

On the Formation of Benzonitrile from Benzaldehyde and Ammonia. III. A Role of the Existing Base^{1,2)}

Akira MISONO, Tetsuo OSA and Seiichiro KODA

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

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In the preceding paper,¹⁾ the authors reported on the mechanism of the oxidative formation of benzonitrile from benzaldehyde and ammonia in a methanol solution with oxygen catalyzed by some copper compounds. It was assumed that the aldehyde and ammonia reacted to produce benzilideneimine, from which was produced the corresponding nitrile oxidatively. Though it was observed that the basicity played an important role in the oxidation step, its exact role remained ambiguous to be made clear in this paper. The rates of the formation of benzonitrile against various concentrations of cupric chloride as a main catalyst with the concentration of sodium hydroxide being kept constant were observed and are shown in Fig. 1. The reaction rates were almost independent on the concentration of cupric chloride in the region where the concentration of cupric chloride was over a certain limit. From the consideration of this result and of the experimental results reported in the preceding paper,¹⁾ such as

the first-order dependence of the reaction rate upon the concentration of cupric hydroxide as the catalyst (the basicity of the system may be proportional to the concentration of cupric hydroxide), the linear relation of the reaction rate to the concentration of sodium hydroxide and the relation between the basicity and the activity of catalysts, the rate-determining step of the formation of the nitrile would be the deprotonation of benzilideneimine and the oxidation reaction of the formed anion or the corresponding sodium salt would be sufficiently fast. Of course, in the case when the concentration of cupric ion is very small, the rate-determining step may be alternatively the oxidation step of the formed anion.

To investigate on this oxidation step further, the oxidation of the sodium derivative of benzophenoneimine was tried. This stable N-unsubstituted imine was selected in place of the unstable benzilideneimine. Though some difference may be between these two imines, the reaction may begin at the position of the imino-group (=N-H) in both of the imines. The sodium derivative of benzophenoneimine, which was prepared from benzophenoneimine and sodium amide in benzene (or tetrahydrofuran), was oxidized with suspended cupric chloride after the removal of unreacted sodium amide. The oxidation reaction seemed to proceed rapidly, judging from the observation that the characteristic deep red color of the sodium derivative disappeared immediately after the contact of the derivative with the oxidant. The corresponding oxidative dimerization product, benzophenoneazine was obtained in an about 70% yield. The fact that a complex of benzophenoneimine with cuprous chloride, $\text{CuCl} \cdot \text{Ph}_2\text{C}=\text{NH}$, was detected as a by-product may mean that the oxidation step is an one-electron transfer reaction. Benzophenoneimine may be resulted from the hydrolysis of the sodium derivative, as a trace of water could exist in the oxidant or the solvent. The oxidation reaction of the sodium derivative may proceed much faster than the oxidation reaction of the parent imine by cupric chloride, judging from the fact that the complex of benzophenoneimine with cupric chloride, $\text{CuCl}_2 \cdot 2\text{Ph}_2\text{C}=\text{NH}$, is observed to be stable at room temperature.³⁾ Potassium permanganate and manganese dioxide

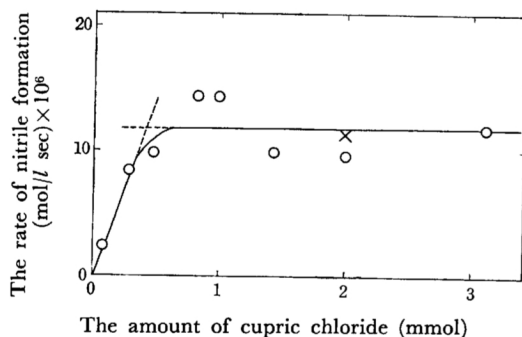


Fig. 1. The dependence of the reaction rate on the concentration of cupric chloride.

Initial conditions:

CuCl_2	0.095—3.11 mmol
NaOH	3.00 mmol
NH_3	103 mmol
Benzaldehyde	30 mmol
Solvent (+ NH_3)	100 ml
Reaction temperature	$29.5 \pm 0.2^\circ\text{C}$

×: the corrected value from the datum in the preceding paper¹⁾ according to the equation;

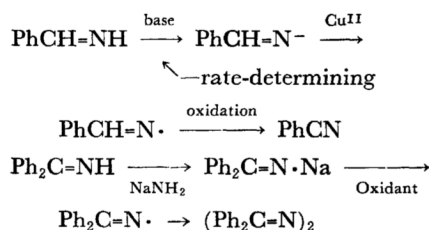
$$\text{the rate} \propto \frac{[\text{NH}_3][\text{benzaldehyde}]}{([\text{NH}_3] + [\text{Benzaldehyde}])}$$

1) Part I: A. Misono, T. Osa and S. Koda, This Bulletin, **40**, 912 (1967).

2) Part II: *ibid.*, **40**, 2875 (1967).

3) A. Misono, T. Osa and S. Koda, *ibid.*, **41**, 373 (1968).

also oxidized the sodium derivative to the ketazine in gross yields of 51% and 22%, respectively. Palladium chloride and silver nitrate also oxidized the sodium derivative to the ketazine, though not quantitatively observed. As for other oxidants, Morton⁴⁾ oxidized the sodium derivative to benzophenone oxime by air and to benzophenone azine by iodine in a yield of 17%. From the consideration of the above stated observations, the oxidation of the imines may plausibly proceed as follows.



Experimental

The Oxidation of Benzaldehyde and Ammonia with Oxygen Catalyzed by Cupric Chloride and Sodium Hydroxide. The materials and the reaction apparatus were all the same as in the preceding paper.¹⁾ The procedure were also same except the following treatments before the start of the reaction; the methanol containing ammonia and sodium hydroxide was introduced in the flask and was stirred for 15 min. Then the introduction of oxygen gas was started. When 10 min passed after the beginning of the introduction of oxygen, the given amount of cupric chloride was added to at one time. When additional 5 min passed, benzaldehyde was introduced to start the reaction.

The Oxidation of the Sodium Derivative of Benzophenoneimine. All treatments were carried out at room temperature under dried nitrogen before the oxidation products were separated by filtration.

Oxidation by Cupric Chloride in Benzene. In 20 ml of benzene, 1 g (26 mmol) of sodium amide and 1.890 g (10.4 mmol) of benzophenoneimine (prepared from phenylmagnesium bromide and benzonitrile,⁵⁾ bp

146.5–148°C/7.5 mmHg) were agitated for 1 hr. Then, undissolved substances were separated and washed with 10 ml of benzene. The filtrate together with the washing was added to 2.708 g (20.1 mmol) of cupric chloride (prepared through dehydration by thionyl chloride from commercial cupric chloride dihydrate⁶⁾) and the mixture was stirred for 3 hr. Then 20 ml of benzene was added to the mixture, and the resulted mixture was filtered. After stripping off benzene, 1.281 g (gross yield, 68%, mp 148–156°C) of yellow solid of benzophenone azine became available (recry. from ethanol, mp 164.5°C, lit.⁷⁾ 164°C. Its infrared spectrum agreed with that of an authentic sample.⁸⁾ Found: C, 55.57; H, 3.87; N, 5.00%. Calcd for $\text{CuCl} \cdot \text{C}_{13}\text{H}_{11}\text{N}$: C, 55.71; H, 3.96; N, 5.00%.

In tetrahydrofuran as a solvent, benzophenone azine was obtained in a 72% yield after a similar treatment.

Oxidation by Potassium Permanganate. In 20 ml of benzene, 1 g of sodium amide and 1.905 g (10.5 mmol) of benzophenoneimine were agitated together for 1 hr, and treated similarly. The filtrate was added to 1.591 g (10.1 mmol) of potassium permanganate. The mixture was stirred for 2.5 hr and then kept for 40 hr at standing. The resulted mixture was treated similarly. Solids with little liquids remained after the removal of benzene. The mixture was again dissolved in 100 ml of ethanol with 10 ml of benzene. The solution was concentrated, then the resulting precipitate was separated at –30°C. The precipitate, 0.959 g (51%, mp 160.5–161.5°C) in weight, proved to be benzophenone azine (recry. from ethanol, 164.8°C). From the filtrate, 0.769 g (40%) of yellow liquid, which was mainly benzophenoneimine, contaminated with a little benzophenone, judging from its infrared spectrum, was obtained.

The oxidation by activated manganese dioxide (prepared from potassium permanganate⁹⁾) of the sodium derivative of benzophenoneimine for 3 hr yielded benzophenone azine in a 22% gross yield after similar treatments.

6) A. R. Pray, "Inorganic Syntheses," **5**, 153 (1957).

7) J. Guenzet, *Compt. rend.*, **251**, 2970 (1960).

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4) A. A. Morton and J. R. Stevens, *J. Am. Chem. Soc.*, **53**, 2769 (1931).

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