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Liquid-phase Oxidation of Anthracene in Acetic Acid by Copper(II) Chloro Complexes

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Synopsis. Copper(II) chloro complexes contribute to the liquid-phase oxidation of anthracene in acetic acid. Products of the oxidation were anthrone, anthraquinone, 9-acetoxyanthracene, and 9-chloroanthracene.

It is known that the copper(II) chloro complexes[1-4] are formed by the reactions of copper(II) salts with alkali chlorides both in aqueous and nonaqueous solutions. Although the catalytic activities of copper(II) salts in liquid-phase oxidation are generally low, it was observed that the addition of lithium chloride highly improved the activity of copper(II) acetate in liquid-phase oxidation. No chain reaction in liquid-phase oxidation of a polynuclear aromatic hydrocarbon had been reported before the work[5] of Mahoney. There appears to be general agreement that a polynuclear aromatic hydrocarbon is not readily oxidized in liquid-phase oxidation. In this paper, the activities of copper(II) chloro complexes and the reaction products in the liquid-phase oxidation of anthracene are reported.

Experimental

Materials. Acetic acid was distilled after refluxing with $KMnO_4$. The water content in the distllate was determined by the Karl-Fischer method and the water removed with the equivalent amount of acetic anhydride. Copper(II) acetate (reagent grade) and lithium chloride (reagent grade) were dried at 115 and 120 °C in vacuum respectively. Lithium acetate (reagent grade) was used without further purification. Commercial oxygen was purified by passing through 30% aqueous potassium hydroxide solution and concd sulfuric acid. Anthracene was dissolved in xylene, the solution poured into methanol and the precipitated anthracene dried in vacuum.

Oxidation Procedure. Oxidation was performed in a closed system using an apparatus equipped with a gas burette and oxygen absorption was followed by a manually controlled gas burette filled with mercury. The reaction was performed under the partial pressure of oxygen by which the rate of the oxidation was not affected.

Measurements. UV and visible absorption spectra were recorded with a Hitachi spectrophotometer model 124. The water content in acetic acid was determined with a Karl-Fischer apparatus, Kyoto Electronic Industry Ltd. MK-SS.

Analyses of Reaction Products. The reaction mixture was diluted with water and extracted with benzene which was removed in vacuum. The extracts were analyzed with a Yanagimoto model 550-TF gas chromatograph using a 2.25 m column of 30% Apieason grease L on Celite 545 at 190 °C and a 2 m column of 10% Silicone OV-17 on Chromosorb WAW at 230 °C. Gas-mass spectral analysis was performed with a JEOL model JMSD100-JGC20K spectrometer equipped with a 2 m column of 10% Silicone OV-17 on Chromosorb WAW.

Results and Discussion

Effect of Copper(II) Chloro Complexes. The following equilibrium exists in a mixture of acetic acid and lithium chloride.

$$AcOH + LiCl \rightleftarrows LiOAc + HCl \qquad (1)$$

In a mixture of copper(II) acetate and hydrogen chloride, the following equilibria[4] have been proposed.

$$Cu_2(OAc)_4 + 2HCl \rightleftarrows 2CuCl(OAc) + 2AcOH \qquad (2)$$

$$Cu_2(OAc)_4 + 4HCl \rightleftarrows 2CuCl_2 + 4AcOH \qquad (3)$$

Further, the following equilibria[4] in a mixture of lithium chloride and copper(II) chloride in acetic acid have also been reported.

$$CuCl_2 + LiCl \rightleftarrows LiCuCl_3 \qquad (4)$$

$$LiCuCl_3 + LiCl \rightleftarrows Li_2CuCl_4 \qquad (5)$$

It is also known that copper(II) acetate exists mainly as the dimer[6] in acetic acid. In these experiments, the absorption maximums at 685 and 365 nm which were observed when copper(II) acetate was dissolved in acetic acid decreased and disappeared upon addition of lithium chloride respectively. This suggests that a part of the dimer of copper(II) acetate is converted into the monomer by the addition of lithium chloride and that copper(II) chloro complexes are formed. No oxygen absorption was detected when the oxidation of anthracene without any additive was performed at 90 °C in acetic acid. The rate of oxygen absorption in the oxidation of anthracene with copper(II) acetate was low but improved on addition of lithium chloride. However, without copper(II) acetate in the oxidation of anthracene, no oxygen absorption was observed either on adding lithium chloride or lithium acetate. A part of these results is shown in Table 1. Accordingly lithium chloride, lithium acetate and hydrogen chloride formed by the reaction of lithium chloride with acetic acid were not effective in the oxidation of anthracene directly. Moreover, the rate of oxygen absorption in the oxidation

TABLE 1. EFFECTS OF COPPER(II) ACETATE AND LITHIUM CHLORIDE ADDITION ON THE OXIDATION OF ANTHRACENE AT 90 °C

Anthracene mol/l	Copper(II) acetate $Cu_2(OAc)_4$ mol/l	Lithium chloride mol/l	Initial rate of oxygen absorption mol/l·s
0.05	—	0.01	0 (reaction time 240 min)
0.05	0.01	—	1.3×10^{-7}
0.05	0.005	0.01	2.9×10^{-6}
0.05	0.01	0.01	4.2×10^{-6}

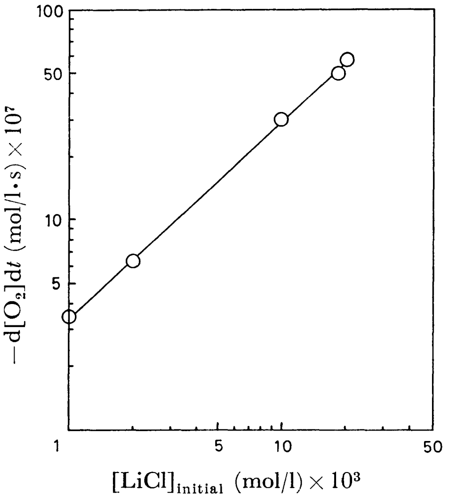

Fig. 1. Effect of $[LiCl]_{initial}$ at 90 °C under conditions, $[LiCl]_{initial} = 2 \times [Cu_2(OAc)_4]_{initial}$.
$[LiCl]_{initial}$: initial concentration of added lithium chloride.
$[Cu_2(OAc)_4]_{initial}$: initial concentration of added copper (II) acetate dimer.

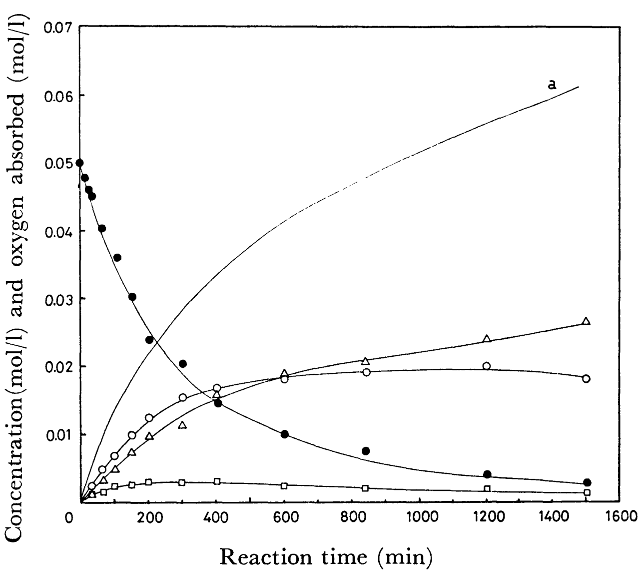

Fig. 2. Time course of oxidation of anthracene at 90 °C.
anthracene : 0.05 mol/l
copper(II) acetate $Cu_2(OAc)_4$: 0.005 mol/l
lithium chloride : 0.01 mol/l
●: Anthracene, □: 9-acetoxyanthracene, ○: anthrone, △: anthraquinone, a: oxygen absorbed.

of anthracene with copper(II) acetate and lithium acetate was low. Thus the increase of oxygen absorption rate is presumed to be related to the formation of copper(II) chloro complexes.

Effect of Added Amount of Copper(II) Acetate and Lithium Chloride on Oxygen Absorption Rate. When the molar ratio of copper(II) acetate dimer to lithium chloride is 0.5, the effect of various amounts of added copper(II) acetate and lithium chloride is shown in Fig. 1. Initial rates of oxygen absorption increase as concentrations of added copper(II) acetate and lithium chloride increase. That is, some copper(II) chloro complexes formed from copper(II) acetate and lithium chloride effectively work for the liquid-phase oxidation. The rates of oxygen absorption are approximately proportional to the added amounts of copper(II) acetate and lithium chloride under the experimental conditions.

Reaction Products. Anthraquinone, anthrone, 9-acetoxyanthracene, and 9-chloroanthracene were identified as reaction products by gas chromatography and gas-mass spectrometry. Formation of 10,10′-bianthrone was not observed. No generation of carbon dioxide from the reaction solution was detected. Typical patterns of production of anthraquinone, anthrone, and 9-acetoxyanthracene, decrease of anthracene, and oxygen absorption are shown in Fig. 2. 9-Chloroanthracene was detected in trace amounts. At the initial stage of oxidation, anthrone was a main product. 9-Acetoxyanthracene was produced at the initial stage of oxidation and then remained nearly constant in the reaction solution.

References

1) C. A. Angell and D. M. Gruen, *J. Am. Chem. Soc.*, **69**, 1038 (1947).

2) M. Baaz, V. Gurmann, G. Hampel, and J. R. Masaguer, *Monatsh. Chem.*, **93**, 1416 (1962).

3) C. Furlani and G. Morpurgo, *Theor. Chim. Acta*, **1**, 102 (1963).

4) K. Sawada, H. Ohtaki, and M. Tanaka, *J. Inorg. Nucl. Chem.*, **34**, 3455 (1972).

5) L. R. Mahoney, *J. Am. Chem. Soc.*, **86**, 444 (1964).

6) M. Kato, H. B. Jonassen, and J. C. Tanning, *Chem. Rev.*, **64**, 99 (1964).