On the Mechanism of Oxidation by Cuprous Chloride, Pyridine and Air. II. The Mechanism of Formation of Azobenzene from Aniline*

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Terent'ev et al.[1] reported that when aerial oxidation of aniline was carried out in a pyridine solution catalyzed by cuprous chloride, azobenzene was obtained in a good yield. In Part I of this series, the details of this reaction were studied and it was considered that the actual oxidant of this oxidation was "oxidant A" obtained by aerial oxidation of cuprous chloride pyridine complex[2]. In this paper, the mechanism of this reaction is discussed.

Experimental

Materials.—Aniline (b. p. 184～185°C), *o*-toluidine (b. p. 199～200°C) and *o*-anisidine (b. p. 225°C) were redistilled immediately before use. Extra chemical pure grade *p*-toluidine (m. p. 44～45°C) and *p*-anisidine (m. p. 56～57°C) were used. Cuprous acetate pyridine complex was prepared as follows. When cupric acetate (3.8 g., 2/100 mol.) in pyridine (50 cc.) was refluxed for 2 hr., deep blue crystals were formed (cupric acetate pyridine complex). A mixture of metallic copper (0.5 g. excess) and the above pyridine solution of cupric acetate pyridine complex was stirred at 60°C in a stream of nitrogen until the color of the solution was turned to dark yellow.

(1) Attempted Aerial Oxidation of Aniline Catalyzed by the Copper Acetate Complexes.—(a) A mixture of aniline (2.0 g., 2.2/100 mol.) and the above-mentioned cuprous acetate pyridine complex in pyridine was stirred for 5 hr. at 30°C in a stream of air. The resulting mixture was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). After removal of the ether, a trace of residue was obtained. The residue was dissolved with light petroleum (b. p. 40～60°C) and chromatographed on activated alumina (Wako Pure Chemical Industries, Ltd.). All the substance remained on top of the activated alumina. No azobenzene was obtained. The color of the aqueous layer was blue.

(b) Potassium hydroxide (1.1 g., 2/100 mol.) in methyl alcohol (10 cc.) was added to a cupric acetate pyridine complex in pyridine (described in the preparation of cuprous acetate pyridine complex). A mixture of aniline (2.0g., 2.2/100 mol.) and the resulting copper complex was stirred at 80°C for 5 hr. in a stream of air. The resulting mixture was treated as in Experiment 1a. The same results as in Experiment 1a were obtained.

(2) Oxidation of Substituted Anilines.—(a) A mixture of *p*-toluidine (2.2 g., 2/100 mol.), cuprous chloride (2.0 g., 1/100 mol.) and pyridine (50 cc.) was stirred for 5 hr. at room temperature in a stream of air. The resulting mixture was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). After removal of the ether, the residue was dissolved with benzene, and chromatographed on activated alumina. 4,4'azotoluene (2.0 g., 90%) was obtained; m. p. 142～143°C (Lit. 143°C). It was identified with 4,4'azotoluene by a mixed melting point determination and an analysis.

Anal. Found: C, 80.10; H, 6.92; N, 13.16.

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

2) K. Kinoshita, Part I of this series in This Bulletin, **32**, 777 (1959).

Calcd. for $C_{14}H_{14}N_2$: C, 80.00; H, 6.66; N, 13.33%.

A trace of black substance remained on top of the activated alumina.

(b) A mixture of *p*-anisidine (2.5 g., 2/100 mol.), cuprous chloride (2.0 g., 1/100 mol.) and pyridine (50 cc.) was treated as in Experiment 2a. 4,4'Azoanisol (2.2 g., 88%) was obtained; m. p. 162~163°C (Lit. 163°C). It was identified with 4,4'azoanisol by a mixed melting point determination and an analysis.

Anal. Found: C, 69.54; H, 5.96; N, 11.47. Calcd. for $C_{14}H_{14}O_2N_2$: C, 69.42; H, 5.78; N, 11.57%.

A trace of black substance remained on top of the activated alumina.

(c) A mixture of *o*-toluidine (2.2 g., 2/100 mol.), cuprous chloride (2.0 g., 1/100 mol.) and pyridine (50 cc.) was treated as in Experiment 2a. The resulting mixture was acidified with $6N\text{-}H_2SO_4$, and extracted with ether (500 cc.). After removal of the ether, the residue was distilled with steam; then a large amount of substance remained in the vessel. From the distillate 2,2'-azotoluene (0.3 g., 14%) was obtained; m. p. 54~55°C (Lit. 55°C). It was identified with 2,2'-azotoluene by a mixed melting point determination and an analysis.

Anal. Found: C, 79.93; H, 6.89; N, 13.19. Calcd. for $C_{14}H_{14}N_2$: C, 80.00; H, 6.66; N, 13.33%.

The aqueous layer was dark violet.

(d) A mixture of *o*-anisidine (2.5 g., 2/100 mol.), cuprous chloride (2.0 g., 1/100 mol.) and pyridine (50 cc.) was treated as in Experiment 2a. 2,2'-Azoanisol (0.4 g., 16%) was obtained; m. p. 153~154°C (Lit. 153°C). It was identified with 2,2'-azoanisol by a mixed melting point determination and an analysis.

Anal. Found: C, 69.41; H, 5.98; N, 11.44. Calcd. for $C_{14}H_{14}O_2N_2$: C, 69.42; H, 5.78; N, 11.57%.

A large amount of substance remained on the activated alumina. There were some substances which did not dissolve in ether. The color of the aqueous layer was dark violet.

(3) Oxidation of Hydrazobenzene.—Cuprous chloride (2.0 g., 1/100 mol.) in pyridine (50 cc.) was oxidized with air for 2 hr. at room temperature. When hydrazobenzene (2.0 g., 1.1/100 mol.) was added to the resulting copper complex, the color of the solution was turned to yellow. The yellow solution was stirred for 1 hr. at room temperature in a stream of air. From the resulting mixture azobenzene (1.9 g., 95%) was obtained; melted at 67~68°C alone or with an authentic sample of azobenzene.

(4) Competitive Oxidation of Aniline and *p*-Anisidine.—A mixture of aniline (3.6 g., 4/100 mol.), *p*-anisidine (5.0 g., 4/100 ml.), cuprous chloride (1.0 g., 1/200 mol.) and pyridine (50 cc.) was stirred at room temperature in a stream of air. The resulting mixture was acidified with $6N\text{-}H_2SO_4$ and filtered. The residue was continuously extracted for 24 hr. with light petroleum (b. p. 40~60°C, 100 cc.). A trace of black substance remained. From the extract 4,4'azoanisol was separated; this melted at 163~164°C alone or with an authentic sample of 4,4'azoanisol. When the reaction was carried out for 30 min. and 60 min., the obtained 4,4'azoanisol amounted to 1.2 g. and 2.3 g. respectively, and the residues, after removal of the mother liquor, were 0.1 g. and 0.2 g., respectively.

Results and Discussion

Since it was reported that the chlorine ion in cupric chloride complexes was easily substituted³⁾, chlorine ion in "oxidant A" I may also be substituted by aniline or methyl alcohol (Reactions 1 and 2). On the other hand, acetate ion in cupric acetate complexes may not be substituted easily by the above compounds (Ref. 3).

$$\underset{\text{I}}{C_6H_5NH_2 + Cu(II)\text{-}Cl} \rightleftarrows \underset{\text{II}}{[C_6H_5NH_2Cu(II)]^+Cl^-} \qquad (1)$$

$$CH_3OH + Cu(II)\text{-}Cl \rightleftarrows [CH_3OH\text{-}Cu(II)]^+Cl^- \qquad (2)$$

An excess of methyl alcohol retards the aerial oxidation of aniline²⁾—it may be caused by a competition between Reactions 1 and 2. Cuprous acetate pyridine complex or hydroxy cupric acetate pyridine complex has no catalytic activity to the aerial oxidation of aniline (Table I). From these facts II may be considered as an intermediate in this reaction.

TABLE I. CATALYTIC ACTIVITY OF COPPER ACETATE COMPLEX

Pyridine complex* of copper salts	Temp. °C	Azobenzene g.(%)
Cuprous chloride**	25	1.5(75)
Cuprous acetate	30	0
Cuprous acetate	60	0
Cuprous acetate	80	0
Hydroxy cupric acetate	80	0

Aniline (2.0 g., 2.2/100 mol.) was treated for 5 hr.

* Cf. Experiment 1.

** Cupric chloride pyridine complex was reduced by metallic copper.

Syrkin et al. reported that in ammino complexes, the basic properties of the nitrogen atom were reduced, but that the acidic properties correspondingly increased⁴⁾. By the reaction between II and I which is considered to be a strong base²⁾, a proton is removed from II to form an intermediate III.

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3) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

4) Y. K. Syrkin et al., "Structure of Molecules and the Chemical Bond", Interscience Publisher, New York (1950), p. 387.

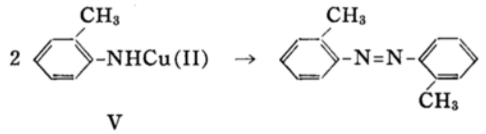
$$\underset{\text{II}}{[\mathrm{Cu(II)\text{-}NH_2C_6H_5}]^+\mathrm{Cl}^-} \rightarrow \underset{\text{I}}{\mathrm{Cu(II)}}\text{-}\underset{\text{III}}{\mathrm{NHC_6H_5}} \qquad (3)$$

By aerial oxidation of an equimolar mixture of aniline and *p*-anisidine catalyzed by a small amount of cuprous chloride, 4,4′azoanisol is selectively obtained in the early stage of this reaction (Experiment 4). This result suggests that IV reacts with another IV to produce 4,4′azoanisol (Reaction 4), because the reaction between IV and free amines, may accompany 4-methoxy azobenzene with 4,4′azoanisol, even in the early stage of this reaction.

$$2\ \underset{\text{IV}}{(p\text{-})\mathrm{CH_3OC_6H_4NH\text{-}Cu(II)}}$$
$$\rightarrow (p\text{-})\mathrm{CH_3OC_6H_4N=NC_6H_4OCH_3}(p\text{-}) \qquad (4)$$

By aerial oxidation catalyzed by cuprous chloride in a pyridine solution, *p*-toluidine and *p*-anisidine are converted into the corresponding azo compounds almost quantitatively, while *o*-toluidine and *o*-anisidine are converted into the corresponding azo compounds only in a poor yield, although many other products are formed besides the azo compounds (Table II).

It was reported that the yield of azo compounds from substituted anilines were hardly affected at all by the position of the substituents in these amines, if these azo compounds were produced from the dimerisation of intermediate free radicals[5,6]. On the other hand, the steric hindrance of ortho substituent in V may interfere with the approach of two nitrogen atoms to decrease the yield of 2,2′-azotoluene,



V

(5)

if 2,2′azotoluene is produced from a reaction of V with another V, (Reaction 5). The experimental results prove this to be valid.

TABLE II. OXIDATION OF SUBSTITUTED ANILINES

Amine g.(mol.)	Cu_2Cl_2 g.(mol.)	Time (hr.)	Azocompound g. (%)
p-Toluidine 2.2(2/100)	2.0(1/100)	5	4,4′Azotoluene 2.0 (90)
p-Anisidine 2.5(2/100)	2.0(1/100)	5	4,4′Azoanisol 2.2 (88)
o-Toluidine 2.2(2/100)	2.0(1/100)	5	2,2′Azotoluene 0.3 (14)
o-Toluidine 4.4(4/100)	4.0(2/100)	6	2,2′Azotoluene 0.8 (18)
o-Toluidine 8.8(8/100)	8.0(4/100)	8	2,2′Azotoluene 1.7 (20)
o-Anisidine 2.5(2/100)	2.0(1/100)	5	2,2′Azoanisol 0.4 (16)
p-Toluidine 1.1(1/100)	2.0(1/100)*	5	4,4′Azotoluene** 0.5
o-Anisidine 2.5(2/100)	4.0(2/100)*	20	2,2′Azoanisol** 0.2

* "Oxidant A" was used.
** Absence of air.

Hydrazobenzene is converted into azobenzene almost quantitatively, by aerial oxidation catalyzed by "oxidant A" in a pyridine solution (Experiment 3). Accordingly, it is reasonable to assume that III is converted primarily into hydrazobenzene, which is further oxidized to azobenzene[5,6].

$$2\ \underset{\text{III}}{\mathrm{C_6H_5NH\text{-}Cu(II)}} \rightarrow \mathrm{C_6H_5NH\text{-}NHC_6H_5}$$
$$\rightarrow \mathrm{C_6H_5N{=}NC_6H_5} \qquad (6)$$

In a pyridine solution, it was reported that cuprous salts and complexes increased in their stability[7]. Consequently, the activated complex may be as VI[8]. By the reaction of VI with another VI, hydrazobenzene and cuprous complex are produced. Hydrazobenzene is further oxidized to azobenzen (Reaction 7).

$$\underset{\text{III}}{\mathrm{C_6H_5NH\text{-}Cu(II)}} \rightleftarrows \underset{\text{VI}}{[\mathrm{Cu(I)\text{-}\dot{N}HC_6H_5}]}$$
$$2\ [\mathrm{Cu(I)\text{-}\dot{N}HC_6H_5}] \rightarrow \mathrm{C_6H_5NH\text{-}NHC_6H_5}$$
$$+\ 2\ \mathrm{Cu(I)}$$
$$\mathrm{C_6H_5NH\text{-}NHC_6H_5} \rightarrow \mathrm{C_6H_5N{=}NC_6H_5} \qquad (7)$$

Summary

(1) Attempted aerial oxidation of aniline, catalyzed by cuprous acetate pyridine complex, is unsuccessful even at 80°C.

(2) By the aerial oxidation of equimolar mixture of aniline and *p*-anisidine, catalyzed by a small amount of cuprous chloride, 4,4′azoanisol is selectively obtained in the early stage of this reaction.

(3) By the aerial oxidation catalyzed by cuprous chloride in a pyridine solution, the yields of the azo compounds, which are produced from *p*-toluidine and *p*-anisidine, are almost quantitative. On

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5) K. H. Pausacker, *J. Chem. Soc.*, **1953**, 1989.

6) K. H. Pausacker et al., ibid., **1954**, 4003.

7) J. E. B. Landles, ibid., **1942**, 802.

8) R. E. Connick, *J. Phys. Chem.*, **56**, 21 (1952). In this remark, he described the activated complex in which oxidized cyanide ion was combined with $[Cu(CN)_3]^{2-}$ in the oxidation of cyanide ion with cupric ion.

the other hand, the yields of the azo compounds, which are produced from *o*-toluidine and *o*-anisidine, are very poor.

(4) In this reaction, it is postulated that an intermediate [Cu(II)-NHC_6H_5] is initially formed, and that hydrazobenzene and cuprous complex are produced by the bimolecular reaction of this intermediate.

(5) Hydrazobenzene is converted into azobenzene almost quantitatively under the same condition as aniline is oxidized.

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