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On the Formation of Benzonitrile from Benzaldehyde and Ammonia. I. with Copper Catalysts

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The mechanism of the oxidative formation of benzonitrile from benzaldehyde with ammonia in a methanol solution catalyzed by some copper compounds is discussed, as well as the dependence of the activity on the basicity of the catalysts. On the basis of such kinetic data as the rate of nitrile formation related to the concentration of cupric hydroxide as a catalyst, the effect of the water added, and the effect of the sodium hydroxide added, benzilideneimine was confirmed to be an important intermediate. The rate of nitrile formation could be explained fairly quantitatively on the assumption that aldehyde and ammonia react to produce benzilideneimine, from which is produced the corresponding nitrile *via* the imine radical. Cupric hydroxide, cuprous chloride, and cupric chloride with sodium hydroxide or sodium methoxide are active catalysts, but cupric acetate and cupric chloride are not so active. This difference is found to be due to the basicity of the catalysts. Some other results are also discussed.

Brackman and Smit1) reported a method of sinthesizing nitriles by treating with oxygen a methanolic solution of the corresponding aldehydes, containing ammonia, sodium methoxide, and cupric chloride. They applied their method to various aldehydes and also proposed a mechanism for this reaction, but without sufficient discussions based on experimental data. Fischer2) also investigated this reaction, comparing it with a similar reaction taking hydrobenzamide as the

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1) W. Brackman and P. J. Smit, *Rec. Trav. Chim.*, **82**, 757 (1963).

2) E. Fischer, *J. Prakt. Chem.*, **29**, 199 (1965).

starting meterial in place of benzaldehyde. However, he did not discuss the possible mechanism kinetically. We had taken a great interest in this reaction, regarding it as one model of liquid-phase ammoxidation reactions. We supposed that the reaction mechanism could be clarified by using kinetic measurements. Moreover, we used as catalysts several kinds of copper compounds, the activity of which could be explained in terms of their basicity.

The outline of this reaction is as follows. Using methanol as a solvent and a copper compounds as a catalyst, benzaldehyde (we used benzaldehyde as a convenient representative of the aldehydes), and ammonia were placed in a reactor kept at a moderate temperature. Oxygen gas was continuously bubbled into the reactor; the main product was found to be benzonitrile.

Results

The system chosen for this investigation was the oxidation of benzaldehyde in a methanolic solution containing ammonia at 29.5±0.2°C and at atmospheric pressure, using as a catalyst cupric hydroxide, which was not used by the foregoing investigators.[1,2)

A typical reaction path is shown in Fig. 1. The rate of nitrile formation, which was small at the initial step, became larger as the reaction progressed for a definite time. Afterward, the reaction rate kept rather constant. It was, therefore, adopted as a kinetic datum for discussions.

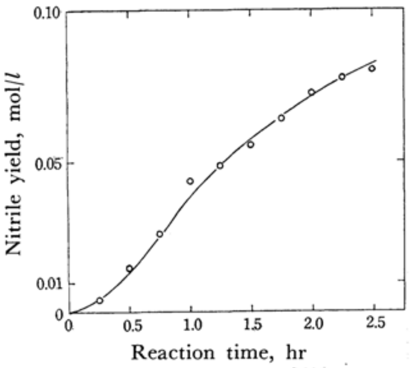

Fig. 1. An example of benzonitrile yield to reaction time.
Initial conditions

$Cu(OH)_2$	0.002 mol
NH_3	0.089 mol
Benzaldehyde	0.030 mol
Solvent (+NH_3)	100 ml

The oxygen uptake rate would be the most convenient measure for discussing the mechanism kinetically, but it could not be measured exactly because of the co-existence of ammonia in methanol and also in the gas phase.

In addition to the main reaction-producing nitrile, the formation of benzoic acid, hydrobenzamide, and methyl benzoate, as well as the oxidation of methanol, were known to be side reactions, but their amounts were too small to be taken into consideration in any discussion of the reaction mechanism. Methyl benzoate was produced in a yield of several mol% of the benzonitrile formed in any experiments (analyzed by means of infrared spectroscopy and gas chromatography; conditions: column, 10% glutaronitrile on diasolid L, 2m, column temperature, 130°C). The formation of hydrobenzamide was neglected because a rapid equilibrium might be assumed to exist between hydrobenzamide and benzilideneimine. This assumption will be discussed later. Benzoic acid was formed in a yield of several mol% of the formed benzonitrile, according to Fischer.2) The co-existence of the oxidation of methanol is considered to have little effect on the kinetics of the benzonitrile formation.

The reaction solution showed blue in any catalyst system as long as oxygen existed in the reactor, but it gradually became pale yellow within one day or so after the interruption of the oxygen supply. This solution, however, immediately became blue when oxygen was reintroduced. This fact shows that the oxidation of copper(I) to copper(II) proceeds sufficiently rapidly compared to that of some organic compounds.

The dependence of the reaction rate (the nitrile formation rate) upon the concentration of cupric hydroxide used as a catalyst is shown in Fig. 2. The value of the slope was 1.19, as calculated by the method of least squares.

Various amounts of water were added in advance

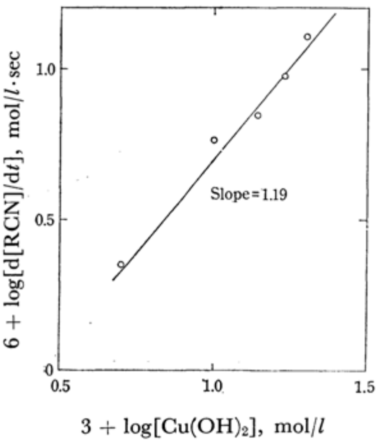

Fig. 2. Dependence of the reaction rate upon the concentration of cupric hydroxide.
Initial conditions

$Cu(OH)_2$	0.0005—0.002 mol
NH_3	0.089 mol
Benzaldehyde	0.030 mol
Solvent (+NH_3)	100 ml

to the reaction mixture, while the concentration of cupric hydroxide was kept constant (0.017 mol/*l*). The dependence of the rate of nitrile formation is shown in Fig. 3. The reciprocal of the reaction rate could be linearly related to the amount of water added.

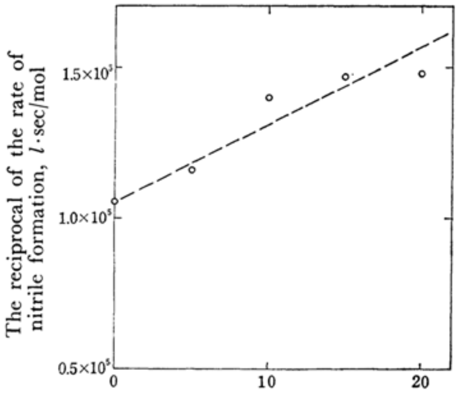

Fig. 3. Dependence of nitrile formation rate upon the amount of water added.

Initial conditions

$Cu(OH)_2$	0.0017 mol
NH_3	0.089 mol
Benzaldehyde	0.030 mol
Solvent ($+NH_3$)	100 m*l*
H_2O	0—0.034 mol

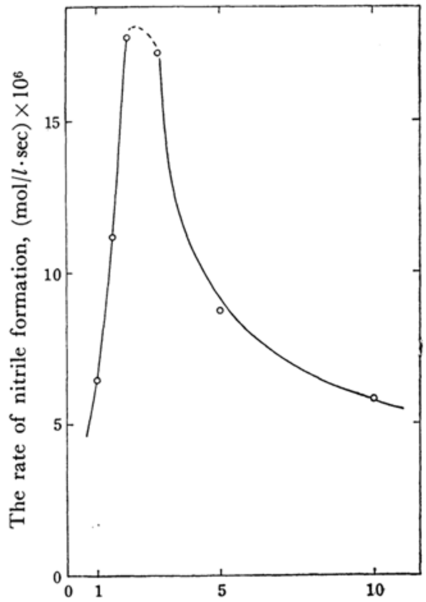

Fig. 4. The effect of sodium hydroxide.

Initial conditions

$CuCl_2$	0.002 mol
NH_3	0.089 mol
Benzaldehyde	0.030 mol
Solvent ($+NH_3$)	100 m*l*
NaOH	0—0.02 mol

The effect of the sodium hydroxide added to the reaction mixture is shown in Fig. 4. In this series of experiments cupric chloride was used as a catalyst in place of cupric hydroxide.

Fischer²⁾ reported on the effect on the nitrile yield of the sodium methoxide added to a reaction mixture which was saturated with ammonia and which contained cupric chloride as a catalyst. He showed that the yield increased with the amount of sodium methoxide added in advance; this is contrary to our observation, but this contradiction could be solved, as will be explained later.

We used cupric hydroxide, cuprous chloride, cupric acetate ($Cu(acetate)_2 \cdot H_2O$), cupric chloride with equimolar sodium methoxide, and cupric chloride with equimolar sodium hydroxide as catalysts; their activities were explained on the basis of their relative basicity. These results are shown in Fig. 5. The activity increases with the relative basicity.

Ammonium chloride, which had previously been added to a reaction mixture containing cupric hydroxide or cuprous chloride, considerably diminished the rate of nitrile formation, as is shown in Fig. 6. The methanol solution of a catalyst and ammonia with ammonium chloride is rather weakly basic, as is shown in Table 1.

The effect of the lithium chloride added to the reaction mixture is shown in Fig. 7. Lithium

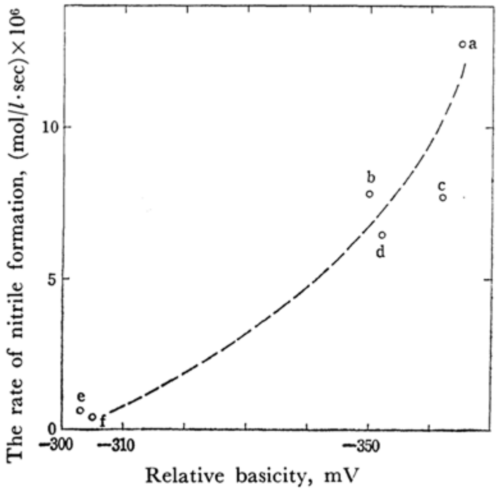

Fig. 5. The relation between the activity and the basicity of catalysts.

Initial conditions

Copper salt	0.002 mol
NH_3	0.089 mol
Benzaldehyde	0.030 mol
Solvent ($+NH_3$)	100 m*l*

a: $Cu(OH)_2$, b: CuCl,
c: $CuCl_2$+equimolar $NaOCH_3$,
d: $CuCl_2$+equimolar NaOH,
e: $CuCl_2$, f: $Cu(acetate)_2 \cdot H_2O$

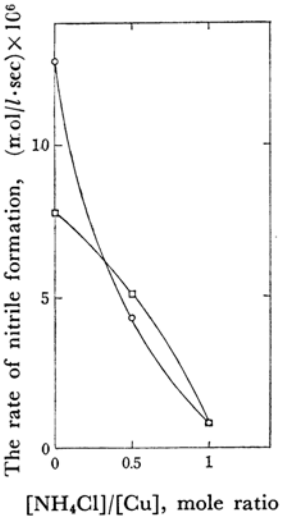

Fig. 6. The effect of ammonium chloride added to the reaction mixture.

Initial conditions

Copper salt	0.002 mol
(○: $Cu(OH)_2$, □: CuCl)	
NH_3	0.089 mol
Benzaldehyde	0.030 mol
Solvent ($+NH_3$)	100 m*l*
NH_4Cl	0—0.002 mol

TABLE 1. THE BASICITY OF CATALYSTS IN METHANOL-AMMONIA

Catalyst	Concentration of catalyst mol/*l*	Relative basicity mV
$CuCl_2$	0.0087	−303
CuCl	0.0100	−350
$Cu(acetate)_2 \cdot H_2O$	0.0098	−305
$Cu(OH)_2$	0.0100*	−365
$CuCl_2$ $+NaOH$	0.0101 0.0106	−352
$CuCl_2$ $+NaOCH_3$	0.0098 0.0101	−362
CuCl $+NH_4Cl$	0.0099 0.0115	−326
CuCl $+LiCl$	0.0099 0.099	−358

Solvent: 0.205 N ammoniacal methanol
*: not perfectly dissolved

chloride does not lower the basicity of the solution, contrary to the case of ammonium chloride (Table 1).

Discussion

We wish to propose a mechanism according to the equations shown in Fig. 8.

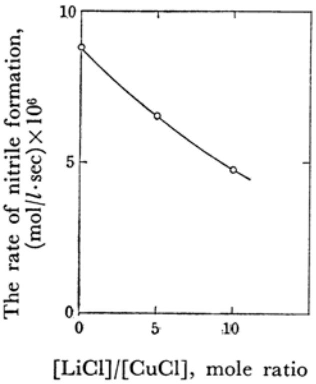

Fig. 7. The effect of lithium chloride added to the reaction mixture.

Initial conditions

CuCl	0.002 mol
NH_3	0.089 mol
Benzaldehyde	0.030 mol
Solvent ($+NH_3$)	100 m*l*
LiCl	0—0.02 mol

The oxidation of copper(I) will proceed rapidly, as is supported by the qualitative observations described before and as is generally assumed in cases of oxidation reactions catalyzed by copper salts in the liquid phase.[3]

The nitrile formation rate is estimated according to the scheme given in Fig. 8, on the following three assumptions:

1) The nitrile formation reaction from the imine radical is sufficiently fast in comparison with those in former steps; that is,

$$d[RCH{=}N\cdot]/dt = 0$$

Then,

$$0 = d[RCH{=}N\cdot]/dt = k_3'[RCH{=}NH][Cu(OH)_2] - A$$

A: rate of nitrile formation

$$\therefore\ A = k_3'[Cu(OH)_2][RCH{=}NH] = k_3[RCH{=}NH]$$

Therefore, the rate of the nitrile formation reaction is equal to that of the imine radical formation reaction, assuming that no reaction of the imine radical proceeds.

2) It is probable that a rapid equilibrium exists between benzilideneimine and hydrobenzamide. Ogata *et al.*[4] investigated kinetically the reaction between benzaldehyde and ammonia, which produces hydrobenzamide in methanol as a solvent, and concluded that the production of α-aminoalcohol or its dehydration reaction is the rate determining step; they based this conclusion on the observation that the reaction is a first-order one in both benzaldehyde and ammonia. They concluded that the intermediate, α-aminoalcohol or benzilideneimine, reacts rapidly to produce hydrobenzamide by some means, but they did not investigate

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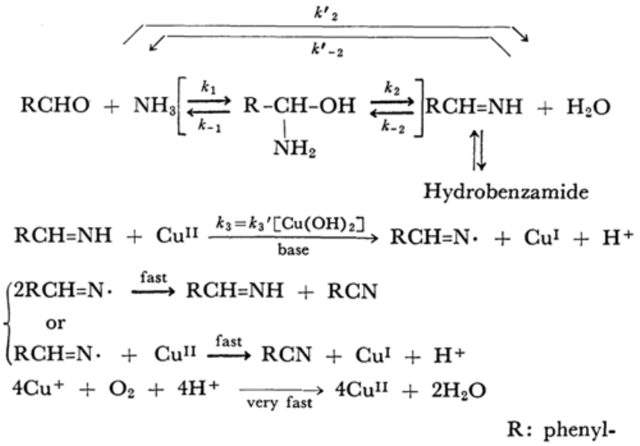
[3] E. Ochiai, *Tetrahedron*, **20**, 1831 (1964).

[4] Y. Ogata, A. Kawasaki and N. Okumura, *J. Org. Chem.*, **29**, 1985 (1964).



$$\mathrm{RCHO} + \mathrm{NH_3}\left[\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{R\text{-}\underset{\displaystyle NH_2}{\underset{|}{C}H}\text{-}OH} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}}\right]\mathrm{RCH{=}NH} + \mathrm{H_2O} \qquad (k'_2,\ k'_{-2};\ \mathrm{RCH{=}NH} \rightleftarrows \text{Hydrobenzamide})$$

$$\mathrm{RCH{=}NH} + \mathrm{Cu^{II}} \xrightarrow[\text{base}]{k_3=k_3'[\mathrm{Cu(OH)_2}]} \mathrm{RCH{=}N\cdot} + \mathrm{Cu^I} + \mathrm{H^+}$$

$$\begin{cases} \mathrm{2RCH{=}N\cdot} \xrightarrow{\text{fast}} \mathrm{RCH{=}NH} + \mathrm{RCN} \\ \quad\text{or} \\ \mathrm{RCH{=}N\cdot} + \mathrm{Cu^{II}} \xrightarrow{\text{fast}} \mathrm{RCN} + \mathrm{Cu^I} + \mathrm{H^+} \end{cases}$$

$$\mathrm{4Cu^+} + \mathrm{O_2} + \mathrm{4H^+} \xrightarrow[\text{very fast}]{} \mathrm{4Cu^{II}} + \mathrm{2H_2O}$$

R: phenyl-

Fig. 8. Reaction mechanism.

these steps because of their rapidity. Moreover, it is known that hydrobenzamide with water produces benzaldehyde and ammonia in some yield under the same reaction conditions.

Fischer[2] observed that the nitrile was produced at almost the same rate whether benzaldehyde or hydrobenzamide was used as the starting material.

These facts told us that a rapid equilibrium will be reached between hydrobenzamide and benzilideneimine. It was, however, so difficult to take this equilibrium into consideration exactly that we were forced to assume the equation:

$$[\mathrm{RCH{=}NH}]_{\mathrm{actual}} = [\mathrm{RCH{=}NH}]_{\mathrm{total}} \times p$$

(p=a constant, regardless of any other reactions) $[\mathrm{RCH{=}NH}]_{\mathrm{total}}$ is the concentration of benzilideneimine when it is assumed that no hydrobenzamide is produced from benzilideneimine. $[\mathrm{RCH{=}NH}]_{\mathrm{actual}}$ is the concentration of benzilideneimine which actually exists in the mixture.

3) The amount of the aldehyde consumed multiplied by that of the ammonia consumed is assumed to be negligibly small. This is correct in the earlier part of the reaction procedure.

According to the first and second assumptions above,

$$\mathrm{d}(a-x)/\mathrm{d}t = -k_2'(a-x)(b-x) + k'_{-2}wp(x-y) \tag{1}$$

$$\mathrm{d}y/\mathrm{d}t = k_3p(x-y) \tag{2}$$

t: reaction time
a: the initial concentration of the aldehyde
b: the initial concentration of ammonia
x: the concentration of aldehyde (or ammonia) consumed
y: the concentration of the imine radical (=nitrile) produced
w: the concentration of water added in advance

Then, using the third assumption,

$$y = c(1 + (\beta_2/(\beta_1 - \beta_2))e^{-\beta_1 t} - (\beta_1/(\beta_1 - \beta_2))e^{-\beta_2 t})$$

$$c = ab/(a+b)$$

$$\beta_1 + \beta_2 = k'_2(a+b) + k'_{-2}wp + k_3p$$

$$\beta_1\beta_2 = k'_2k_3p(a+b)$$

and the maximum rate of the nitrile formation is;

$$(\mathrm{d}y/\mathrm{d}t)_{max} = c(\beta_1\beta_2/(\beta_1 - \beta_2)) \times [(\beta_2/\beta_1)^{-(\beta_2/(\beta_2-\beta_1))} - (\beta_2/\beta_1)^{-(\beta/(\beta_2-\beta_1))}] \tag{3}$$

This relation can be simplified as follows:

Case 1: $k'_2(a+b),\ k'_{-2}wp \gg k_3p$

$$(\mathrm{d}y/\mathrm{d}t)_{max} = k'_2k_3pab/[k'_2(a+b) + k'_{-2}wp] \tag{4}$$

Case 2: $k'_2(a+b) \gg k'_{-2}wp,\ k_3p$

$$(\mathrm{d}y/\mathrm{d}t)_{max} = k_3pab/(a+b) \tag{5}$$

Case 3: $k_3p \gg k'_2(a+b) \gg k'_{-2}wp$

$$(\mathrm{d}y/\mathrm{d}t)_{max} = k'_2ab \tag{6}$$

The rate of nitrile formation obtained by the experimental measurements will be considered to be proportionate to the maximum rate as calculated from Eqs. (4)—(6).

All the experiments, except the series in which some water is added in advance, belong to Case 2 or Case 3.

The results shown above can be explained with these kinetic equations ((4)—(6)).

a) The effect of the sodium hydroxide added (*cf.* Fig. 4).

There is some probability that a part of the copper catalyst is precipitated when larger amounts of sodium hydroxide are added. In these experiments, however, because of the presence of an excess of ammonia, the precipitation proceeds in too small a extent, if at all, especially during the earlier parts of the reaction, to make the dependence of the reaction rate upon the concentration of sodium hydroxide such as is shown in Fig. 4. Therefore, some other explanations are necessary.

According to Ogata *et al.*,⁴⁾ the second-order rate constant of the reaction between benzaldehyde and ammonia in a methanolic solution at 30°C is $(2\pm 0.5)\times 10^{-4}$ l/mol·sec over rather wide regions of the concentrations of the two reactants. This value can be converted into the rate of nitrile formation under our reaction conditions;

$$d[\mathrm{RCN}]/dt = (5.4 \pm 1.4)\times 10^{-5}\ \mathrm{mol}/l\cdot\mathrm{sec}$$

which, in general, is quite a bit larger than the rates measured in our experiments. This suggests that the reaction proceeds according to Case 2, except for the experiments in which larger amounts of sodium hydroxide are added. The increase in the amount of sodium hydroxide seems to make the k_3 rate constant larger. On the contrary, the k'_2 rate constant diminishes with the increase in the amount of sodium hydroxide, according to Ogata *et al.*,⁴⁾ who observed that the second-order rate constant of the reaction between benzaldehyde and ammonia diminished from a value of 2.46×10^{-4} l/mol·sec (when the concentration of potassium hydroxide (they used potassium hydroxide instead of sodium hydroxide) is zero) to a value of 0.94×10^{-4} l/mol·sec (when the concentration is equal to 0.247 mol/l). Then, on the assumption that the effect of sodium hydroxide is almost the same as that of potassium hydroxide, the value of k'_2ab may be estimated as about $(2.65\times 0.7)\times 10^{-5}$ mol/l·sec in the experiment in which ten times as much sodium hydroxide as cupric chloride is added (the concentration of sodium hydroxide is 0.2 mol/l).

Because the measured value of the rates of nitrile formation will, of course, be quite small in comparison with the values calculated from Eqs. (4)—(6), as is clear from the treatment of these equations, the reaction will proceed approximately according to Case 3 when a larger amount of sodium hydroxide is added to the reaction mixture, though the value, $(2.65\pm 0.7)\times 10^{-5}$ mol/l·sec might still be sufficiently large for the application of Case 2.

The appearance of the maximum point in the curve showing the dependence of the rate of nitrile formation upon the amount of sodium hydroxide added can thus be explained. Investigating the effect of the addition of sodium methoxide on the yield of nitrile, Fischer²⁾ found no maximum point in the curve. The reason for this is perhaps that the concentration of ammonia was sufficiently large for the application of Case 2, for the solvent methanol was saturated with ammonia in his experiments.

b) The dependence of the reaction order upon the concentration of cupric hydroxide (*cf.* Fig. 2)

In Case 2, it is expected that the rate of nitrile formation depends upon the first order of the concentration of cupric hydroxide. The observed value, 1.19, could be recognized as nearly one.

c) The effect of the water added (*cf.* Fig. 3).

When some water is added, Case 1 will be applied; then Eq. (4) may be rewritten as follows:

$$1/(d[\mathrm{RCN}]/dt) \propto 1+\mathrm{constant}\times[\mathrm{H_2O}]$$

Fig. 3 shows this relation roughly.

d) The dependence of the reaction order upon the other variables.

The data of Fischer²⁾ shows that the reaction is almost first order; as a reaction medium, he used a methanolic solution saturated with ammonia all through the reaction progress, with cupric chloride with sodium methoxide as a catalyst. When Eq. (5) is applied:

$$(dy/dt)_{max} = k_3pab/(a+b) \approx k_3pa \qquad (b \gg a)$$

the reaction is considered to proceed with a first-order dependence on the concentration of benzaldehyde.

Benzilideneimine hydrochloride was prepared according to the method of Busch⁵⁾ (mp ∼180°C) to be used as a starting material in place of benzaldehyde, but the results obtained were all qualitative because of the ambiguity in the reaction progresses. Four grams of benzilideneimine hydrochloride were suspended in 100 ml of pyridine. To this mixture there was added 10 ml of triethylamine, and it was stirred vigorously for thirty minutes or so. (A part of the benzilideneimine was set free. *Cf.* Tolbert *et al.*⁶⁾) The remaining precipitate was separated off, to the solution there was added 4 mmol of a catalyst, and oxygen gas was bubbled in for five hours at 30°C. In the resulting mixture, after the volatile components had been distilled off, the nitrile was examined by means of a study of the infrared spectra. The following order in the activity of the catalysts was found:

$$\mathrm{CuCl_2\cdot 2H_2O} + t\text{-BuONa (saturated in 100 m}l\text{ pyridine)} \approx \mathrm{CuCl} > \mathrm{CuCl_2\cdot 2H_2O}$$

A similar reaction was carried out using benzene as a solvent in place of pyridine, and cupric naphthenate+sodium *t*-butoxide as a catalyst, but no nitrile was detected.

The order of activity shown above holds for the reactions adopting benzaldehyde as the starting material. Thus benzilideneimine seems to execute an important role in these reactions.

As is shown in the brackets in Fig. 8, benzaldehyde and ammonia together probably produce α-aminoalcohol at the first step; its concentration will not be so small as that of benzilideneimine. Then the following reaction might proceed to produce benzamide:

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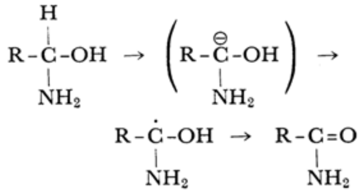
5) M. Busch, *Ber.*, **29**, 2143 (1896).

6) T. L. Tolbert and B. Houston, *J. Org. Chem.*, **28**, 695 (1963).



$$\mathrm{R{-}\overset{\displaystyle H}{\underset{\displaystyle NH_2}{C}}{-}OH} \rightarrow \left(\mathrm{R{-}\overset{\ominus}{\underset{\displaystyle NH_2}{C}}{-}OH}\right) \rightarrow \mathrm{R{-}\underset{\displaystyle NH_2}{\dot{C}}{-}OH} \rightarrow \mathrm{R{-}\underset{\displaystyle NH_2}{C}{=}O}$$

In fact, Nakagawa *et al.*[7] obtained aromatic amides in high yields from the corresponding aldehydes and ammonia by oxidizing them with nickel peroxide in ether as a solvent at temperatures below 0°C. The present authors also obtained a mixture of nitrile and amide form benzaldehyde and ammonia by oxidizing them with potassium permanganate in benzene or *t*-butanol as solvents. (The details of this reaction will be published in the future.) These observations show that the reactions assumed above actually proceeded in some cases. Therefore, we expected to detect benzamide in this reaction catalyzed by copper compounds, a reaction was carried out at 0°C. (The formation of amide is superior to that of nitrile at lower temperatures, according to Nakagawa *et al.*[7]) However, we failed to do so. Besides, Fischer[2] observed that very little nitrile was produced when benzamide was used as the starting material under similar conditions. Parameswaran *et al.*[8] reported a method of synthesizing nitriles from aldehydes and ammonia in a benzene solvent; in this method they used lead tetraacetate as the oxidant. It is not clear from their report, but probably few or none of the corresponding amides were produced, if the high yield of nitriles is considered.

These facts possibly mean that the copper compound and perhaps lead tetraacetate have no ability to eliminate hydrogen from α-aminoalcohol in any way. α-Aminoalcohol (or its anion) may, then, be expected to have a more noble redox potential or a lower acidity than benzilideneimine (or its anion).

The foregoing discussion altogether supports the mechanism shown in Fig. 8, excluding the reactions starting from the benzilideneimine radical, which are very difficult to make clear by means of kinetical treatments.

The relation between the activity and the basicity of the catalysts is shown in Fig. 5. The addition of ammonium chloride to the reaction mixture diminishes the rate of nitrile formation considerably. This means that the catalysts shall be at least stronger bases than ammonia, and that the basicity executes an important role in the oxidation reaction. The increase in the sodium hydroxide added to a mixture containing cupric chloride as a catalyst makes the rate of nitrile formation larger, at least to a certain extent; the extent is, however, open to question as long as we consider the results of these experiments only.

Many reports have been published on investigations of the oxidation reaction of phenols catalyzed by copper salts.[3,9]

Ochiai,[3] who studied the oxidation reaction of 2, 6-di(*t*-butyl)-phenol by oxygen in a pyridine solution, reported that "cuprous chloride+pyridine" and "cupric chloride+pyridine+hydroxide anion" are active catalysts, while "cupric chloride+pyridine" is not, and that the activity of catalysts is related to their basicity rather than to their redox potentials. He also reported, on the basis of the spectroscopic data, that the active catalysts have a copper-oxygen bond (Cu^{2+}-O^{2-}, Cu^{2+}-OH^-, *etc.*) in their structures. A certain copper-oxygen bond comes to be formed when cuprous chloride is oxidized by oxygen.

In this ammoxidation reaction, also, the dependence of the rate on the basicity of catalysts, and the effect of the lithium chloride added (some of the chloride anions would take the place of ligands containing oxygen (such as O^{2-}, OH^-)) could be explained as in the oxidation of phenols.

Detailed discussions of the possible structures of active catalysts will, however, be very difficult in this reaction because of the complexity of the reaction mechanism; therefore, for the discussions, some model reactions should be investigated.

Experimental

Reagents. *Benzaldehyde.* Benzaldehyde, obtained commercially as a guaranteed reagent, was distilled under reduced pressure in a nitrogen atmosphere just before being used (bp 67°C/15 mmHg, $n^{29.5}$ 1.327). Contact with air was avoided before it was let into the reactor. Gas chromatographic analysis proved that there were no peaks except for the aldehyde. (Conditions: column, 10% carbowax 4000 on diasolid M 2 m; column temperature, 160°C; hydrogen flame detector.)

Ammonia. Ammonia was obtained commercially in a bomb and was put through a potassium hydroxide layer in order to remove any moisture. The ammonia was absorbed to a certain content in methanol in advance.

Methanol. Methanol was commercially obtained as a guaranteed reagent, and then dehydrated by magnesium and distilled (bp 64.2—64.7°C, n^{30} 1.542). It was feared that the distilled methanol might contain some magnesium methoxide, but such methoxide, if any, was under 2×10^{-4} mol/l in concentration. The methanol used in all the experiments was distilled at one time, so that any possible impurities could be neglected, at least relatively.

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[7] K. Nakagawa, H. Onoe and K. Minami, The Annual Meeting of the Chemical Society of Japan, 3N221 (1966).

[8] K. N. Parameswaran and O. M. Friedman, *Chem. & Ind.*, **1965**, 988.

[9] G. F. Endres, A. S. Hay and J. W. Eustance, *J. Org. Chem.*, **28**, 1300 (1963).

Oxygen. Oxygen in a bomb obtained commercially was dried through calcium chloride and silica-gel layers.

Copper Compounds. Cuprous chloride, cupric hydroxide, and cupric acetate ($Cu(acetate)_2 \cdot H_2O$) of a reagent grade were commercially obtained and were used without further purification. Cupric chloride dihydrate of a reagent grade was obtained commercially; it was dehydrated by thionyl chloride[10] and used without further purification. The quantities of these reagents were the same throughout the investigation.

Other Reagents. The sodium hydroxide, ammonium chloride, lithium chloride, and sulfuric acid were all guaranteed reagents. Ether and 1-heptanol were of reagent grade. Water was purified by ion exchange processes.

Experimental Method—Kinetic Investigation. *Apparatus* (*cf.* Fig. 9). A 200 m*l*, round-bottomed flask was equipped with an oxygen-inlet tube. The gas was cooled in a condenser chilled with water, and then in a trap cooled with dry ice and methanol under −50°C, in order to remove the volatile reagents; then, it was introduced into a 11 *l* gas holder and recycled to the inlet tube (the flow speed was 18 *l*/hr). The 200 m*l* flask was set in a thermostat controlled at a temperature of 29.5±0.2°C. The reaction solution in the reactor was then stirred sufficiently vigorously, at a constant speed, throughout the investigation by a magnetic stirrer.

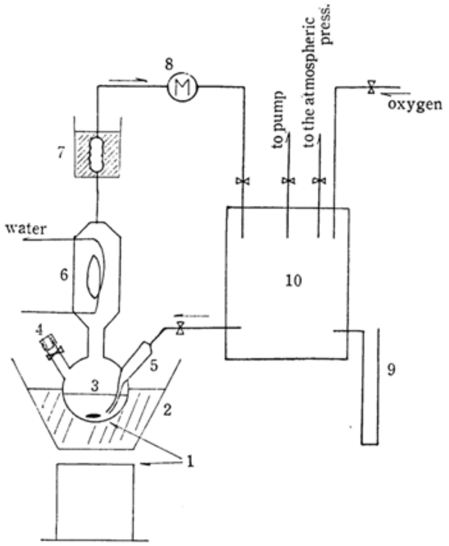

Fig. 9. Apparatus for the oxidation reaction. 1) magnetic stirrer, 2) thermostat, 3) 200 m*l* flask 4) sampling inlet, 5) inlet tube of oxygen, 6) condenser, 7) dry ice-methanol trap, 8) circulating moter, 9) manometer, 10) 11 *l* gas holder

Experimental Method. At first, ammonia was absorbed in methanol and titrated with 1 N hydrochloric acid (bromothymol blue indicator). The reaction apparatus was made vaccuous, and then oxygen was introduced into it until the atmospheric pressure was reached. This procedure was repeated several times until the oxygen present was over 99% in volume. The pressure in the apparatus was controlled at atmospheric pressure throughout the reaction progress by removing or introducing oxygen. One hundred milliliters of a methanol solution of ammonia, a catalyst, and some other additives, if necessary, were introduced to the reactor, and the mixture was stirred, while oxygen was circulated through, for 1 hr. Then, benzaldehyde was introduced at one time to start the reaction. At constant intervals 1 m*l* portions of the reaction solution were sampled out and added to 2 m*l* portions of the 1 N sulfuric acid solution, to which were added 1 m*l* portions of diethyl ether containing 1-heptanol (as an internal standard for gas chromatographic analysis); the ether layer was then analyzed gas chromatographically. The yield of nitrile was estimated by using a calibration curve prepared under the same processes as were actually used. (Gas chromatographic conditions: column, 10% carbowax 4000 on diasolid M 2 m; column temperature, 160°C; flow speed of nitrogen, 60 m*l*/min; hydrogen flame detector.)

Experimental Method—Measurement of the Relative Basicity. The electro-motive force (mV unit) was measured between a glass electrode and a saturated calomel electrode in methanol containing ammonia and copper salt by the use of a pH meter (Toyo Rica Co.). These two electrodes had been kept in methanol for a long time before being used. When two minutes had passed after the electrodes had been introduced into the stirred solution, the electromotive force was measured in order to compare it relatively. The values thus obtained, however, are significant only relative to the other values.

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[10] A. R. Pray, "Inorganic Syntheses," Vol. V, p. 153 (1957).