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THE OXIDATION OF ACROLEIN CATALYZED BY A METAL POLYPHTHALOCYANINE

Takao HARA, Yasukazu OHKATSU,* and Tetsuo OSA*
Department of Chemistry, Faculty of Engineering, Yokohama National University, Ohoka, Minami-ku, Yokohama 233
*Department of Industrial Chemistry, Faculty of Engineering, the University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Kinetic studies on the homogeneous liquid-phase oxidation of acrolein using a metal polyphthalocyanine as a catalyst revealed that the rate of chain initiation (Ri) can be expressed as Ri = k_1(acrolein)(cat)(O_2). The rate constant k_1 is determined as $(6.3 \pm 0.3) \times 10^{-2}$ $M^{-2}sec^{-1}$ at 40 °C in benzene. The result may indicate that a phthalocyanine - O_2 complex abstracts the aldehyde hydrogen to initiate the oxidation.

In the previous paper,1) it was reported that a metal polyphthalocyanine (Me-polyPc) catalyzes the oxidation of cumene by activating an oxygen molecule to form a phthalocyanine - O_2 complex, which abstracts the tertiary hydrogen of cumene to initiate the reaction. In the present work, the proposed initiation mechanism is confirmed by the kinetic study in the oxidation of acrolein. The kinetic study on the homogeneous liquid-phase oxidation was carried out according to the new method using the oxygen analyzer of 777 model manufactured by Toshiba - Beckman Co.2) A 22 ml reactor equipped with the sensor of the analyzer was filled up with benzene as a solvent and a certain amount of the catalyst. The solution containing a desirable concentration of oxygen was prepared by bubbling corresponding gaseous mixture of oxygen and nitrogen. Immediately after a certain amount of acrolein was charged into the reactor, the reaction system filled with the solution was closed. The continuous change of the concentration of dissolved oxygen corresponding to the amount of oxygen absorbed was recorded by the 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 hours. When a small amount of pyridine was added, the concentration of oxygen began to decrease and became asymptotically zero towards the end of the reaction. The effect of pyridine was similar with that reported in the oxidation of cumene, and in the case of acrolein it should be noticed that the presence of pyridine was indispensable to initiate 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 initiation step proposed in the previous paper,$^{1)}$ the stationary state treatment gives the following theoretical rate equation.

$$
\begin{aligned}
&\mathrm{RH} + \mathrm{cat} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{R\cdot} \\
&\mathrm{R\cdot} + \mathrm{O_2} \xrightarrow{k_2} \mathrm{RO_2\cdot} \\
&\mathrm{RO_2\cdot} + \mathrm{RH} \xrightarrow{k_3} \mathrm{RO_2H} + \mathrm{R\cdot} \\
&2\ \mathrm{R\cdot} \xrightarrow{k_4} \\
&\mathrm{R\cdot} + \mathrm{RO_2\cdot} \xrightarrow{k_5} \text{non radical products} \\
&2\ \mathrm{RO_2\cdot} \xrightarrow{k_6}
\end{aligned}
$$

where RH denotes acrolein molecule

$$
-d\mathrm{O_2}/dt = [\, k_1(\mathrm{RH})(\mathrm{cat})(\mathrm{O_2})]^{1/2}\ \frac{k_2k_4^{-1/2}(\mathrm{RH})(\mathrm{O_2})}{(\mathrm{RH}) + (k_2k_4^{-1/2}/\ k_3k_6^{-1/2})(\mathrm{O_2})}
$$

The rate constants, $k_2k_4^{-1/2}$ and $k_3k_6^{-1/2}$, are reported as 3.7×10 and 5.5×10^{-2} ($M^{-1/2}\mathrm{sec}^{-1/2}$) respectively, in the oxidation initiated by di-t-butyl diperoxyoxalate in benzene at 40 °C.$^{3)}$ Consequently the constant k_1 can be calculated in various reaction conditions (Table 1). Runs 1-4 show the effect of the catalyst concentration. The decrease of chain length with the increase of the catalyst concentration may be partly ascribed to the termination of radicals, considering that the negative catalyst effect$^{4)}$ 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, chain length was given as close to 30, the value of which showed a good accordance with that obtained in the oxidation catalyzed by $\mathrm{Co(acac)_3}$.$^{5)}$ The constant k_1 is given as $(6.3 \pm 0.3) \times 10^{-2}\ M^{-2}\mathrm{sec}^{-1}$ in each reaction condition.

The influence of the concentration of oxygen can be determined in an experiment in the homogeneous liquid-phase oxidation. In the run 5, the oxidation rate decreased with the decrease of the concentration of oxygen after some induction period. During the oxidation, the change of the concentration of acrolein could be 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 replaced as follows :

$$-dO_2/dt = k_1^{1/2}k_2k_4^{-1/2}A^{3/2}B^{1/2}(O_2)^{3/2} \ / \ [\ A + (k_2k_4^{-1/2}/k_3k_6^{-1/2})(O_2)],$$

where A and B denote the concentration of acrolein (0.48 M) and the catalyst (4.72×10^{-3} M), respectively. Then k_1 can be calculated from the differential value of the decreasing curve of oxygen (the rate of oxidation) at each concentration of oxygen (Table 2). The constant k_1 is given as $(6.6 \pm 0.2) \times 10^{-2}$ M^{-2} sec^{-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 of concentrations of the catalyst, acrolein and oxygen, which supported the initiation mechanism proposed previously : a phthalocyanine - O_2 complex abstracts hydrogen of a reactant to initiate the reaction.

Table 1. Effect of the concentrations of acrolein and the catalyst on the rate of oxidation

Run	$-dO_2/dt$ $\times 10^6$ M sec^{-1}	(RH) M	$(O_2)^*$ $\times 10^3$ M	(cat) $\times 10^3$ M	Ri $\times 10^8$ M sec^{-1}	Chain length	k_1 $\times 10^2$ M^{-2} sec^{-1}
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

*The concentration of oxygen at which the rate of oxidation reaches 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.

Table 2. Effect of the concentration of oxygen on the rate of oxidation

(O_2) x10^3 M	$-dO_2/dt^*$ x10^6 Msec^{-1}	Ri x10^8 Msec^{-1}	Chain length	k_1 x10^2 M^{-2}sec^{-1}
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

*The rate of oxidation at each concentration of oxygen.

Reaction conditions : initial concentration of acrolein, 0.48 M; of the catalyst, 4.7 x10^{-3} M; and of oxygen, 6.8 x10^{-3} M (0.89 atm. of partial pressure of oxygen), pyridine added, 1.0 ml; 40 °C in benzene.

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