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# MECHANISM OF CATALYSIS BY METAL COMPLEXES IN AUTOXIDATION OF AN OLEFIN

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**Abstract**—A preliminary study in the autoxidation of cyclohexene has been made of the mechanism of catalysis by transition metal stearates and phthalocyanines. A study of the working state of catalysts by absorption spectra and ESR spectral measurements during reaction has led to the conclusion that metal stearates participate in the autoxidation by the Haber-Weiss mechanism and that metal ions in two different valence states are associated, bringing about interaction absorption and ESR broadening. It is suggested that metallophthalocyanines participate in the autoxidation in several ways depending on the central metal ion.

## INTRODUCTION

Many papers[1] published on the autoxidation of olefins catalysed by metal salts or complexes have been concerned with the kinetics of oxygen uptake or the production of reaction products or intermediates. Many authors[2–5] have approved the mechanism:

$$\left\{\begin{array}{l} ROOH + M^{+n} \rightarrow RO\cdot + OH^- + M^{+n+1} \\ ROOH + M^{+n+1} \rightarrow ROO\cdot + H^+ + M^{+n} \end{array}\right. \qquad (1)$$

and suggested the formation of metal-hydroperoxide complexes such as $M^{+n}$—ROOH. The state of the catalyst during reaction, i.e., the mode of coexistence of $M^{+n}$ and $M^{+n+1}$ and the structure of the metal-hydroperoxide complex, have scarcely been studied directly, e.g., by structure analysing methods.

This paper reports a preliminary study on the working states of catalysts (stearates of copper, cobalt or manganese and phthalocyanines of copper, cobalt, iron or manganese) in the autoxidation of cyclohexane by means of absorption spectroscopy, ESR spectroscopy and others. Metal stearates have long chain ligands while metallophthalocyanines have a rather rigid planar ligand. It has been suggested that metallophthalocyanines activate the oxygen molecule in autoxidation reactions.[6,7] An attempt has also been made to establish the relationship between the spatial or electronic structure and the catalytic activity of a catalyst.

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[1] Summarized in a recent monograph: *Autoxidation and Antioxidants* (Edited by W. O. Lundberg), Interscience (1961); and a review: E. T. Denisov and N. M. Emanuel, *Usp. Khim.* **29**, 1409 (1960).

[2] A. J. Chalk and F. Smith, *Trans. Faraday Soc.* **53**, 1214 (1957).

[3] M. H. Dean and G. Skirrow, *Trans. Faraday Soc.* **54**, 849 (1958).

[4] D. Benson and L. H. Sutcliffe, *Trans. Faraday Soc.* **55**, 2107 (1959).

[5] H. Berger and A. F. Bickel, *Trans. Faraday Soc.* **57**, 1325 (1961).

[6] N. Uri, *Nature, Lond.* **177**, 1177 (1956).

[7] H. Kropf, *Liebigs Ann.* **637**, 73 (1960).

## RESULTS AND DISCUSSION

### I. *Metal stearates*

The kinetic behaviour of oxygen uptake in these reactions was found to be nearly identical with that of autoxidation of cyclohexene catalysed by metal heptoates as studied by Chalk and Smith.[2] The three stearates studied, except for small differences are similar to each other in catalytic behaviour.

The colour of a reaction mixture, with manganese stearate (abbreviated as $Mn(St)_2$ below) or cobalt stearate ($Co(St)_2$) as catalyst, turns gradually brown during the reaction. Using copper stearate ($Cu(St)_2$) as catalyst, the light blue reaction mixture turns greenish yellow. A precipitate was observed during these reactions; being brown in the case of $Mn(St)_2$ catalyst, greenish brown in the case of $Co(St)_2$, and greenish yellow in the case of $Cu(St)_2$.

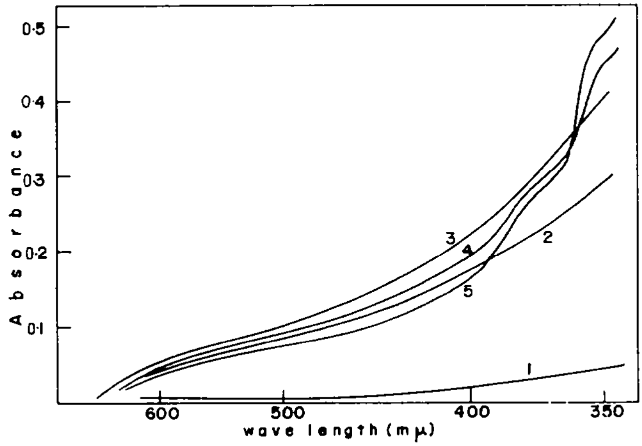

FIG. 1. The absorption spectra during a reaction catalysed by manganese stearate at 60·0°C, at reaction times (1) 0 min, (before addition of cyclohexene), (2) 2 min, (3) 7 min, (4) 50 min, (5) 148 min; $[Mn] = 9{\cdot}6 . 10^{-5}$ mole/l, $RH = 4{\cdot}9 . 10^{-2}$ moles, $[RH] = 3{\cdot}27$ mole/l.

The absorption spectra of a reaction mixture in which $Mn(St)_2$ was the catalyst are shown in Fig. 1; the absorption increased rapidly at first then decreased gradually with time in the visible region, while in the near UV region (<400 mμ) a spectrum with certain fine structures appeared the intensity of which increased with time. Similar spectral changes were also observed using $Co(St)_2$ or $Cu(St)_2$ as catalysts. Addition of t-butyl hydroperoxide to these catalyst solutions brought about similar spectral changes although the spectrum in the near UV region was not observed. This spectrum in the near UV region was found to be due to the cyclohexenone formed and identified by gas chromatography. The rate of oxygen pressure decrease and the absorbance at 460 mμ of the reaction mixture were plotted against reaction time as shown in Fig. 2.

The absorbance at 460 mμ at the maximum point of the absorbance curve in the Fig., $\log I_0/I = 0{\cdot}13$, corresponds to $\log \epsilon = 3{\cdot}1$ per mole of manganese. The optical absorptions of a $Mn^{2+}$ or $Mn^{3+}$ species in the visible region are usually due to forbidden d-d transitions, so that the $\log \epsilon$ value of a $Mn^{2+}$ or $Mn^{3+}$ species is

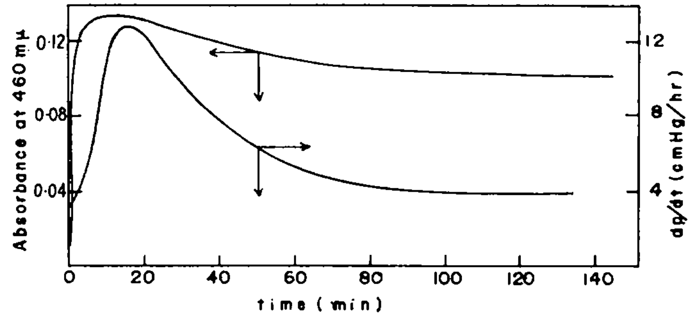

FIG. 2. The changes of absorbance at 460 mμ and rate of oxygen pressure decrease with time in the reaction cited in Fig. 1.

not so large, being 1·69 at 575 mμ for $[Mn(acac)_2(OH_2)_2]^-$.[8] This intense absorption without appreciable fine structure, therefore, cannot be due to $Mn^{2+}$ or $Mn^{3+}$ species only, but due to the interaction between $Mn^{2+}$ and $Mn^{3+}$ species through bridges such as $OH^-$, ketone or alcohol formed, as is often observed in such systems as $Cu^+—Cl^-—Cu^{2+}$,[9] $Fe^{2+}—Cl^-—Fe^{3+}$,[10] and $Sn^{2+}—Cl^-—Sn^{4+}$.[11]

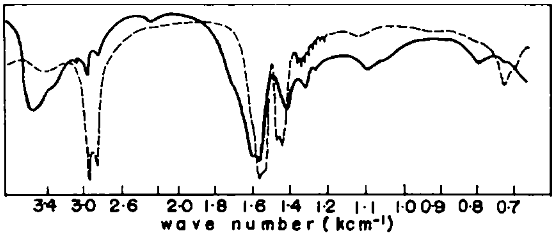

FIG. 3. IR spectra of the precipitate (solid line) and the unused catalyst (dashed line) in the case of $Mn(St)_2$ catalyst.

The gradual decrease of optical absorbance of the reaction mixture shown in Fig. 2 may indicate the loss of such a species giving rise to interaction colour, from the solution in the form of precipitate. A chemical analysis showed that the manganese content of the precipitate was 7·1–9·0 wt%. The IR spectrum of the precipitate as well as that of the unused catalyst is shown in Fig. 3. The bands at 3400 $cm^{-1}$, 1100 $cm^{-1}$ and 800 $cm^{-1}$ in the spectrum of the precipitate, which are not observed in that of the unused catalyst, may be assigned to stretching vibrations of an O—H bond, a C (secondary)—O bond, and out-of-plane deformation vibrations of a C—H bond adjacent to a C=C bond, respectively. Although a weak band at 3400 $cm^{-1}$ is observed in the spectrum of the unused catalyst too, this would be due to moisture adsorbed. The figure also shows that the band at about 1600 $cm^{-1}$ of the precipitate is broader than that of the unused catalyst and that they deviate from one another. This suggests that the precipitate contains another type of carboxyl group than coordinated stearate groups, coordinated carbonyl groups or C=C groups.

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[8] G. H. Cartridge, *J. Amer. Chem. Soc.* 74, 6015 (1952).

[9] H. McConnell and N. Davidson, *J. Amer. Chem. Soc.* 72, 3168 (1950).

[10] H. McConnell and N. Davidson, *J. Amer. Chem. Soc.* 72, 5557 (1950).

[11] C. I. Browne, R. P. Craig and N. Davidson, *J. Amer. Chem. Soc.* 73, 1946 (1951).

The chemical analysis and the IR spectrum, thus, suggest that the composition of the precipitate is approximately $Mn(St)_2(OH^-)(C_6H_9OH)$ or $Mn(St)_2(OH^-)(C_6H_8O)$ (weight content of metal: calc. 7·36 wt% or 7·38 wt%; found 7·1–9·0 wt%). The composition of the precipitate in the case of $Co(St)_2$ or $Cu(St)_2$ catalyst was found to be approximately $M(St)(OH^-)(C_6H_9OH)$ or $M(St)(OH^-)(C_6H_8O)$ (weight content of metal: calc. 12·7%, found 16% for cobalt; calc. 13·5%, found 16% for copper).

Some results of ESR measurement are shown in Table 1 and Fig. 4. The spectra for high concentration of manganese (Table 1) have no hyperfine structures, but hyperfine structures are resolved for lower concentration of manganese (Fig. 4).

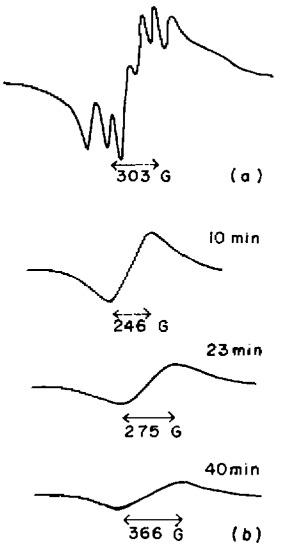


Fig. 4. ESR spectra of the systems: (a) benzene solution of $Mn(St)_2$, at 30°C; $[Mn^{2+}] = 6{\cdot}0 \,.\, 10^{-5}$ mole/l, (b) reaction mixture in benzene at 30°C at reaction times indicated; $[Mn^{2+}]_0 = 4{\cdot}8 \,.\, 10^{-5}$ mole/l, $[RH]_0 = 1{\cdot}5$ mole/l.

Table 1. The results of ESR measurement on manganese stearate catalyst[a]

| Reaction system | Temp (°C) | $(Mn^{2+})_0$ (M) | $(CH)_0$ (M) | Reaction time (min) | $\Delta H_{msl}$ (G) | Intensity |
|---|---|---|---|---|---|---|
| $Mn(St)_2$[b] | 31 | $1{\cdot}2 \,.\, 10^{-4}$ | 0·0 | | 182 | 100[d] |
| $Mn(St)_2 + CH + O_2$[b] | 31 | $1{\cdot}0 \,.\, 10^{-4}$ | 1·5 | 20 | 224 | 79 |
| $Mn(St)_2 + CH + O_2$[c] | 21 | $3{\cdot}5 \,.\, 10^{-4}$ | 2·0 | 7 | 278 | decrease ↓ |
| | | | | 48 | 414 | |
| | | | | 93 | 706 | |
| $Mn(St)_2$ + t-BuOOH[c] | 21 | $3{\cdot}5 \,.\, 10^{-4}$ | | 10 | 640 | |

[a] All the spectra listed here were of a single peak of Lorentian type, almost symmetrical, without hfs. [b] Solvent: benzene. [c] Solvent: 10% ethanol-benzene. [d] For unit concentration of manganese.

The absence of hyperfine structures may be caused in part by association of manganese stearate molecules. In associated state hyperfine lines may coalesce into a single line by exchange interaction. The spectrum of the reaction mixture of low concentration of manganese, which had hyperfine structures before addition of cyclohexane, lost its hyperfine structure, becoming a single broad line that broadened with time (Fig. 4). The spectra of the reaction mixtures without hyperfine structures also broadened with time (Table 1). Addition of t-butyl hydroperoxide broadened the spectrum of manganese stearate, but addition of cyclohexanol (tried in place of cyclohexenol, which was expected to be produced during reaction), cyclohexanone or methylvinyl ketone (in place of cyclohexenone) did not make any appreciable change in the spectrum of manganese stearate solution. A precipitate was not observed within the reaction time in these experiments. These ESR results may be explained as follows:

(1) At room temperature, the spectrum of $Mn^{2+}$ species can be observed, but that of $Mn^{3+}$ species cannot.

(2) $Mn^{2+}$ stearate, when of high concentration, is associated in organic solvents and shows no hyperfine structures on account of exchange interaction.

(3) $Mn^{2+}$ stearate, during reaction, is associated with $Mn^{3+}$ species formed by oxidation of $Mn^{2+}$, and there may be another exchange interaction between their electron clouds direct or via the bridges such as $OH^-$ or cyclohexenol.

(4) The broadening of the spectrum may be due to the life-time effect; i.e., there may be an electron transfer reaction between $Mn^{2+}$ and $Mn^{3+}$ ions in such an associated state or other effects which shorten the life-time of the $Mn^{2+}$ state.

(5) Hydroperoxide, cyclohexanol, cyclohexanone or methylvinyl ketone may coordinate to $Mn^{2+}$ ion, but may not make any appreciable change in its spectrum if it is only coordinated to $Mn^{2+}$ without changing the valence state of the manganese.

Thus, the interpretation that $Mn^{2+}$ and $Mn^{3+}$ coexist during reaction and that they are associated probably in the form of $Mn^{2+}—X—Mn^{3+}$ does not conflict with the results of absorption spectra or ESR spectra.

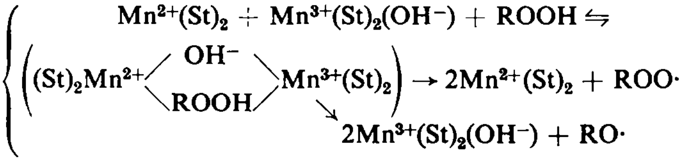
From the results and discussions mentioned, a possible, though not unique nor conclusive mechanism of catalysis for manganese stearate catalyst could be suggested as follows.

Early stage:

$$\mathrm{ROOH} + \mathrm{Mn^{2+}(St)_2} \rightleftharpoons (\mathrm{Mn^{2+}(St)_2(ROOH)}) \rightarrow \mathrm{Mn^{3+}(St)_2(OH^-)} + \mathrm{RO\cdot} \tag{2}$$

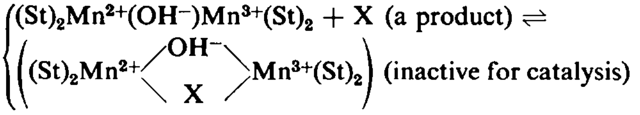
$$\left\{\begin{array}{l} \mathrm{ROOH} + \mathrm{Mn^{3+}(St)_2(OH^-)} \rightleftharpoons (\mathrm{Mn^{3+}(St)_2(OH^-)(ROOH)}) \\ \qquad\qquad\qquad \rightarrow \mathrm{Mn^{2+}(St)_2} + \mathrm{ROO\cdot} + \mathrm{H_2O} \end{array}\right. \tag{3}$$

Intermediate stage:

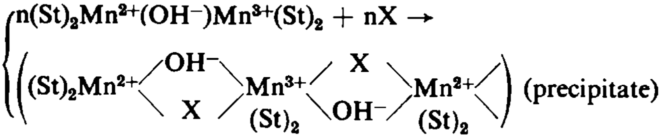


$$\left\{\begin{array}{l} \qquad \mathrm{Mn^{2+}(St)_2} + \mathrm{Mn^{3+}(St)_2(OH^-)} + \mathrm{ROOH} \leftrightarrows \\ \left(\mathrm{(St)_2Mn^{2+}} \begin{array}{c} \mathrm{OH^-} \\ \mathrm{ROOH} \end{array} \mathrm{Mn^{3+}(St)_2}\right) \rightarrow 2\mathrm{Mn^{2+}(St)_2} + \mathrm{ROO\cdot} \\ \qquad\qquad\qquad \searrow 2\mathrm{Mn^{3+}(St)_2(OH^-)} + \mathrm{RO\cdot} \end{array}\right. \tag{4}$$

Later stage:



$$\left\{\begin{array}{l} \mathrm{(St)_2Mn^{2+}(OH^-)Mn^{3+}(St)_2} + \mathrm{X}\ \text{(a product)} \rightleftharpoons \\ \left(\mathrm{(St)_2Mn^{2+}} \begin{array}{c} \mathrm{OH^-} \\ \mathrm{X} \end{array} \mathrm{Mn^{3+}(St)_2}\right)\ \text{(inactive for catalysis)} \end{array}\right. \tag{5}$$



$$\begin{cases} n(St)_2Mn^{2+}(OH^-)Mn^{3+}(St)_2 + nX \rightarrow \\ \left((St)_2Mn^{2+}\langle {}^{OH^-}_{X} \rangle \underset{(St)_2}{Mn^{3+}} \langle {}^{X}_{OH^-} \rangle \underset{(St)_2}{Mn^{2+}} \right) \text{ (precipitate)} \end{cases} \quad (6)$$

In the case of cobalt or copper stearate catalysts, one of the stearate groups attached to a metal ion may be substituted by $OH^-$, another product, or a solvent molecule in the precipitate, as is inferred from the chemical analysis mentioned above.

The rate of oxygen uptake diminished remarkably after a maximum point with the progress of reaction as shown in Fig. 2. This may be due to inhibition by products such as $OH^-$, alcohol or ketone as is shown in the above equations, and in part due to the precipitation of active metal ion.

Recently, Ingold *et al.*[12] reported that the rate of decomposition of tetralin hydroperoxide by $Co(OAc)_2$ depends on the 2nd power of the concentration of $Co(OAc)_2$ in acetic acid or polar solvent, but on the 1st power if it is a weakly polar solvent. This result may reasonably be understood by the mechanism (Eq. 4), in which one obtains:

$$-d[ROOH]/dt = k[ROOH][Co^{2+}{-}X{-}Co^{3+}] \quad (7)$$

In a weakly polar solvent, the position of the equilibrium (8)

$$Co_2^{2+}L_m + X + Co^{3+}L_n \overset{K}{\rightleftharpoons} (LCo^{2+}{-}X{-}Co^{3+}L) + 2L \quad (8)$$

would be almost completely moved to the right of the equation so that

$$[Co_2^{2+}{-}X{-}Co^{3+}] \doteqdot \tfrac{1}{2}[Co]_{total},$$

and therefore,

$$-d[ROOH]/dt \propto [Co]_{total} \quad (9)$$

But as [L] is large in acetic acid, the position of equilibrium would be moved to the left of the equation, so that:

$$[Co^{2+}{-}X{-}Co^{3+}] = K[Co^{2+}][Co^{3+}][X]/[L]^2 = K'[Co]_{total}^2$$

and

$$-d[ROOH]/dt \propto [Co]_{total}^2 \quad (10)$$

## II. *Metallophthalocyanines*

The optical absorption measurement during reaction revealed that FePc (abbreviation of iron phthalocyanine) and CoPc are liable to undergo decomposition by the hydroperoxide formed, that CuPc is not appreciably decomposed within the reaction time (up to 8 hr) and that MnPc is decomposed at a moderate rate. Fig. 5 shows the spectra of the reaction mixtures, the solvent of which was α-chloronaphthalene–benzene. Fig. 6 shows the time course of oxygen pressure change in these reactions. In reactions catalysed by FePc or CoPc, the oxygen uptake seemed to proceed in two stages; the rate of oxygen pressure decrease was nearly constant for a while and then increased. An induction period was observed in reactions catalysed by CuPc. Kinetic results on the rate of oxygen uptake are summarized as follows for MnPc and CuPc (Table 2).

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[12] Y. Kamiya, S. Beaton, A. Lafortune and K. U. Ingold, *Canadian J. Chem.* **41**, 2020, 2034 (1963).

CoPc and FePc are very liable to undergo decomposition by hydroperoxide as mentioned above, but they catalysed the autoxidation together with decomposition. This suggests free radical character of the decomposition according to, for example, the following equation:

$$\mathrm{nROOH} + \mathrm{Fe^{2+}Pc} \rightarrow \mathrm{RO\cdot} + \mathrm{OH^-} + \mathrm{Fe^{3+}X} \tag{11}$$

X, products of the decomposition of Pc group, at first attached to $Fe^{3+}$ would inhibit the access of hydroperoxide to $Fe^{3+}$, but as hydroperoxide accumulated, X would be expelled from the coordination sites of $Fe^{3+}$ and then the reaction would be accelerated.

CuPc is reported to catalyse the autoxidation of cumene by the oxygen activating mechanism of Kropf.[7] A mechanism of initiation similar to that of Kropf can suitably be applied for our case; i.e.,

$$\left\{\begin{array}{l}\mathrm{CuPc} + \mathrm{O_2} \rightleftharpoons (\mathrm{CuPc})^{\delta+}\mathrm{O_2}^{\delta-}\\ (\mathrm{CuPc})^{\delta+}\mathrm{O_2}^{\delta-} + (\mathrm{RH, ROOH}) \rightarrow \mathrm{CuPc} + \mathrm{ROO\cdot} + \mathrm{R\cdot} + \mathrm{H_2O_2}\end{array}\right. \tag{12}$$

This mechanism, together with the usually postulated propagation mechanism and bimolecular termination mechanism, does not conflict with the kinetic result mentioned. The induction period may be the period of hydroperoxide accumulation, which is required by the second reaction of the Eq. (12), or one in which an unknown deactivation reaction of active free radical such as ROO· or RO· predominates. In the complex $(\mathrm{CuPc})^{\delta+}\mathrm{O_2}^{\delta-}$, $\delta$ may not be so large, although Kropf[7] postulated it as unity for the observed spectrum during reaction (Fig. 5c) is not very different from that of CuPc, while the spectrum of $(\mathrm{CuPc})^+$ is reported to be very different from that of CuPc.[13]

Recently it has been reported[14] that MnPc is capable of being in several valence states (+2, +3, +4), depending on solvent, irradiation of light and whether oxygen is present. MnPc prepared by us in air and sublimed in vacuum were greenish black needles, being weakly paramagnetic (1·13 B.M.) and in benzene containing α-chloronaphthalene showed an optical spectrum (Fig. 5d) corresponding to the $(\mathrm{Mn^{III}—OH})\mathrm{Pc}$ denoted by Calvin *et al.*,[14] and a sharp single ESR spectrum ($\Delta H_{msl}$ = 4 Gauss). It is also reported[15] that diamagnetic metallophthalocyanines (NiPc, ZnPc, etc.) show a sharp ESR line. This fact suggests the free radical character or triplet character of the Pc ligand. In α-chloronaphthalene MnPc also may have a free radical character as is inferred from the ESR spectrum. This free radical character of MnPc may bring about catalytic activity for radical autoxidation and the kinetic behaviour of catalysis different from other phthalocyanines (Fig. 6). The addition of cyclohexene under the reaction conditions brought about a slight but definite change in the optical spectrum of MnPc as shown in Fig. 5d. This suggests coordination of RH or ROOH to the central manganese ion. A probable mechanism of initiation is:

$$\left\{\begin{array}{l}(\mathrm{Mn^{3+}—OH})\mathrm{Pc} + \mathrm{XH} \rightleftharpoons (\mathrm{Mn^{3+}—XH})\mathrm{Pc} \text{ or } (\mathrm{Mn^{3+}(OH)XH})\mathrm{Pc}\\ \xrightarrow{+\mathrm{nO_2}} \mathrm{Mn^{3+}Y} + \mathrm{X\cdot} + \mathrm{HO_2}^-\end{array}\right. \tag{13}$$

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[13] A. E. Cahill and H. Taube, *J. Amer. Chem. Soc.* 73, 2847 (1951).

[14] G. Engelsma, A. Yamamoto, E. Markham and M. Calvin, *J. Phys. Chem.* 66, 2517 (1962).

[15] R. Neiman and D. Kivelson, *J. Chem. Phys.* 35, 162 (1961).

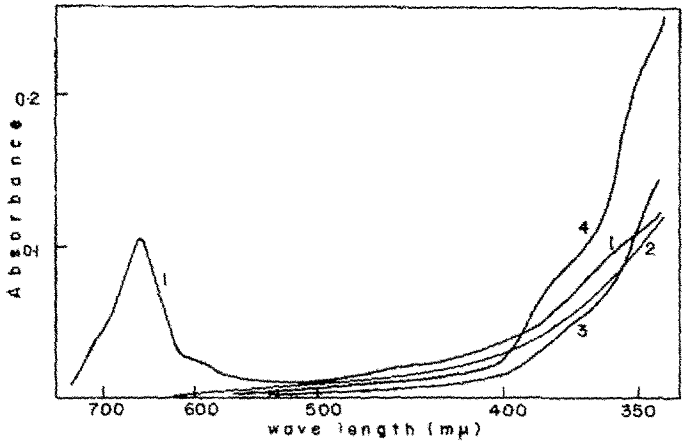

FIG. 5a. Absorption spectra during a reaction catalysed by FePc at 60°C, at reaction times (1) 0 min (before addition of cyclohexene), (2) 4 min, (3) 29 min, (4) 139 min; $[\mathrm{FePc}]_0 = 2{\cdot}1 \,.\, 10^{-6}$ mole/l, RH $= 4{\cdot}9 \,.\, 10^{-2}$ moles, [RH] $= 3{\cdot}27$ mole/l.

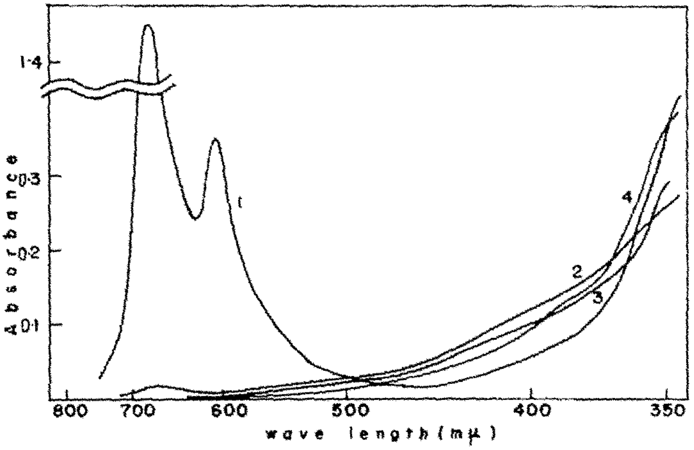

FIG. 5b. Absorption spectra during a reaction catalysed by CoPc at reaction times (1) 0 min, (2) 2 min, (3) 33 min, (4) 108 min; $(\mathrm{CoPc})_0 = 9{\cdot}3 \,.\, 10^{-6}$ mole/l.

Y is one of the decomposition products of Pc. With free radical character Pc may take part in the radical fission of XH like a radical initiator. MnPc, however, was not found to catalyse the autoxidation in pyridine, in which MnPc can form (Mn(IV) = O)Pc according to Calvin *et al.*[14] This fact may be explained by the inhibiting action of pyridine, which occupies the coordination sites of MnPc, making it not accessible for XH.

### III. *Comparison between metal stearates and metallophthalocyanines*

(1) All the transition metal stearates studied participate in the autoxidation by the Haber–Weiss mechanism,[16] (Eq. 1); i.e., they decompose an intermediate product, hydroperoxide, forming free radicals. On the other hand, metallophthalocyanines

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[16] F. Haber and J. Weiss, *Proc. Ror. Soc.* **A147**, 332 (1934).

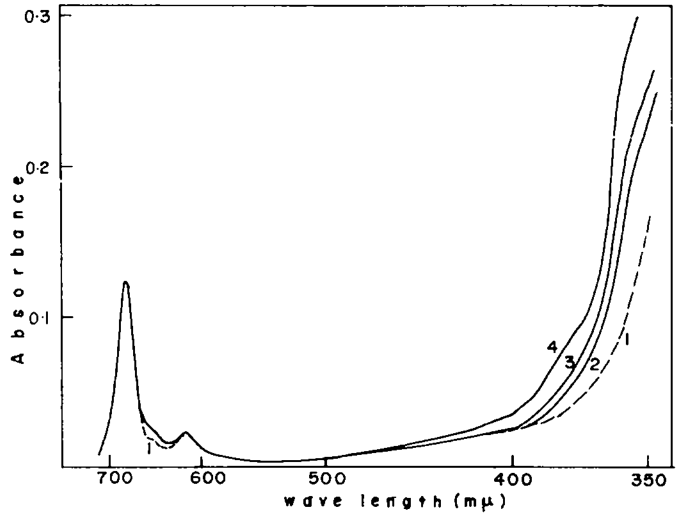

FIG. 5c. Absorption spectra during reaction catalysed by CuPc at reaction times (1) 0 min, (2) 3 min, (3) 33 min, (4) 129 min; $(CuPc)_0 = 5{\cdot}7 \,.\, 10^{-7}$ mole/l.

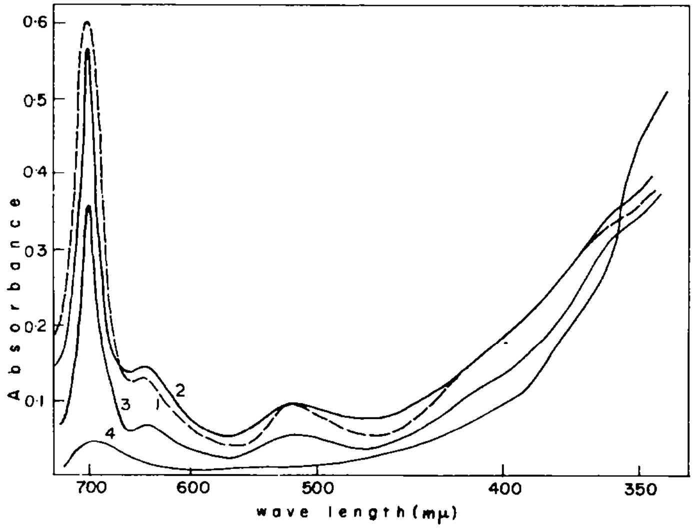

FIG. 5d. Absorption spectra during reaction catalysed by MnPc at reaction times (1) 0 min, (2) 2 min, (3) 49 min, (4) 245 min, $[MnPc]_0 = 1{\cdot}2 \,.\, 10^{-6}$ mole/l.

participate in the autoxidation in several ways. It was suggested that CoPc and FePc are liable to undergo decomposition and decompose hydroperoxide at the same time, that CuPc activates the oxygen molecule, and that MnPc acts like a radical initiator.

(2) These differences in catalysis between metal stearates and metallophthalocyanines may be due to differences in electronic structure. The electronic structure of a transition metal stearate is almost the same as an aquo complex and can easily change its valence by the action of an oxidant or a reductant. When a metallophtalocyanine changes the valence of central metal ion, its electronic structure is so greatly

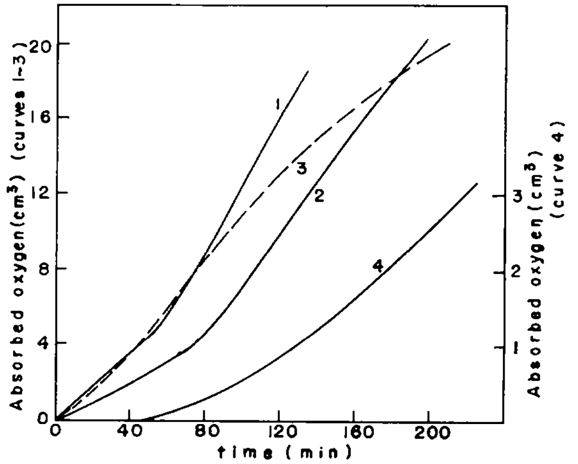

FIG. 6. The time courses of oxygen pressure decrease in the reactions cited in Fig. 5, catalysed by (1) FePc, (2) CoPc, (3) MnPc and (4) CuPc.

TABLE 2. KINETIC EXPRESSION OF OXYGEN UPTAKE RATE
$(-d(O_2)/dt)_{catalyst} = k(catalyst)^m P_{O_2}{}^n$ (at 60°C)

| Catalyst | Range of catalyst concentration (M) | Range of oxygen pressure (mmHg) | m | n |
|---|---|---|---|---|
| CuPc | $7{\cdot}7 \,.\, 10^{-7}$–$1{\cdot}9 \,.\, 10^{-7}$ | 730–275 | 0·4 | 0·5 |
| MnPc | $14 \,.\, 10^{-6}$–$3{\cdot}6 \,.\, 10^{-7}$ | 643–279 | 1·0 | 0·4–0·5 |

affected that its stability may be changed appreciably. Some metallophthalocyanines, therefore, may change valence with difficulty, or be decomposed by oxidation or reduction (CoPc and FePc). Some metallophthalocyanines have an affinity for the oxygen molecule due to a charge transfer from the central metal ion to oxygen, like the oxygen carrying heme enzymes (CuPc and MnPc). Pc is a large pi-electron system, probably with low lying triplet states or a tendency to lose or accept an electron becoming a doublet state. These states may be favourable for initiation of a free radical reaction (MnPc).

## EXPERIMENTAL

Cyclohexane was purified by the method used by Chalk and Smith.[8] Metal stearates were prepared by the reaction between sodium stearate and metal chloride and washed with hot water. Metallophthalocyanines were prepared by usual methods,[17] and purified by sublimation in vacuum. They were identified by comparison of their IR spectra with those obtained by other authors.[18] The rate of oxygen uptake was measured by a constant pressure reaction apparatus, volume change being recorded automatically. The absorption spectra of reaction mixtures and the rate of oxygen pressure decrease were measured at the same time with a vessel equipped with a quartz cell and

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[17] *The chemistry of synthetic dyes and pigments* (Edited by H. A. Lubs). Reinhold (1955).

[18] A. A. Ebert and H. B. Gottlieb, *J. Amer. Chem. Soc.* **74**, 2806 (1952); A. N. Sidorov and A. N Terenin, *Dokl. Akad. Nauk SSSR* **104**, 575 (1955).

a manometer. The ESR spectra of catalyst solutions or reaction mixtures were recorded on a Japan Electron Optics Lab. ESR Spectrometer Model JES-3B.

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