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Catalytic Activity of Metal Polyphthalocyanines in Autoxidation Reactions[1)]

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The oxidation of cumene and acrolein was carried out using metal polyphthalocyanines as a catalyst. The catalyst activated an oxygen molecule to form a phthalocyanine–O_2 complex, which then abstracted the hydrogen atom of a reactant to initiate the oxidation. The catalyst had no effects on the decomposition of cumene hydroperoxide, formed selectively in the oxidation of cumene. The addition of a small amount of pyridine induced a drastic shortening of the induction period as well as a considerable increase in the oxidation rate. The initiation mechanism assumed on the basis of findings on the desorption of oxygen from the catalyst and on the effect of pyridine was confirmed by a kinetic study of the homogeneous liquid-phase oxidation of acrolein.

Metal phthalocyanines have been used as catalysts in the autoxidation of such hydrocarbons as cumene.[2–6)] Kropf proposed that, in the oxidation of cumene below 100 °C, copper phthalocyanine activated a molecular oxygen through its coordination with the metal ion to form a phthalocyanine–O_2 complex, which then abstracted the tertiary hydrogen of cumene to initiate the oxidation.[2)] However, Min'kov and Keier reported that a unimolecular decomposition of cumene hydroperoxide occurred at 40—70 °C, whereas a higher-order decomposition occurred at 90—110 °C; they concluded that the catalytic activity of copper phthalocyanine was associated not with the activation of oxygen, but with the decomposition of the hydroperoxide, over both temperature ranges.[3)] Furthermore, a polymeric metal phthalocyanine (metal polyphthalocyanine, Me-polyPc) was also used as a catalyst in the liquid-phase autoxidation.[5,6)] Inoue *et al.* presumed, in the oxidation of acetaldehyde ethylene acetal, that metal ions, especially Fe(II) ions, located in the conjugated system of phthalocyanines might act as active sites for the activation of oxygen as well as for the decomposition of the hydroperoxide. From the above description, it can be understood that the role of a phthalocyanine catalyst in an autoxidation reaction has not yet been clarified univocally.

In this investigation, many kinds of metal polyphthalocyanines were synthesized and used as catalysts for the decomposition of cumene hydroperoxide and the liquid-phase oxidation of cumene; this was done in order to elucidate how the catalyst affects the activation of oxygen and/or the decomposition of the hydroperoxide. Besides, the results obtained by the kinetic study of the homogeneous liquid-phase oxidation of acrolein supported the proposed initiation mechanism; that is, a phthalocyanine–O_2 complex abstracts the hydrogen atom of a reactant to initiate the oxidation.

Experimental

Materials. The metal polyphthalocyanines were synthesized according to the method reported by Epstein and Wildi.[7)] Copper–Iron polyphthalocyanine, for example, was prepared in the following manner. A mixture of 1,2,4,5-tetracyanobenzene (4.00 g), $CuCl_2$ (0.80 g), $FeCl_2$ (0.70 g), and urea (0.25 g) was ground sufficiently and was then heated at 300 °C under a nitrogen atmosphere for 18 hr. The mixture was then heated for two additional hours at 350 °C. The resulting solid was washed with methanol to remove the unchanged metal chlorides; the catalyst thus obtained will be called a "crude" polyphthalocyanine below. Then the solid was extracted with boiling pyridine until the greenish color of the extract faded out, resulting in the removal of not only monomeric but also oligomeric metal phthalocyanine. The residue was dried and heated at 350 °C/10^{-1} mmHg for 30 hr; this will be called a "purified" polyphthalocyanine.

TABLE 1. ELEMENTAL ANALYSIS OF METAL POLYPHTHALOCYANINES

Me–polyPc	C	H	N
Cu–polyPc			
Found:	57.5%	1.53%	24.4%
Calcd 1:	57.1	1.0	26.7
Calcd 2:	61.9	1.0	28.8
Co–polyPc			
Found:	53.3	1.96	27.1
Calcd 1:	57.8	1.0	27.1
Calcd 2:	61.8	1.0	29.0

Calcd 1 and 2 are obtained as the structure of Me–polyPc is $[Me(C_6H_2(CN)_4)_2]_n$ and $Me(C_6H_2(CN)_4)_4$, respectively.

Eleven kinds of catalysts were obtained as a dark solid-powder and were not dissolved in any organic solvents. No data have been obtained on the molecular weight of the catalysts. Considering that when a monomeric phthalocyanine and a polymeric one in which the degree of polymerization remain low are slightly dissolved in boiling pyridine they assume a characteristic color, the molecular weight of the "purified" catalyst may be quite large. This was also presumed because the IR absorption peak ascribed to the terminal -CN group in the catalysts was not observed.[8)] The results of the elemental analyses of some catalysts are shown in Table 1. If the structure of a Me-polyPc thus obtained is similar to that of a monomeric phthalocyanine, its molecular formula can be expressed as $Me(C_6H_2(CN)_4)_4$. When the degree of polymerization becomes sufficiently large, the expression may be transformed to $[Me(C_6H_2(CN)_4)_2]_n$. The results shown in Table 1 also indicate that the prepared catalysts are highly-polymerized phthalocyanines. The metal contents in Cu–Fe polyPc were measured by the spectrophotometric method reported by Underwood.[9] Copper and iron ions existed in the catalyst in the ratio of 2.7: 4.1, an iron-rich catalyst being thus prepared. The total contents of metal ions in Cu–Fe polyPc were 86 and 160% of the theoretical values when calculated by means of the molecular formulae of $[Me(C_6H_2(CN)_4)_2]_n$ and $Me(C_6H_2(CN)_4)_4$ respectively. However, no data have yet been obtained with respect to the disposition of the two kinds of metal ions in the enlarged conjugated system.

Procedure. The catalytic decomposition of cumene hydroperoxide and the oxidation of cumene were carried out using the apparatus and the procedure described in a previous paper.[10]

The kinetic study of the homogeneous liquid-phase oxidation of acrolein was carried out according to a new method using an oxygen analyzer, model 777, manufactured by the Toshiba-Beckman Co.[11] A 22 ml reactor equipped with a sensor of the analyzer was filled with benzene as a solvent and a certain amount of a catalyst. A solution containing a desirable concentration of oxygen was prepared by bubbling of the corresponding gaseous mixture of oxygen and nitrogen. Immediately after a certain amount of acrolein has been charged into the reactor, the reaction system filled with the solution was closed. The continuous change in the concentration of dissolved oxygen corresponding to the amount of oxygen absorbed was recorded by the analyzer.

The behavior of oxygen on metal polyphthalocyanines was examined in the following manner. A "purified" metal polyphthalocyanine stored under a nitrogen atmosphere was charged into a 100 ml flask and heated at 350 °C/10^{-2} Torr for 5 hr. The catalyst was then cooled to room temperature and allowed to be in contact with pure oxygen for 24 hr. Then the atmosphere was removed again, and the inner pressure was strictly maintained at 2.1×10^{-2} Torr for 3 hr. The temperature was then raised to about 350 °C at a constant rate of 2 °C per min, and the increase in the inner pressure was measured.

Results and Discussion

The decomposition reaction of cumene hydroperoxide was carried out at 82 °C in a *p*-xylene solution. As is illustrated in Fig. 1, cumene hydroperoxide was not decomposed within 4 hr in the presence of "purified" Cu–Fe polyPc, Cu–polyPc, or Fe–polyPc, whereas it was almost completely decomposed after 4 hr using the "crude" Cu–Fe polyPc catalyst. The valency of a transition metal ion or ions can be changed in the conjugated-ring system of a phthalocyanine. When cumene hydroperoxide is catalytically decomposed through the Haber-Weiss mechanism,[12] the catalytic activity generally depends on the redox potential of a metal ion. The redox potentials of monomeric phthalocyanines were obtained in a pyridine solution as −0.98 and −0.49 V *vs.* SCE with regard to iron and cobalt phthalocyanine respectively.[13] Considering that the reduction potential of a hydroperoxide is −0.7 to −0.8 V,[14] a monomeric phthalocyanine, especially iron phthalocyanine, can possibly decompose the hydroperoxide. On the other hand, the potential of a polymeric phthalocyanine may be decreased with the enlargement of the π-electrons conjugated ring system; chelation is recognized to make a metal ion stable and, consequently, to lower the potential. The "purified" metal polyphthalocyanine is considered not to decompose cumene hydroperoxide because of its lower redox potential. The opposite results mentioned above relating to the decomposition of a hydroperoxide may be ascribed to the degree of purification of a metal polyphthalocyanine.

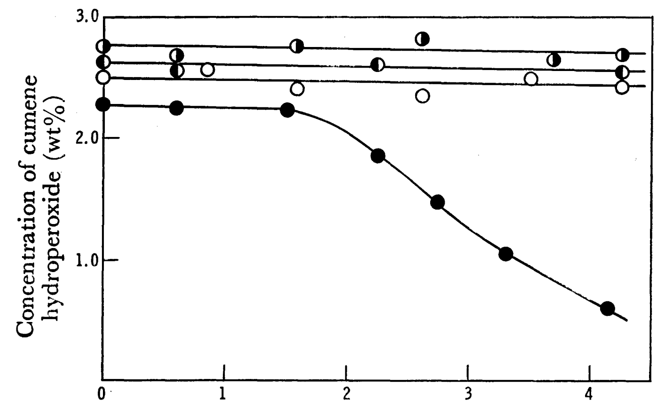

Fig. 1. The decomposition of cumene hydroperoxide by metal polyphthalocyanines. Reaction conditions; Me–polyPc 4.9×10^{-3} M, solvent *p*-xylene, at 81.5°C. ○ Cu–Fe polyPc, ◑ Cu–polyPc, ◐ Fe–polyPc, ● crude Cu–Fe polyPc.

The behavior of oxygen on a metal polyphthalocyanine was examined in order to confirm the mechanism of the activation of oxygen. Oxygen was desorbed from a metal polyphthalocyanine as the temperature rose. The differential pressure per centigrade of the desorbed oxygen is plotted against the temperature in Fig. 2. The first peak of Cu–Fe polyPc was also observed either in the case of Cu–polyPc or Fe–polyPc in the temperature range of 80—150 °C, but the second peak was characteristic of Cu–Fe polyPc. In addition, the first peak of Cu–polyPc existed over a higher temperature range than that of Fe–polyPc. These results imply that a strongly-chemisorbed oxygen existed on a

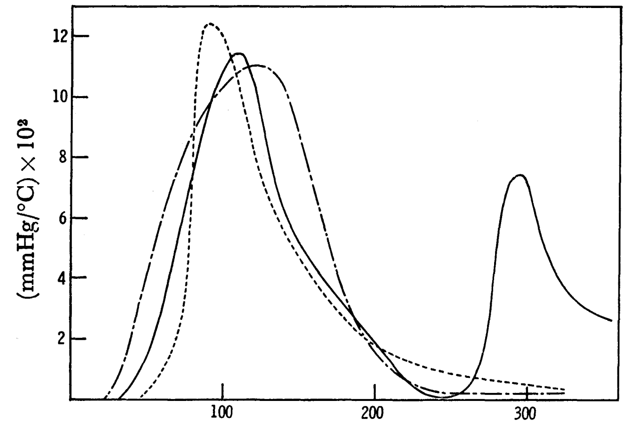

Fig. 2. Desorption of oxygen on metal polyphthalocyanines Me–polyPc 180 mg, —— Cu–Fe polyPc, —·— Cu–polyPc, ------ Fe–polyPc.

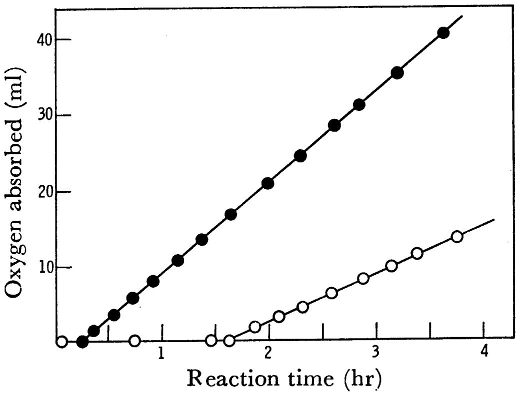

Fig. 3. The oxidation of cumene with Cu–Fe polyPc. Reaction conditions; cumene 0.652 M, Cu–Fe polyPc 4.82×10^{-3} M, in *p*-xylene at 81.5 °C. ● with pyridine, 2.25×10^{-1} M.

metal polyphthalocyanine catalyst, especially on Cu–Fe polyPc; that is, the catalyst activates a molecular oxygen, as has been described by Inoue *et al.*[5]

It was examined in the oxidation of cumene whether or not the activated oxygen could abstract a hydrogen atom to initiate the oxidation. The oxidation of cumene in *p*-xylene was carried out at 82 °C using a metal polyphthalocyanine in the presence and in the absence of pyridine. No oxygen was absorbed without the catalyst for 6 hr, while in the presence of Cu–Fe polyPc the uptake of oxygen started at a steady rate after an induction period of 100 min (Fig. 3). A drastic shortening of the induction period as well as a considerable increase in the oxidation rate were induced by the presence of a small amount of pyridine. A similar absorption curve of oxygen was also obtained when pyridine was added after one hour. The oxidation under the reaction conditions shown in Fig. 3 gave cumene hydroperoxide as the only product. The active oxygen in the hydroperoxide was estimated to be 1.9×10^{-3} mol after a 4 hr reaction time; this amount corresponded to 108% of the amount of oxygen absorbed. This means that a "purified" metal polyphthalocyanine can produce cumene hydroperoxide selectively without its decomposition.

TABLE 2. EFFECT OF METAL IONS IN POLYPHTHALOCYANINES

Metal	$-\mathrm{d}O_2/\mathrm{d}t$ $\times 10^6$ M s^{-1}	Induction period, min
Cu–Fe	2.36	14
Cu–Fe[a)]	2.38	10
Cu–Co	1.76	12
Cu–Mn	1.69	17
Cu	1.51	0
Co	1.41	18
Cr	1.30	8
Fe–Co	1.27	19
Mn	1.26	23
Fe	1.17	5
Co–Mn	1.13	33
Fe–Mn	0.57	16

Reaction conditions were the same as in Fig. 4.
a) under the same reaction condition

Table 2 illustrates the effects of metal ions in polyphthalocyanines on the rate of oxidation and shows that metal polyphthalocyanines including a copper ion are more effective; the order of activity is different from that reported in the oxidation of acetaldehyde ethylene acetal.[5] The active order of copper, iron, and copper–iron polyphthalocyanines is found to correspond to the order of the peak temperature based on the desorption of oxygen from the catalysts, as is shown in Fig. 2. That is to say, the catalysts on which oxygen is chemisorbed more strongly may be active in initiating the oxidation, resulting in an increase in the oxidation rate. This suggests that the metal ion, particularly the copper ion, is effective in forming its complex with oxygen, which may abstract the tertiary hydrogen of cumene.

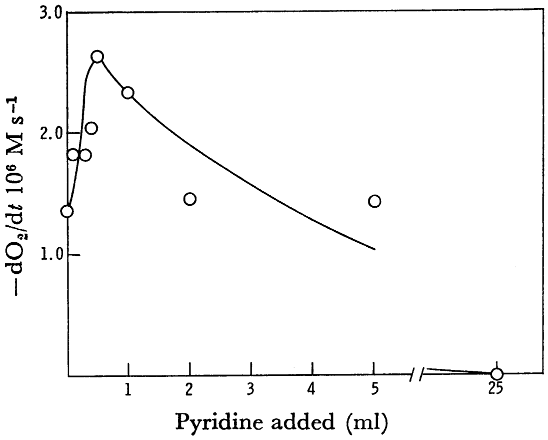

Fig. 4. Effect of pyridine on the rate of oxidation. Reaction conditions; cumene 0.652 M, Cu–Fe polyPc 4.80×10^{-3} M, in *p*-xylene at 81.5 °C, total volume of the solution 55 ml.

The effect of pyridine on the oxidation rate was also examined (Fig. 4). The absorption rate of oxygen varied considerably depending on the amount of pyridine added, though Inoue *et al.* related only a negative effect of added pyridine. The maximum rate was obtained when 0.5 ml of pyridine was added to 55 ml of the total volume of the oxidation solution; this rate was 2.1 times that in the absence of pyridine. The excess addition showed rather a negative effect on the rate, and the oxidation did not proceed over 6 hr in the presence of more than 25 ml of pyridine. Though almost the same absorption rate was given in the case of the addition of 5.0 ml as that observed in the absence of pyridine, the induction period was shortened to 9 min.

With respect to pyridine, Elvidge and Lever found that manganese phthalocyanine could carry an oxygen molecule reversibly in a pyridine solution.[15] Calvin *et al.* explained this oxygen-carrying mechanism by a spectrophotometric method and pointed out the activation of oxygen by the coordination of pyridine at the *trans*-position. The effect of pyridine on this oxidation of cumene, consequently, may also be related to the initiation mechanism with which a metal polyphthalocyanine is concerned. However, the activation mechanism by Calvin *et al.* cannot be applied to a metal polyphthalocyanine, because it is completely insoluble in the reaction solution. As the distance between the layers of the planar crystalline of a monomeric phthalocyanine was reported to be 3.38 Å,17) there is no room for pyridine to enter between the layers of the catalyst to activate a molecular oxygen at the *trans*-position.

On the other hand, Barret *et al.* reported that iron phthalocyanine formed a 1 : 6 adduct with aniline, four molecules of aniline being coordinated with the conjugated system, and two, with the central metal, iron.18) This explanation may make it possible to consider that an adequate amount of pyridine is coordinated with the conjugated-ring system of a metal polyphthalocyanine and acts in the same manner as that at the *trans*-position to facilitate the activation of oxygen at the central metal ions on the surface of the catalyst by moving electrons through the ring system. This can lead to the shortening of the induction periods to approximately 10 min. The excess amount of pyridine may occupy all the coordination sites including metal ions to deactivate the catalyst. The decrease in the oxidation rate upon the addition of more than 5.0 ml of pyridine may be ascribed to the decrease in the amount of available activated oxygen. This consideration is supported by the result that the oxidation did not occur in such solvents as DMF and DMSO, which have higher coordination strengths. Besides, the negative effect of pyridine may be partly attributed to the formation of a charge-transfer complex between the cumylperoxy radical and pyridine, as has been reported by Thomas.19)

The assumed initiation mechanism involving the activation of oxygen by the catalyst is confirmed by the kinetic study. The method of the homogeneous liquid-phase oxidation is suitable for the investigation of the effect of oxygen on the rate of oxidation, because the transfer-process of oxygen from the gas phase to the liquid phase is not involved in the measurement of the absorption rate of oxygen.11) The oxidation of acrolein was studied instead of that of cumene, as the reaction temperature was limited below 45 °C by the use of the oxygen analyzer.

Acrolein was not oxidized even in the presence of Cu–Fe polyPc at 40 °C in benzene; the concentration of dissolved oxygen remained constant over 24 hr. When a small amount of pyridine was added, the concentration of oxygen began to decrease and assymptotically became zero towards the end of the reaction. The effect of pyridine was similar to that described in the oxidation of cumene, and it should be noticed in the case of acrolein that the presence of pyridine was indispensable to the initiation of the oxidation. The kinetic study was carried out with pyridine (5.6×10^{-1} M), where the accelerating effect on the rate was observed.

Assuming that the autoxidation proceeds through the known chain mechanism including the assumed initiation step, the stationary-state treatment gives the following theoretical rate equation:

$$\mathrm{RH} + \mathrm{cat} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{R\cdot}$$

$$\mathrm{R\cdot} + \mathrm{O_2} \xrightarrow{k_2} \mathrm{RO_2\cdot}$$

$$\mathrm{RO_2\cdot} + \mathrm{RH} \xrightarrow{k_3} \mathrm{RO_2H} + \mathrm{R\cdot}$$

$$\left.\begin{array}{l} 2\mathrm{R\cdot} \xrightarrow{k_4} \\ \mathrm{R\cdot} + \mathrm{RO_2\cdot} \xrightarrow{k_5} \\ 2\mathrm{RO_2\cdot} \xrightarrow{k_6} \end{array}\right\} \text{non-radical products}$$

where RH denotes the acrolein molecule

$$-\mathrm{dO_2}/\mathrm{d}t = [k_1(\mathrm{RH})(\mathrm{cat})(\mathrm{O_2})]^{1/2} \times \frac{k_2 k_4^{-1/2}(\mathrm{RH})(\mathrm{O_2})}{(\mathrm{RH}) + (k_2 k_4^{-1/2}/k_3 k_6^{-1/2})(\mathrm{O_2})}$$

The rate constant, $k_2 k_4^{-1/2}$ and $k_3 k_6^{-1/2}$, have been reported to be 3.7×10 and 5.5×10^{-2} ($\mathrm{M^{-1/2}\,s^{-1/2}}$) respectively in the oxidation initiated by di-*t*-butyl diperoxyoxalate in benzene at 40 °C.20) Consequently, the k_1 constant can be calculated under various reaction conditions (Table 3). Runs 1—4 show the effect of the catalyst concentration. The decrease in the chain length with the increase in the catalyst concentration may be partly ascribed to the termination of radicals by the catalyst, considering that a negative catalyst effect21) was observed at higher concentrations of the catalyst. Runs 1 and 5—7 show the dependence on the concentration of acrolein. In the case of a constant concentration of the catalyst, the chain length was given as close to 30. The k_1 constant is given as $(6.3 \pm 0.3) \times 10^{-2}$ $\mathrm{M^{-2}\,s^{-1}}$ under all the reaction conditions.

TABLE 3. EFFECT OF THE CONCENTRATION OF ACROLEIN AND THE CATALYST ON THE RATE OF OXIDATION

Run	$-\mathrm{dO_2}/\mathrm{d}t$ $\times 10^6$ $\mathrm{M\,s^{-1}}$	(RH) M	$(\mathrm{O_2})^{a)}$	(cat)	R_i $\times 10^8$ $\mathrm{M\,s^{-1}}$	Chain length	k_1 $\times 10^2$ $\mathrm{M^{-2}\,s^{-1}}$
			$\times 10^3$ M				
1	5.10	0.34	1.39	4.72	13.7	37	6.1
2	3.55	0.34	1.39	2.31	6.6	54	6.1
3	2.64	0.34	1.39	1.22	3.7	72	6.3
4	1.85	0.34	1.20	0.76	2.0	94	6.3
5	14.3	0.48	3.05	4.72	45.1	32	6.6
6	3.00	0.20	1.63	4.72	10.0	30	6.4
7	1.49	0.14	1.30	4.72	5.3	28	6.3

a) The concentration of oxygen at which the rate of oxidation reached maximum. Reaction conditions: amount of pyridine added, 1.0 ml; 40 °C in benzene; initial concentrations of oxygen were set as about 2.0×10^{-3} M except the case of the run 5.

The influence of the concentration of oxygen can be determined in an experiment in the homogeneous liquid-phase oxidation. In Run 5, the oxidation rate decreased with the decrease in the concentration of oxygen after a certain induction period. During the oxidation, the change in the concentration of acrolein was negligible because the ratio of the concentration of acrolein to that of oxygen was set as about 10^2. The theoretical rate equation can be transformed as follows:

$$-\mathrm{dO_2}/\mathrm{d}t = \frac{k_1^{1/2} k_2 k_4^{-1/2} A^{3/2} B^{1/2} (\mathrm{O_2})^{3/2}}{A + (k_2 k_4^{-1/2}/k_3 k_6^{-1/2})(\mathrm{O_2})}$$

where A and B denote the concentrations of acrolein (0.48 M) and the catalyst (4.72×10^{-3} M) respectively. Then k_1 can be calculated from the differential value

TABLE 4. EFFECT OF THE CONCENTRATION OF OXYGEN ON THE RATE OF OXIDATION

(O_2) $\times 10^3$ M	$-dO_2/dt^{a)}$ $\times 10^6$ M s^{-1}	R_i $\times 10^8$ M s^{-1}	Chain length	k_1 $\times 10^2$ M^{-2} s^{-2}
3.05	14.3	45.1	32	6.6
2.67	13.1	39.7	33	6.6
2.29	11.6	33.6	33	6.5
1.91	10.2	28.5	36	6.6
1.53	8.57	22.9	37	6.7
1.14	6.67	17.0	39	6.6
0.76	4.50	11.0	41	6.4
0.38	2.21	5.8	38	6.8

a) The rate of oxidation at each concentration of oxygen. Reaction conditions: initial concentration of acrolein, 0.48 M; of the catalyst, 4.7×10^{-3} M; and of oxygen, 6.8×10^{-3} M (0.89 atm. of partial pressure of oxygen); pyridine added, 1.0 ml; 40 °C in benzene.

of the decreasing curve of oxygen (rate of oxidation) at each concentration of oxygen (Table 4). The k_1 constant is given as $(6.6\pm 0.2)\times 10^{-2}$ M^{-2} s^{-1} over the range of concentration of oxygen from 0.38 to 3.05×10^{-3} M.

The value of k_1 did not change with the change in the concentrations of the catalyst, acrolein and oxygen, which supported the initiation mechanism: a phthalocyanine–O_2 complex abstracts the hydrogen of a reactant to initiate the oxidation.

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