344. *Catalytic Properties of the Phthalocyanines. Part IV. Chemiluminescent Reactions.*

By A. H. Cook.

The ability of iron pigments of the phthalocyanine type in common with hæmin to catalyse the chemiluminescent oxidation of luminol is recorded. The oxidation of fluorescent phthalocyanines of metals of Group II and also of chlorophyll by organic peroxides at elevated temperatures is usually accompanied by emission of red light.

Tamamushi (*Naturwiss.*, 1937, **20**, 318), following Gleu and Pfannstiel (*J. pr. Chem.*, 1936, **146**, 137; cf. Albrecht, *Z. physikal. Chem.*, 1928, **136**, *A*, 321), has observed that hæmin catalyses the chemiluminescent oxidation of 5-aminophthalaz-1 : 4-dione (luminol) either by hydrogen peroxide or by oxygen.

Iron pigments of the phthalocyanine type having a ring structure resembling that of hæmin also promote the production of light by luminol under similar conditions. Thielert and Pfeiffer have noted (*Ber.*, 1938, **71**, 1399) the similar catalytic effect of some iron complex compounds, including iron phthalocyanine, in which iron is bound in the anion or cation or in a neutral complex. The effects have their origin in the metal atom, for, whilst porphyrin-like structures seem to be peculiarly suited for the chemiluminescent reaction in association with iron, others may in combination with iron also exhibit activity. Nevertheless, differences in behaviour (*e.g.*, among iron salicylaldehyde diamine compounds) make it impossible to trace any connection between structure and catalytic activity.

In experiments using hydrogen peroxide, 10 c.c. of a 0·1% solution of 5-aminophthalaz-1 : 4-dione in 0·1% aqueous sodium hydroxide were treated with 3 c.c. of 0·3% hydrogen peroxide (Merck's perhydrol) in water, and approx. 1 mg. of finely powdered pigment added, any luminescence being observed in a darkened chamber. Ferrous and chloroiron phthalocyanines produced the strongest emission of light, although iron octaphenylporphyrazine (octaphenyltetrazaporphin) and its derivatives were all markedly active. Chromium phthalocyanine produced a weak emission of light and manganese, molybdenum, hydroxyaluminium, platinum, cerium, di-iodotin and 4-chlorocopper phthalocyanines catalysed the reaction so feebly that the emitted light was only just discernible. In all other cases (mercury, magnesium, chloroaluminium, beryllium, nickel, lead, 4-nitrocopper phthalocyanines, copper and magnesium naphthalocyanines, a copper thiophen pigment, magnesium, copper, and zinc octaphenyltetrazaporphins and their complexes with acids, metal-free pigments, etc.) no activity was detected. Deposits of the iron pigments on charcoal (1 : 100) (prepared as in Part I; this vol., p. 1763) were feebly active; the emitted light was more readily observed when barium sulphate was the carrier. Deposits of other metal phthalocyanines on carbon were inactive (vanadium, nickel, copper, zinc). Of crystalline derivatives of iron octaphenyltetrazaporphin (these preparations will be described in a later communication), those with pyridine, aniline, and quinoline increased in activity in this order, the free pigment and a hydrochloride taking up an intermediate position.

The luminescence produced by the strongest of these catalysts (iron phthalocyanine) is somewhat surpassed by that of hæmin. Whilst, however, the action of hæmin is not inhibited by a moderate concentration of hydrocyanic acid, that of iron phthalocyanine is very considerably and that of chloroiron phthalocyanine practically completely inhibited under comparable conditions. The effect of hydrocyanic acid on a deposit of iron phthalocyanine on barium sulphate is less pronounced than its effect on the free pigment, this insensitivity recalling the similar behaviour noted in Part I.

Drew and Garwood (J., 1937, 1843; this vol., p. 791) have obtained evidence that the formation of a peroxide of the aminophthalazdione is probably an essential stage in the chemiluminescent oxidation, so the iron catalyst functions by promoting what is probably the further rearrangement or disruption of the peroxide. The catalytic reaction is to be regarded, therefore, as a special example of the general decomposition of peroxides described in Part III (this vol., p. 1774). In agreement with this view, the same pigments are catalytically active in both cases, ionised iron possessing catalytic activity to a minor degree only (if a solution of a ferrous or ferric salt is slowly added in place of a solid pigment in the above luminescent oxidations, each drop produces a momentary flash of light on entering the alkaline hydrazide solution, but the precipitated hydroxide is quite inactive).

A stream of oxygen may be used as the oxidising agent: here again the iron pigments are the only ones to exhibit appreciable activity, although the emission of light is feebler than with hydrogen peroxide.

In Part III the effect of pigments of the phthalocyanine class on the decomposition of organic peroxides was described. Normally (*i.e.*, at room temperature) only the iron pigments have any noticeable effect, but at considerably higher temperatures some are oxidised with emission of light. Pigments possessing this property are all complexes with metals of Group II of the periodic table which are normally markedly fluorescent in solution. These include beryllium, magnesium, and zinc phthalocyanine, magnesium α- and β-naphthalocyanines, magnesium octaphenyltetrazaporphin and thionaphthalocyanine, of which beryllium phthalocyanine gives the most brilliant luminescence. The only exceptions to the above generalisation which have been so far observed are magnesium pyridinoporphyrazine and zinc octaphenyltetrazaporphin, which, although brightly fluorescent, are stable to organic peroxides under quite drastic conditions. Magnesium octanitrophenyltetrazaporphin is, unlike the unnitrated pigment, not fluorescent and has not been observed to undergo chemiluminescent oxidation. On the other hand, it is even more remarkable that chlorophyll with a strong fluorescence is active in emitting light under these conditions.* A large number of phthalocyanines and related pigments containing other metals (lithium, sodium, aluminium, calcium, vanadium, chromium, molybdenum, iron, cobalt, nickel, copper, manganese, silver, tin, cerium, mercury, lead) were found to be inactive. Included among these are pigments (those of iron and to a lesser extent of some other metals) which are capable of catalysing the decomposition of peroxides at lower temperatures. Noteworthy also is the fact that addition compounds of magnesium octaphenyltetrazaporphin with acids (*e.g.*, oxalic acid) are not fluorescent (unlike the parent pigment) and are surprisingly stable towards organic peroxides, no chemiluminescent oxidation being observed in these instances. Deposits of the active pigments on charcoal were also active, but this was possibly due in part to elution of the pigment by the boiling solvent. Helberger (*Naturwiss.*, 1938, **26**, 316) has also noticed the emission of light by boiling tetralin containing peroxide in presence of magnesium phthalocyanine or tetrabenzporphin, or zinc phthalocyanine.

The luminescence, which is remarkable for its glowing red colour (in most low-temperature chemiluminescent oxidations the light emitted is blue-green), is best observed in relatively high-boiling hydrocarbons, which form or contain preformed peroxides, by heating to boiling in presence of a minute amount of the active pigment. As the boiling point is approached, the liquid glows with a bright crimson colour clearly visible in day-

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* Since the above was written, Rothemund has recorded (*J. Amer. Chem. Soc.*, 1938, **60**, 2005) the emission of light when solutions of chlorphyll or magnesium or zinc salts of porphins in tetralin, xylene, *p*-cymene or bromo*cyclo*hexane are heated.

light; the luminescence persists for 30 secs. or more, the time depending upon the amounts of pigment and peroxide originally present. Particularly suitable are pinene, tetralin, and octalin, the brilliance paralleling the peroxide content as judged by the relative evolution of heat on decomposition with iron phthalocyanine (Part III). The effect is still more pronounced with a prepared solution of tetralin peroxide in tetralin.

In all cases where luminescence is observed oxidation of pigment also takes place, but oxidation, even in those cases where the pigment is known to be potentially active, is not inevitably accompanied by emission of light and indeed the chemiluminescence is certainly dependent on other factors (*e.g.*, solvent and temperature) to a large and possibly preponderating extent. Thus a temperature of 150—180° appears to be necessary even under otherwise favourable conditions; for example, the effect is completely lacking in *cyclo*hexene containing peroxide at its boiling point, is somewhat dull in pinene (b. p. 156°), but brilliant in tetralin (b. p. 208°) and Δ^2-octalin. The luminescence is not quenched by moderate additions of aromatic amines or phenols, or by nitriles (*e.g.*, phenylacetonitrile). In other solvents (paraffin, b. p. 190—200°, decalin, chloronaphthalene, aniline, anisole, phenylacetonitrile, etc.) no emission of light was observed even in presence of benzoyl peroxide, nor could chemiluminescence be induced by substances which, as shown in Part III, are probably oxidised through an intermediate peroxide (*e.g.*, cholesteryl acetate). Nevertheless, in many such instances the pigment is oxidised.

Work on the emission spectra of these substances and their relation to the fluorescence spectra is in progress.

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