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Liquid-phase Oxidation of Anthracene in Acetic Acid by Use of Copper(II) Chlorocomplexes. II.[1] Kinetic Study

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A kinetic study was performed on the oxidation of anthracene by use of copper(II) chlorocomplexes, which were produced in reactions of copper(II) acetate with lithium chloride in acetic acid. When the pressure of oxygen was high enough that the rate of oxidation was not affected, the result was as follows:

$$-\frac{dO_2}{dt} \propto [RH]^1\,[Cu_2(OAc)_4]_0^{1/2}\,[LiCl]_0^{1/2-0}.$$

A kinetic approximation to the experimental result was attempted.

It is known that metal ions[2–4] decompose hydroperoxides and that metal ions[5,6] in their higher valency may oxidize substrates and generate free radicals.

$$ROOH + M^{(n+1)+} \xrightarrow{k_1} ROO\cdot + H^+ + M^{n+} \qquad (1)$$

$$ROOH + M^{n+} \xrightarrow{k_2} RO\cdot + OH^- + M^{(n+1)+} \qquad (2)$$

$$RH + M^{(n+1)} \xrightarrow{k_3} RH^{\dagger} + M^{n+} \qquad (3)$$

$$RH^{\dagger} \xrightarrow{k_4} R\cdot + H^+ \qquad (4)$$

On the other hand, it is known that copper(II) chlorocomplexes[7–19] are formed in reactions of Cu^{2+} with Cl^- in molten salts, and in aqueous and nonaqueous solutions. We previously reported that liquid-phase oxidation[1] of anthracene was effected by these chlorocomplexes, producing mainly anthraquinone. It is interesting to learn the role of these chlorocomplexes at the initiation stage of the oxidation.

The mechanism of autoxidation of anthracene is complex and not yet clearly explained in spite of great interest. In this paper, we report a kinetic study of the oxidation of anthracene by use of copper(II) chlorocomplexes formed by the reactions of copper(II) acetate with lithium chloride in acetic acid.

Experimental

The experimental procedures were the same as those described in the previous paper,[1] with the following exceptions. Gas compositions of the mixtures of oxygen and nitrogen in the reaction vessels were determined on a Yanagimoto model GCG 550-TF gas chromatograph with TCD detector, using helium gas as a carrier. The reactions were performed according to the method of Morimoto and Ogata.[20] The reactions, except for the experiments on the effect of partial pressure of oxygen, were performed under 6.1×10^{-1} bar partial pressure of oxygen, at which pressure the rates of oxidations were not affected. Iodometry was performed in a nitrogen atmosphere.

Results and Discussion

Kinetics. How the initial rates of oxygen absorption depend on concentrations of anthracene, initially added copper(II) acetate, and initially added lithium chloride is shown in Table 1. The rate is expressed as

$$-\frac{dO_2}{dt} = k_{obsd}[RH]^1\,[Cu_2(OAc)_4]_0^{1/2}\,[LiCl]_0^{1/2}$$

Table 1. Effect of concentrations of anthracene, copper(II) acetate, and lithium chloride on initial rate of oxygen absorption at 90 °C

$\frac{[RH]}{\text{mol dm}^{-3}}$	$\frac{[Cu_2(OAc)_4]_0}{\text{mol dm}^{-3}}$	$\frac{[LiCl]_0}{\text{mol dm}^{-3}}$	$\frac{-dO_2/dt}{\text{mol dm}^{-3}\,\text{s}^{-1}}$	$\frac{k_{obsd}}{\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$	$\frac{k'_{obsd}}{\text{dm}^{3/2}\,\text{mol}^{-1/2}\,\text{s}^{-1}}$
0.008	0.0050	0.010	4.5×10^{-7}	7.9×10^{-3}	7.9×10^{-4}
0.010	0.0050	0.010	5.7×10^{-7}	8.1×10^{-3}	8.1×10^{-4}
0.020	0.0050	0.010	1.1×10^{-6}	7.7×10^{-3}	7.7×10^{-4}
0.030	0.0050	0.010	1.7×10^{-6}	7.9×10^{-3}	7.9×10^{-4}
0.040	0.0050	0.010	2.3×10^{-6}	8.0×10^{-3}	8.0×10^{-4}
0.050	0.0050	0.010	2.9×10^{-6}	8.2×10^{-3}	8.2×10^{-4}
0.050	0.0005	0.010	8.4×10^{-7}	7.5×10^{-3}	7.5×10^{-4}
0.050	0.0010	0.010	1.3×10^{-6}	7.9×10^{-3}	7.9×10^{-4}
0.050	0.0033	0.010	2.4×10^{-6}	8.4×10^{-3}	8.4×10^{-4}
0.050	0.0100	0.010	4.2×10^{-6}	8.4×10^{-3}	8.4×10^{-4}
0.050	0.0050	0.001	8.3×10^{-7}	7.4×10^{-3}	—
0.050	0.0050	0.002	1.2×10^{-6}	7.5×10^{-3}	—
0.050	0.0050	0.003	1.6×10^{-6}	8.1×10^{-3}	—
0.050	0.0050	0.005	2.1×10^{-6}	8.2×10^{-3}	—
0.050	0.0050	0.015	2.9×10^{-6}	—	8.2×10^{-4}
0.050	0.0050	0.020	2.9×10^{-6}	—	8.2×10^{-4}
0.050	0.0050	0.030	2.9×10^{-6}	—	8.2×10^{-4}

at $[LiCl]_0$ of 0.0001—0.01 mol dm^{-3}. The rate is

$$-\frac{dO_2}{dt} = k'_{obsd}[RH]^1\,[Cu_2(OAc)_4]_0^{1/2}$$

at $[LiCl]_0$ of 0.01—0.03 mol dm^{-3}. The rate shows zeroth-order dependence with respect to $[LiCl]_0$ in a large excess of $[LiCl]_0$. The dependency of this rate on the partial pressure of oxygen is shown in Fig. 1. The rate was nearly proportional to the partial pressure of oxygen of 1.3×10^{-1}—4.8×10^{-1} bar, while the rate was zeroth-order with respect to the partial pressure of oxygen of 4.8×10^{-1}—6.1×10^{-1} bar.

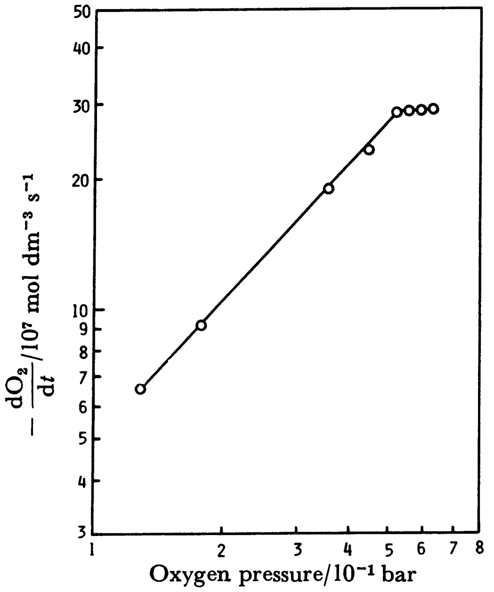


Fig. 1. Effect of oxygen pressure on initial rate of oxygen absorption at 90 °C.
[RH]: 0.05 mol dm^{-3}, $[Cu_2(OAc)_4]_0$: 0.005 mol dm^{-3}, $[LiCl]_0$: 0.01 mol dm^{-3}.

Reaction. No induction period was observed. The possibility of the accumulation of peroxide was investigated at [RH] of 0.05 mol dm^{-3} under the high pressure of oxygen. The amount of peroxide in the solution was determined to be very small on the basis of iodometry, taking the consumption of sodium thiosulfate by the initially added copper(II) acetate into account. Since the variation of the spectrum at the early stage of the reaction was small, there was presumably no prominent variation in kinds or amounts of species of copper(II) salts and copper(II) chlorocomplexes during this period. The amount of oxygen absorption was measured during the period, and the rate of oxygen absorption was calculated. After the period, the absorption near 685 nm was found to increase. This was because a portion of the copper(II) chlorocomplexes or of the monomer of copper(II) acetate changed to the dimer[21,22] of copper(II) acetate again.

Kinetic Approximation. On the basis of kinetics, a tentative mechanism was deduced. M^{2+} and M^+ represent copper(II) ion as active species and copper(I) ion as active species, respectively. Within the range of $[LiCl]_0$ of 0.001—0.01 mol dm^{-3}, the following is assumed:

$$[M^{2+}] \propto [Cu_2(OAc)_4]_0^{1/2}\,[LiCl]_0^{1/2}.$$

And within the range of $[LiCl]_0$ of 0.01—0.03 mol dm^{-3}, the following is assumed:

$$[M^{2+}] \propto [Cu_2(OAc)_4]_0^{1/2}.$$

As shown in Eqs. 3 and 4, RH may react with M^{2+} to give R·.[23,24] R· and oxygen molecule combine to give ROO·.

$$R\cdot + O_2 \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} ROO\cdot \qquad (5)$$

ROO· reacts with RH to give ROOH and R·.

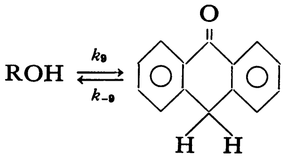
$$ROO\cdot + RH \xrightarrow{k_6} ROOH + R\cdot \qquad (6)$$

As shown in Eqs. 1 and 2, ROOH reacts with M^{2+} and M^+. RO· is generated from ROO· and then reacts with RH.

$$2ROO\cdot \xrightarrow{k_7} 2RO\cdot + O_2 \qquad (7)$$

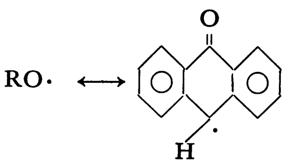
$$RO\cdot + RH \xrightarrow{k_8} ROH + R\cdot \qquad (8)$$

Equation 9 has been reported for the keto-enol tautomerism between 9-anthrol and anthrone.[25-28]

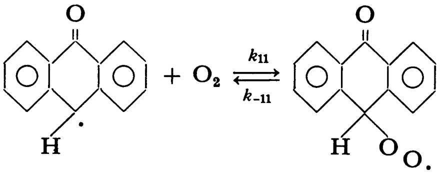


(9)

RO· resonates in the following way and may react with an oxygen molecule.[29-32]

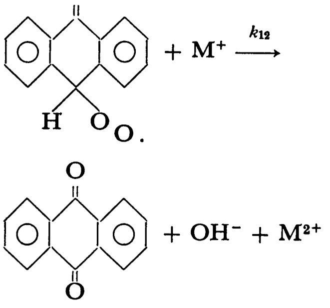


(10)



(11)

By reference to works,[32-34] we thought that the peroxyl radical may react with M^+.



(12)

Steady-state treatment is applied in Eqs. 1—12. On the basis of the experimental results,

$$\frac{d[ROOH]}{dt} \approx 0,$$

$$-\frac{d[M^{2+}]}{dt} \approx 0.$$

Therefore,

$$-\frac{\mathrm{d}O_2}{\mathrm{d}t} \approx (k_1[\mathrm{ROOH}]\,[\mathrm{M}^{2+}] + k_3[\mathrm{RH}]\,[\mathrm{M}^{2+}])$$

$$\times\left(\frac{3}{2} + \frac{1+\dfrac{k_{-11}}{k_{12}[\mathrm{M}^+]}}{2k_{11}[\mathrm{O}_2]} \times k_8[\mathrm{RH}]\right),$$

$$\frac{\mathrm{d}[\mathrm{anthraquinone}]}{\mathrm{d}t} \approx k_1[\mathrm{ROOH}]\,[\mathrm{M}^{2+}] + k_3[\mathrm{RH}]\,[\mathrm{M}^{2+}],$$

$$\frac{\mathrm{d}[\mathrm{anthrone}]}{\mathrm{d}t} \approx \frac{1+\dfrac{k_{-11}}{k_{12}[\mathrm{M}^+]}}{k_{11}[\mathrm{O}_2]}$$

$$\times k_8(k_1[\mathrm{ROOH}]\,[\mathrm{M}^{2+}] + k_3[\mathrm{RH}]\,[\mathrm{M}^{2+}])\,[\mathrm{RH}].$$

Since, on the basis of the experimental result, [ROOH] may be very small,

$$\frac{k_3[\mathrm{RH}]}{[\mathrm{ROOH}]} \gg k_1.$$

The relation between the rate of production of anthrone and the rate of production of anthraquinone is represented:

$$\frac{\mathrm{d}[\mathrm{anthrone}]}{\mathrm{d}t} = G \times \frac{\mathrm{d}[\mathrm{anthraquinone}]}{\mathrm{d}t},$$

where G is a function. Therefore,

$$\frac{-\dfrac{\mathrm{d}O_2}{\mathrm{d}t}}{\dfrac{\mathrm{d}[\mathrm{anthraquinone}]}{\mathrm{d}t}} \approx \frac{1}{2}(3 + G).$$

Here, G may be determined experimentally. For example, G is nearly constant at the early stage of the oxidation shown in Fig. 1,[1] with a value of around 1.4. Therefore, at the early stage of the oxidation,

$$-\frac{\mathrm{d}O_2}{\mathrm{d}t} \approx 2.2k_3[\mathrm{RH}]\,[\mathrm{M}^{2+}],$$

$$\frac{\mathrm{d}[\mathrm{anthraquinone}]}{\mathrm{d}t} \approx k_3[\mathrm{RH}]\,[\mathrm{M}^{2+}],$$

$$\frac{\mathrm{d}[\mathrm{anthrone}]}{\mathrm{d}t} \approx 1.4k_3[\mathrm{RH}]\,[\mathrm{M}^{2+}],$$

$$\frac{-\dfrac{\mathrm{d}O_2}{\mathrm{d}t}}{\dfrac{\mathrm{d}[\mathrm{anthraquinone}]}{\mathrm{d}t}} \approx 2.2.$$

The results of these calculations fit the experimental facts in Fig. 1.[1]

Further, selective production of anthraquinone without production of anthrone could be explained in this mechanism without Eqs. 8 and 9; in this case no approximation is necessary.

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