On the Mechanism of Oxidation by Cuprous Chloride, Pyridine and Air. I. The Properties of the Reaction*

By Keizō KINOSHITA

(Received September 30, 1958)

It was previously reported that by aerial oxidation catalyzed by cuprous chloride in a pyridine solution, benzoin was primarily converted into benzil, which was further oxidized to benzoic acid almost quantitatively[1]. In this reaction, "oxidant A", a product of aerial oxidation of cuprous chloride pyridine complex, is considered to be the actual oxidant[2]. On the other hand, with cupric chloride as a catalyst, no benzoic acid is obtained, although benzoin is converted into benzil almost quantitatively[1].

$$\underset{\text{Benzoin}}{C_6H_5CHOHCOC_6H_5} \xrightarrow[\text{Air}]{Cu_2Cl_2+\text{Pyridine}} 2C_6H_5COOH \quad (1)$$

$$C_6H_5CHOHCOC_6H_5 \xrightarrow[\text{Air}]{CuCl_2+\text{Pyridine}} \underset{\text{Benzil}}{C_6H_5COCOC_6H_5} \quad (2)$$

Terent'ev et al.[3] reported that by aerial oxidation catalyzed by cuprous chloride in a pyridine solution, aromatic amines were converted into the corresponding azo compounds, but that with cupric chloride as a catalyst, these azo compounds were never obtained.

$$2C_6H_5NH_2 \xrightarrow[\text{Air}]{Cu_2Cl_2+\text{Pyridine}} C_6H_5N=NC_6H_5 \quad (3)$$

This paper describes the properties of these reactions.

Experimental

Materials.—Benzil was prepared by oxidation of benzoin with nitric acid, and recrystallized from alcohol, m.p. 94~95°C[4]. Aniline (b.p. 184~185°C) was redistilled immediately before use. Cuprous chloride was prepared by reduction of cupric chloride with sodium sulfite[5], washed with acetone and dried.

(1) Aerial Oxidation of Aniline Catalyzed by Cuprous Chloride in a Pyridine Solution.—A mixture of aniline (2.0 g., 2.2/100 mol.), cuprous chloride (2.0 g., 1/100 mol.) and pyridine (50 cc.) was stirred in a stream of air for 5 hr. at room temperature. The resulting mixture was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). After removal of the ether, the residue was extracted with light petroleum (b.p. 40~60°C), and chromatographed on activated alumina (Wako Pure Chemical Industries, Ltd.). Azobenzene (1.2 g., 60%) was obtained; m.p. 67~68°C. (Lit. 68°C). It was identified with azobenzene by a mixed melting point determination and an analysis.

Anal. Found: C, 79.27; H, 5.57; N, 15.36. Calcd. for $C_{12}H_{10}N_2$: C, 79.12; H, 5.49; N, 15.38%.

(2) Oxidation of Aniline in the Absence of Air.—Cuprous chloride (8.0 g., 4/100 mol.) in pyridine (100 cc.) was oxidized with air for 3 hr. at room temperature. A mixture of aniline (2.0 g., 2.2/100 mol.) and "oxidant A" thus prepared, was stirred for 5 hr. at room temperature in a stream of nitrogen. The resulting mixture was acidified with 6N-H_2SO_4 and extracted with ether. White precipitate remained. From the ether solution, azobenzene (0.5 g.) was obtained as in Experiment 1; m.p. 67~68°C, its melting point was not depressed on admixing with an authentic sample. A trace of red substance remained on top of the activated alumina.

The color of the aqueous layer was at first pale blue, but after the solution was kept in air its color turned to darker blue. The white precipitate was dissoluble in an aqueous ammonia solution. The color of the ammonia solution kept in air turned to blue. These results suggest that cuprous chloride was produced during the oxidation of aniline.

(3) Attempted Aerial Oxidation of Aniline in the Presence of Acetic Acid.—A mixture of aniline (2.0 g., 2.2/100 mol.), cuprous chloride (2.0 g., 1/100 mol.), acetic acid (1.8 g., 3/100 mol.) and pyridine (100 cc.) was treated as in Experiment 1. A trace of red substance remained on top of the activated alumina, and no other neutral substance was obtained. The color of the aqueous solution was blue.

(4) Reaction of Cupric Chloride Pyridine Complex with Potassium Hydroxide.—(a) Cupric chloride (3.4 g., 2/100 mol.) was refluxed in pyridine (50 cc.) until all the precipitate was turned into blue needles. Potassium hydroxide (1.1 g., 2/100 mol.) in methyl alcohol (50 cc.) was added dropwise under stirring to the cooled pyridine solution of cupric chloride pyridine

---

* The present work was presented partly at the Symposium on the Mechanism of Organic Chemical Reaction of the Chemical Society of Japan, held at Osaka in October, 1955, and partly at the similar symposium of the same society, held at Nagoya in October, 1957.

[1] K. Kinoshita, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 48 (1954).

[2] K. Kinoshita, ibid., **75**, 173 (1954).

[3] A. P. Terent'ev et al., *Doklady Akad. Nauk U. S. S. R.*, **1955**, 91—93. [*Chem. Abstr.*, **50**, 4807 (1956).]

[4] R. Adams, "Organic Syntheses", Vol. I, John Wiley & Sons, Inc., New York (1921), p. 25.

[5] W. C. Ferdnelius, "Inorganic Syntheses", Vol. II, McGraw-Hill, New York (1946), p. 1.

complex. The color of the resulting mixture was green.

(b) When potassium hydroxide (1.1 g., 2/100 mol.) in methyl alcohol (50 cc.) was added to the copper complex prepared in Experiment 4a, pale blue precipitate was formed from the green solution.

(5) Oxidation of Benzil with the Copper Complex Prepared in Experiment 4.—(a) A mixture of benzil (2.0 g., 1/100 mol.) and the copper complex prepared in Experiment 4a was stirred at 30°C for 2 hr. in a stream of air. The resulting mixture was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). The ethereal layer was extracted with aqueous sodium carbonate solution. After removal of the ether, the residue was benzil (0.7 g., 35%); this melted at 94∼95°C alone or with an authentic sample of benzil. The aqueous layer was acidified by 6N-H_2SO_4 and extracted with ether. After removal of the ether, the residue was sublimed to give benzoic acid (1.4 g., 57%), m.p. 121∼122°C; its melting point was not depressed on admixing with an authentic sample.

(b) A mixture of benzil (1.0 g., 1/200 mol.) and the copper complex prepared in Experiment 4b was treated as in Experiment 5a. Benzil (0.9 g., 90%) was recovered; m. p. 94∼95°C, its melting point was not depressed with an authentic sample. No benzoic acid was obtained.

(c) When diethylamine (10 g., excess) was added to the copper complex prepared in Experiment 4a, the color of the solution did not change. A mixture of benzil (1.0 g., 1/200 mol.) and the resulting copper complex was treated as in Experiment 5a. Benzoic acid (1.1 g., 90%) was obtained; m. p. 121∼122°C, its melting point was not depressed on admixing with an authentic sample. No benzil was recovered.

(d) When trimethylamine hydrochloride (3.9g., 3/100 mol.) was added to the copper complex prepared in Experiment 4a, blue needles appeared, and trimethylamine was separated. The mixture of benzil (1.0 g., 1/200 mol.) and the resulting copper complex was treated as in Experiment 5a. Benzil (0.9g., 90%) was recovered; it melted at 94∼95°C alone or with an authentic sample of benzil. No benzoic acid was obtained.

(6) Oxidation of Aniline in the Presence of Methyl Alcohol.—(a) A mixture of aniline (2.0 g., 2.2/100 mol.) and the copper complex described in Experiment 4a [prepared from $CuCl_2 \cdot 2H_2O$ (3.4 g.), KOH (1.1 g.), methyl alcohol (10 cc.) and pyridine (50 cc.)] was treated as in Experiment 1. Azobenzene (0.9 g., 45%) was obtained; it melted at 67∼68°C alone or with an authentic sample of azobenzene.

(b) A mixture of aniline (2.0 g., 2.2/100 mol.), cuprous chloride (2.0 g., 1/100 mol.), methyl alcohol (100 cc.) and pyridine (50 cc.) was treated as in Experiment 1. Azobenzene (0.1 g., 5%) was obtained; it melted at 67∼68°C alone or with an authentic sample of azobenzene.

(7) Effect of Bases on "Oxidant A".—(a) Cuprous chloride (2.0 g., 1/100 mol.) in pyridine (50 cc.) was oxidized with air at room temperature for 2 hr.

(b) When potassium hydroxide (1.1 g., 2/100 mol.) in methyl alcohol (50 cc.) was added to the copper complex prepared in Experiment 7a, brown precipitate appeared. Its mixture with benzil (1.0 g., 1/200 mol.) was treated as in Experiment 5a. The same results as in Experiment 5b were obtained.

(c) When diethylamine (10 g., excess) was added to the copper complex prepared in Experiment 7a, no color change occurred. A mixture of benzil (1.0 g., 1/200 mol.) and the resulting copper complex, was treated as in Experiment 5a. The same results as in Experiment 5c were obtained.

(d) When trimethylamine hydrochloride (3.9 g., 3/100 mol.) was added to the copper complex prepared in Experiment 7a, blue needles were formed, and trimethylamine was separated. A mixture of benzil (1.0 g., 1/200 mol.) and the resulting copper complex, was treated as in Experiment 5a. The same results as in Experiment 5d were obtained.

Results and Discussion

By aerial oxidation catalyzed by "oxidant A", aniline is converted into azobenzene in a yield of about 60%. Through the treatment of aniline with "oxidant A" in the absence of air, azobenzene and cuprous chloride are obtained (Table I). These results suggest that "oxidant A" is the actual oxidant in the aerial oxidation of aniline catalyzed by cuprous chloride in a pyridine solution. Similar facts were found in the oxidative cleavage of benzil under the similar condition[2].

TABLE I. OXIDATION OF ANILINE BY CUPROUS CHLORIDE, PYRIDINE AND AIR

Catalyst	Cu_2Cl_2 in the catalyst g. (mol.)	Pyridine cc.	Azobenzene g. (%)
Oxidant A*	8.0 (4/100)	100	0.5**
Cu_2Cl_2	2.0 (2/200)	50	1.2 (60)
Oxidant A	1.0 (1/200)	50	1.2 (60)
Oxidant A	2.0 (2/200)	50	1.2 (60)
Oxidant A	3.0 (3/200)	80	1.2 (60)
Oxidant A	4.0 (4/200)	100	1.2 (60)

Aniline (2.0 g., 2.2/100 mol.) was treated.
* Nitrogen atomosphere.
** Cuprous chloride was obtained.

In the presence of an excess of acidic substance "oxidant A" has no longer its catalytic activity (Table II). The oxidation of benzil is stopped after a definite amount of benzil is oxidized[2], because the produced benzoic acid retards the reaction. On the other hand, "oxidant A" keeps its catalytic activity during the aerial oxidation of aniline, because acidic substance is hardly produced in the reaction.

Table II. Effect of acidic substance

Cu_2Cl_2 g. (mol.)	Acidic substance g. (mol.)	Azobenzene g.
2.0 (1/100)	Acetic acid 1.8 (3/100)	0
2.0 (1/100)	Ammonium chloride 1.6 (3/100)	0
2.0 (1/100)	Trimethylamine hydrochloride* 3.9 (3/100)	0

Aniline (2.0 g., 2.2/100 mol.) was treated in pyridine (100 cc.).
* Trimethylamine was separated.

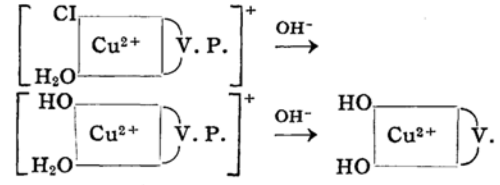
Another catalyst for benzil is obtained from reaction of cupric chloride pyridine complex with a methyl alcohol solution of potassium hydroxide — not with its aqueous solution. With a methyl alcohol solution of potassium hydroxide, cupric chloride pyridine complex—blue needles —turns to a greenish solution, as far as the molar ratio of cupric chloride to potassium hydroxide reaches 1:1.5. Benzil is oxidized to benzoic acid by aerial oxidation catalyzed by this greenish cupric complex—"oxidant B". The amount of oxidized benzil apparently increases in accordance with the amount of added potassium hydroxide (Table III).

Table III. Oxidation of benzil by "oxidant B" and air

$CuCl_2\cdot 2H_2O$* g. (mol.)	KOH g. (mol.)	Benzoic acid g. (%	Sample (recovered) g. (%)
3.4 (2/100)	0	0	1.8 (90)
3.4 (2/100)	0.6 (1/100)	0.6 (25)	1.4 (70)
3.4 (2/100)	1.1 (2/100)	1.4 (58)	0.7 (35)
3.4 (2/100)	1.7 (3/100)	2.0 (82)	0.3 (15)

Benzil (2.0 g., 1/100 mol.) was treated.
* Cf. Experiment 4a.

The following change was postulated in the reaction of dichloro-(2-vinyl pyridine)-copper(II) with potassium hydroxide[6] (Reaction 4). It was reported that by reaction of an aqueous cupric salt pyridine complex solution with equimolar potassium hydroxide, a solution of hydroxy cupric salt pyridine complex ion [**I**] was produced[7] (Reaction 5). All this seems to lead to the conclusion that "oxidant B" is hydroxy cupric chloride pyridine complex.



(4)

$$2\,Cu^{2+}+4\,Py+2\,OH^- \rightleftarrows Py_2Cu(OH)_2CuPy_2{}^{2+} \quad [\mathbf{I}] \qquad (5)$$

(V. P.: Vinyl pyridine, Py: Pyridine).

By aerial oxidation catalyzed by "oxidant B", aniline is converted into azobenzene, although the yield of azobenzene is decreased in the presence of an excess of methyl alcohol. The aerial oxidation of aniline catalyzed by "oxidant A" is also retarded by an excess of methyl alcohol (Table IV).

Table IV. Effect of methyl alcohol on the aerial oxidation of aniline

Copper salt in the catalyst* g. (mol.)		KOH in the catalyst g. (mol.)	Methyl alcohol cc.	Azobenzene g. (%)
Cu_2Cl_2	2.0 (1/100)	0	100	0.1 (5)
$CuCl_2\cdot 2H_2O$	3.4 (2/100)	0	20	0
	3.4 (2/100)	1.1 (2/100)	100	0
	3.4 (2/100)	1.1 (2/100)	20	0.3 (15)
	3.4 (2/100)	1.1 (2/100)	10	0.9 (45)

Aniline (2.0 g., 2.2/100 mol.) was treated.
* Pyridine (50 cc.) was used as a solvent.

When equimolar potassium hydroxide in methyl alcohol is added "oxidant A" or "oxidant B", these complexes are destroyed and their catalytic activity is lost. However, when "oxidant A" or "oxidant B" is treated with excessive diethylamine or benzylamine, they keep their color and their catalytic activity. Through the reaction between trimethylamine hydrochloride and "oxidant A" or "oxidant B", trimethylamine separates. The resulting complexes no longer have their catalytic activity. This fact suggests that "oxidant A" and "oxidant B" have stronger basicity than trimethylamine (Ref. 7).

All the phenomena described above suggest that there is a remarkable resemblance between "oxidant A" and "oxidant B".

Summary

(1) By aerial oxidation of aniline catalyzed by cuprous chloride in a pyridine solution, azobenzene of about 60% is

---

[6] J. F. Pudivin et al., *J. Am. Chem. Soc.*, 78, 2104 (1956).

[7] D. L. Leussing et al., ibid., **79**, 4270 (1957).

produced. In this reaction, the actual oxidant may be considered "oxidant A" which is produced by aerial oxidation of cuprous chloride pyridine complex.

(2) Hydroxy cupric chloride pyridine complex, a reaction product of cupric chloride pyridine complex with a methyl alcohol solution of potassium hydroxide, has a similar catalytic activity.

(3) These two complexes are to be considered strong bases.

(4) These two complexes have a remarkable resemblance to each other.

The author wishes to express his sincere gratitude to Professor Ryozo Goto for his invaluable advice and unfailing encouragement of this work.

Laboratory of Chemistry
School of General Studies
Kyoto University
Sakyo-ku, Kyoto