowered the activity, as is the case with the natural ferment, but it is questionable whether the present results are directly significant, for the effects are almost certainly complicated by unknown adsorption effects, so that the p_H of the bulk of the solution would bear no simple relation to that at the catalyst surface (cf. Sihvonen, *Suomen Kem.*, 1937, **10**, *B*, 25). The mild poisoning action of some added buffers (phosphate and acetate) is, on the other hand, probably a direct specific action such as is exerted on the catalase activity of other iron catalysts, *e.g.*, hæmin (Kuhn and co-workers, *Ber.*, 1926, **59**, 2370; 1927, **60**, 1151).

The catalysis in homogeneous solution is of an apparently unimolecular order, although with very dilute solutions decomposition over a relatively short range (30—50%) is for practical purposes proportional to the time. Similar remarks apply to catalysis by deposits of iron phthalocyanine on barium sulphate or silica gel. Charcoal deposits, however, invariably exhibited an abnormally high initial activity, which soon fell to a steady rate, a property, though usually in much smaller degree, of catalytic charcoals in general (King, J., 1936, 1688). A similar phenomenon is observed with other iron catalysts, and Kuhn and Wassermann (*Annalen*, 1933, **503**, 203) have obtained good evidence that in one instance, at least, *viz.*, the addition of ferric sulphate to αα′-dipyridyl solution, the abnormal catalatic behaviour is due essentially to an active intermediate in the reduction of the ferric complex to the ferrous state by hydrogen peroxide. Hence, it is possible that a ferrous–ferric change is partly responsible for the present phenomenon, although the close similarity between ferrous and ferric phthalocyanines makes experimental verification of this hypothesis somewhat difficult. The "Katalasestoss" is, moreover, a phenomenon exhibited by many heavy-metal catalysts where formal valency changes can hardly be postulated.

Of the many compounds able to catalyse the decomposition of hydrogen peroxide, some have been studied as models of the catalase enzyme (Morgulis, *Ergebn. Physik*, Ascher-Spiro, 1924, **23**, i, 308; Fischer, see Oppenheimer, "Die Fermente," 1927, III, 1115, and Supplements, Pts. 7, 8), but in consequence of the recognition of iron-porphyrin complexes in this and other enzymes, the catalatic properties of these pigments have received increased attention. Although other iron-porphyrins, *e.g.*, meso- and deutero-

hæmin (Euler, Nilsson, and Runehjelm, *Svensk Kem. Tidsk.*, 1929, **41**, 85; Zeile, *Z. physiol. Chem.*, 1930, **189**, 127) possess similar activity, hæmin is exceptional because of its relative stability towards hydrogen peroxide (Kuhn and Brann, *loc. cit.*), but it is noteworthy that in all cases, as with the phthalocyanines, the catalyst becomes inactivated, by complete degradation or otherwise.

In the porphyrin series, the dependence of the absolute magnitude of catalytic activity on slight changes in constitution is a marked factor, *e.g.*, the activities of meso- and deutero-hæmin are 30 times that of hæmin (Kuhn and co-workers, *Ber.*, 1927, **60**, 1151; Euler, Nilsson, and Runehjelm, *loc. cit.*). Among the phthalocyanines, sulphonation results in greatly increased vulnerability towards hydrogen peroxide and lessening in catalytic action. Again, a sensitivity towards specific poisons is shared by both classes of compounds, and both hæmin and iron phthalocyanine are enabled to decompose more hydrogen peroxide when deposited on charcoal, whilst they remain unaffected or even enfeebled on other carriers (Kuhn and Wassermann, *Ber.*, 1928, **61**, 1550). Organic bases have a variable but generally accelerating effect on the catalytic activity of iron-porphyrins (Langenbeck, Hutschenreuter, and Rottig, *Ber.*, 1932, **65**, 1750), an effect due to the formation of parahæmochromogens, and it is probable that the catalysts in the present homogeneous experiments are hæmochromogen analogues.

The similar activities of the iron porphyrins and the present pigments suggest that it is the co-ordinative association of the iron atom with four pyrrole nitrogen atoms which gives rise to potentially catalytically active compounds, the absolute magnitude of the activity being dependent to a small extent on other structural factors. The fact that the fate of the iron pigments varies with the experimental conditions (solution or deposit) makes it likely that the oxidation of the pigment is a side reaction, and that the effects recorded are, to a preponderating extent at least, the result of catalysis by the pigments themselves rather than by active intermediates.

Experimental.

Materials, etc.—Hydrogen peroxide was prepared by diluting Merck's perhydrol with water or water and pure pyridine.

The pigments, except sulphonated iron phthalocyanine, were crystallised, and where possible, were sublimed specimens, most of which were kindly provided by Dr. R. P. Linstead. Iron phthalocyanine was inert towards sulphonating agents (chlorosulphonic acid in chloroform, or sulphuric acid at a high temperature), and was only finally sulphonated by heating it (400 mg.) with excess of chlorosulphonic acid (5 g.) at 100° for 5 hrs. The product was isolated by dilution with water, filtered off, washed with a moderate quantity of water, redissolved in dilute aqueous ammonia, and the filtrate evaporated to small bulk. The free acid then separates as a microcrystalline scale, slightly soluble in water, more soluble in dilute alkali. It is substantially a *monosulphonic acid* (Found: S, 4·63%; N, 16·95. $C_{32}H_{16}O_3N_8SFe$ requires S, 4·94; N, 17·27%). Spectrum: Band maxima in dilute aqueous ammonia, 6900 A. (v. weak), 6320 A. (v. broad).

Catalysts in homogeneous solution were added as solutions of known concentration in 75% pyridine (usually 20 mg. in 50 c.c.). Catalyst deposits were prepared by precipitating a solution of pigment in concentrated sulphuric acid (20 mg. in 40 c.c.) with ice-water (this procedure is obviously only applicable to those pigments which are unaffected by sulphuric acid). Carriers such as silica gel and charcoal were stirred with the acid prior to precipitation. When barium sulphate was employed, the acid solution was rapidly diluted with an aqueous solution of a known weight of barium chloride (*e.g.*, precipitation of a solution of 20 mg. of pigment with 4·166 g. of barium chloride dihydrate yielded a catalyst containing 1 part of pigment deposited on 200 parts of barium sulphate; addition of pigment solution to aqueous barium chloride was less successful). A pure wood charcoal was used (ash, 4·6; Fe, 0·01%).

The fate of the catalyst is indicated by the following experiment.

100 Mg. of iron phthalocyanine were dissolved in 50 c.c. of pyridine, and 3 c.c. of perhydrol added. An immediate and vigorous decomposition, moderated by cooling with water, set in, the blue colour giving place to deep brown. Further quantities of 100 mg. of phthalocyanine were added with perhydrol as required so that eventually 1 g. of the former and 15 c.c. of perhydrol had been used. Further additions of perhydrol were decomposed only slowly. The

solution was kept overnight and evaporated in a vacuum at 50°. The residue was diluted with 75 c.c. of chloroform, and a chocolate-brown, insoluble residue filtered off, washed, and dried in a vacuum (0·55 g.). The iron in this product was partly associated with organic material and soluble in hot pyridine, and partly inorganic, but possessed no appreciable catalatic activity. The filtrate was passed through a 20-cm. column of activated alumina (2 cm. diam.), and the chromatogram washed with chloroform. The coloured zones (in order of decreasing adsorption : brown, 7 cm.; olive-green, 0·5 cm.; blue-green, 4 cm.) were eluted separately with chloroform containing a little pyridine. The two lowest zones yielded only minute amounts of iron phthalocyanine, formed by spontaneous decomposition of the primary peroxide or oxygen addition product (the presence of two zones is possibly to be ascribed to the adsorption of a pyridine addition product). The third elutrate yielded 260 mg. of phthalimide, m. p. and mixed m. p. 231—233°.

The course of decomposition of hydrogen peroxide was normally followed by titration with potassium permanganate. 5 C.c. portions were withdrawn from the reaction flask and titrated with N/100-potassium permanganate, the solutions in 75% pyridine being first diluted with 8—10 vols. of water and treated with 25 c.c. of ice-cold 20% sulphuric acid. In the case of deposits of catalyst, these were first rapidly filtered from 5 or 10 c.c. portions and washed at the pump (filtration through paper was adopted, as the use of sintered glass led to variable results), and the filtrate then acidified and titrated. Mechanical stirring secured uniform suspension in heterogeneous catalyses.

The following are typical figures for homogeneous reactions :

50 C.c. of 0·030N-hydrogen peroxide in 75% pyridine. The titration figures refer to hydrogen peroxide decomposed in 5 c.c. portions in terms of N/100-permanganate at 0°.

Catalyst.						
0·8 Mg. of iron phthalocyanine in 10 c.c. of 75% C_5H_5N	Time (mins.)	15	30	60	105	195
	Titration	0·25	0·40	0·75	1·50	3·45
4·0 Mg. of iron phthalocyanine in 10 c.c. of 75% C_5H_5N	Time (mins.)	15	30	45	75	120
	Titration	1·45	3·20	4·70	6·75	8·50
4·0 Mg. of chloroiron phthalocyanine in 10 c.c. of 75% C_5H_5N	Time (mins.)	15	30	45	75	120
	Titration	0·70	1·65	2·85	5·00	6·60
4·0 Mg. of chromium phthalocyanine in 10 c.c. of 75% C_5H_5N	Time (hrs.)	24	140			
	Titration	1·36	3·65			
4·0 Mg. of iron octaphenyltetrazaporphin in 10 c.c. of 75% C_5H_5N	Time (mins.)	15	30	60		
	Titration	1·20	1·85	3·15		

In all cases where catalysis occurred, the pigment disappeared. With cobalt, as with chromium, the disappearance was only slow and paralleled by the catalysis itself. With sulphonated iron phthalocyanine, disappearance was rapid, and the total catalytic effect only small. Beryllium phthalocyanine apparently exerted a slight effect, but as the pigment in these experiments was always slowly precipitated, possibly as a compound with hydrogen peroxide, the apparent catalysis was almost certainly a phenomenon of a different kind. In no other case where sufficient solubility permitted examination was any catalysis detected.

The following are illustrative of deposited catalysts :

50 C.c. of N/40-hydrogen peroxide + 55 c.c. of water at 0°. In each case a quantity of catalyst preparation containing 2 mg. of pigment was added, and the titres are those of 10 c.c. portions by N/100-permanganate.

Catalyst.						
Iron phthalocyanine on wood charcoal, 1 : 400	Time (mins.)	0	7	12	50	
	Titration	—	3·30	3·65	6·39	
Iron phthalocyanine on wood charcoal, 1 : 200	Time (mins.)	5	10	20	30	
	Titration	5·10	6·75	8·40	9·45	
Iron phthalocyanine on wood charcoal, 1 : 100	Time (mins.)	5	10	20	30	50
	Titration	3·85	5·35	7·00	7·70	9·55
Iron phthalocyanine on wood charcoal, 1 : 66	Time (mins.)	5	10	20	30	40
	Titration	3·75	4·70	5·95	6·70	7·35
400 Mg. of wood charcoal	Time (mins.)	120				
	Titration	0·90				

Iron octaphenyltetrazaporphin was similarly active, but deposits of zinc, platinum, copper, nickel, or vanadium phthalocyanines were inactive.

Experiments with other carriers, poisoning agents, etc., were carried out as described in the introduction.

The titrimetric experiments were in most instances checked by gasometric measurements with an apparatus consisting of a gas burette inside which the pressure could be rapidly adjusted by raising or lowering a reservoir filled with the manometric liquid. The upper part of the burette connected through a three-way tap and flexible tubing with a reaction flask, inside which the catalyst was suspended in an open glass tube out of contact with the hydrogen peroxide solution until equilibrium was attained. The reaction flask was shaken mechanically during each experiment.

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