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# A Kinetic Study of the Metal Ion-catalyzed Glycolysis of Benzonitrile

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The kinetics of the lead ion-catalyzed glycolysis of benzonitrile were studied in the presence of water. The experimental results indicated that the rate of the formation of ammonia followed the first-order rate law with respect to the concentrations of benzonitrile and of water. For the concentration of the catalyst, the rate found was of a 0.44 order. It was observed that the product, $\beta$-hydroxyethyl benzoate, exhibited an inhibiting effect on the glycolysis. The effects of substituents on benzonitrile were found to fit the Hammett rule. The reaction was remarkably influenced by the type of glycol used. The reaction also proceeded through the hydrolysis of benzonitrile, followed by the glycolysis of the benzamide thus formed. The rate of the glycolysis of benzamide was about one-third that of benzonitrile, which is the main reaction in the system. The reaction of imidate formation possessed a small equilibrium constant at a high temperature, but it had a high reaction rate. The proposed mechanism for these glycolysis reactions is as follows: the addition of glycol to benzonitrile yields imidate, which then forms a chelate compound with a metal ion. The imidate activated by the formation of the chelate is easily hydrolyzed by water to form ester and ammonia. This ester tends to chelate to the metal ion and so inhibits the reaction.

The effectiveness of the various kinds of metal compounds on the metal ion-catalyzed glycolysis of terephthalonitrile has been discussed in a previous paper.[1] The heavy metal ions, such as cupric, lead, and zinc ions, have been found to promote the glycolysis of terephthalonitriles. Their catalytic activities have been correlated with the coordination tendency of metal ions.

Kinetic studies of the metal ion-catalyzed glycolysis of benzonitrile are, therefore, important in order to gain a better understanding of the reaction mechanisms. However, no kinetic study of the glycolysis has been found in the literature.

We will attempt here to investigate the reaction kinetics and to propose a mechanism for the metal ion-catalyzed glycolysis of benzonitrile to yield $\beta$-hydroxyethyl benzoate.

## Experimental

**Kinetic Measurements for the Glycolysis of Nitriles and Amides.** The experimental procedure and the methods of measurements for the glycolysis of nitriles and amides were similar to those described in a previous work.[1]

A typical set of reaction conditions used was as follows: a reaction mixture of 0.1 mol of nitrile or amide, 1.5 mol of glycol, 0.1 mol of water, and 0.001 mol of a catalyst was reacted at the reaction temperature of 170°C.

The rate of the formation of ammonia was determined by the titration of samples of the sulfuric acid solution taken from the ammonia-absorbing flask at given intervals. Further, the determination of the rate of the reaction of benzonitrile was carried out by analyzing the samples from the reaction mixture by gas-liquid chromatography at set intervals.

The analytical conditions used were as follows: the heated liquid product in the reaction state was quickly sampled with a micro-syringe (50 $\mu l$) and analyzed by gas-liquid chromatography on a 2 m×6 mm stainless steel column of 25wt% Apiezon L on Chromosorb W at 205°C, using helium as a carrier gas and naphthalene as an internal-standard substance.

The formation of the ester, the main reaction product, was also examined by using gas-liquid chromatography and infrared spectroscopy.

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[1] T. Ikeda, M. Kitabatake, M. Ito and Y. Noguchi, This Bulletin, **41**, 1154 (1968).

**Studies of Imidate Formation from Nitriles.**[2] A reaction mixture of 1.85 g (0.0125 mol) of *m*-nitrobenzonitrile, 124 g (2 mol) of ethylene glycol, and 0.014 g ($0.25 \times 10^{-4}$ mol) of sodium metal was reacted at a given reaction temperature in a 100-m*l* flask immersed in an electrically-heated oil bath stirred by a magnetic apparatus.

Aliquots (5 cc) were withdrawn at intervals, added to a mixture of excess dilute hydrochloric acid and methanol (100 m*l*), and, after 30—45 min, backtitrated to the methyl-orange endpoint.

**Materials.** Isophthalonitrile and terephthalonitrile were prepared by the ammoxidation of *m*- and *p*-xylene respectively; they were purified by recrystallization from dioxane to melting points of 160—161°C and 222—224°C respectively.

The *p*-cyanoacetophenone (mp 54—56°C) was prepared according to the directions proposed by Mowry *et al.*[3]

*p*-Chlorobenzonitrile (mp 93—94°C) was prepared by the usual method from *p*-chloroaniline.

β-Hydroxyethyl *p*-cyanobenzoate (mp 58°C) was prepared by reacting ethylene chlorohydrine with *p*-cyanobenzoic acid sodium salt in a water solution and by recrystallization from water, evaporating under reduced pressure.

β-Hydroxyethyl benzoate was similarly prepared; bp 146—148°C at 10 mmHg.

*m*-Nitrobenzonitrile was a commercial product and was purified by recrystallization from methanol-chloroform; mp 148°C.

Lead acetate, a typical metal ion catalyst, was commercially available with a sufficient purity.

The other materials used in this study were the best commercial products available and were purified by distillation.

## Results and Treatment of Data

**Glycolysis of Benzonitrile.** The conversion of benzonitrile in the presence of water and a catalyst is shown in Fig. 1 as a function of the reaction time. The rates of the formation of ammonia and β-hydroxyethyl benzoate are also given. These results indicate that, in the initial stage of the reaction, the rate of the consumption of benzonitrile is of nearly the same magnitude as the rates of the formation of ammonia and of β-hydroxyethyl benzoate.

In order to ascertain the mass-transfer effect of the rate of reaction, a few experiments were carried out at a faster gas flow rate of nitrogen, while the other conditions were kept constant. The rates of the formation of ammonia were not affected by the nitrogen gas flow rate. It was thus confirmed that the mass-transfer effect was insignificant in this system.

The first-order rate plots of the formation of ammonia observed at 170°C are shown in Fig. 2 for two initial concentrations of benzonitrile. The formation of ammonia and the consumption of benzonitrile are both first-order reactions at low conversions (up to 30% of benzonitrile). A higher conversions, however, the slope of the curve tends to decrease. The difference between the two first-order rate constants in Fig. 2 may be caused by the inhibiting effect of β-hydroxyethyl *p*-cyanobenzoate, which will be discussed later.

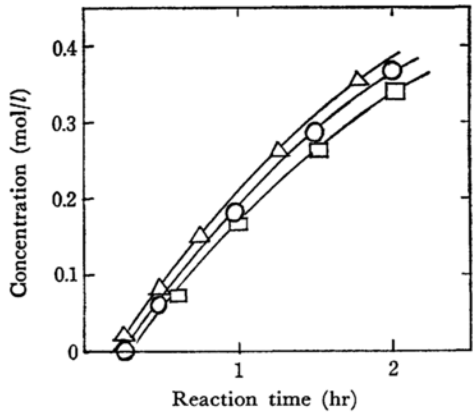

Fig. 1. The quantities of ammonia, ester formation and the reacted benzonitrile.
△: reacted benzonitrile
○: ammonia (formation)
□: ester (formation)
Reaction conditions: Benzonitrile 0.1 mol, E.G. 1.5 mol, $H_2O$ 0.1 mol, $Pb(OAc)_2$ 0.001 mol, Temperature 170°C

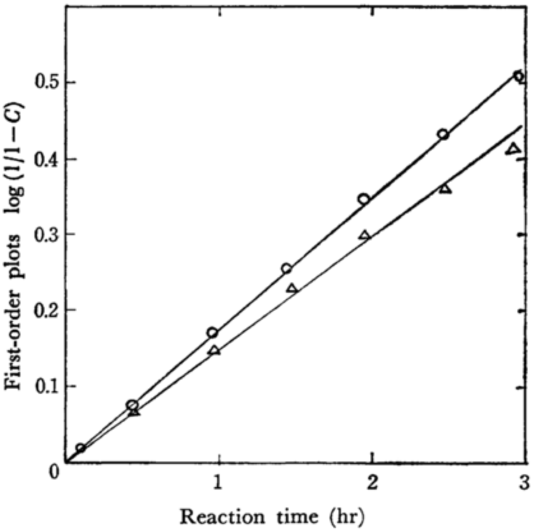

Fig. 2. The first-order formation of ammonia at different initial concentrations of benzonitrile.
○ 0.025 mol of benzonitrile
△ 0.1 mol of benzonitrile
Reaction conditions: E. G. 1.5 mol, $H_2O$ 0.1 mol, Lead acetate 0.001 mol, Temperature 170°C

The first-order rate constants obtained from the initial rate of reaction for the glycolysis of benzonitrile

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[2] F. C. Schaefer and G. A. Peters, *J. Org. Chem.*, **26**, 412 (1961).

[3] D. T. Mowry, M. Renoll and W. F. Huber, *J. Am. Chem. Soc.*, **68**, 1105 (1946).

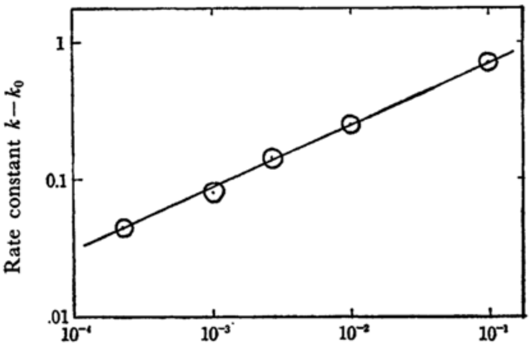

Fig. 3. The first-order rate constant in the glycolysis of benzonitrile *vs.* concentration of catalyst. Reaction conditions: E.G. 1.5 mol, $H_2O$ 0.1 mol, Temperature 170°C, Benzonitrile 0.1 mol
$k_0$: rate constant in the absence of catalyst

in the presence of various concentrations of lead acetate, a typical metal ion catalyst, are plotted in Fig. 3. It should be recalled here that the reaction proceeds slowly even in the absence of any catalyst.[1]

In consideration of such complications, the first-order rate constants, $k$ ($hr^{-1}$), in the glycolysis of benzonitrile can be represented by Eq. (1):

$$k = 0.046 + 4.75\ [\text{catalyst}]^{0.44} \tag{1}$$

The rate of the formation of ammonia may be expressed by an identical equation.

The first-order rate constants in the glycolysis of benzonitrile obtained at 170°C and 150°C are plotted against the initial concentration of water in Fig. 4. The formation of ammonia was found to proceed considerably even in the absence of water. However, the first-order rate of the formation of ammonia increased remarkably with an increase in the concentration of water at the optimum reaction temperature, 170°C. Since the reaction mixture starts refluxing at a concentration of water higher than 1 mol/$l$, the reaction could not be carried out at the above-mentioned temperature, 170°C. The aforementioned first-order rate constant increased gradually up to the concentration of water of 1 mol/$l$ at a lower temperature, 150°C. The effect of water when its concentration is higher than 1 mol/$l$ will be reported in the succeeding paper, as well as the mechanism in the absence of any water in the glycolysis. The chemical equivalent volume of water to benzonitrile is 1 mol/$l$ in the reaction system.

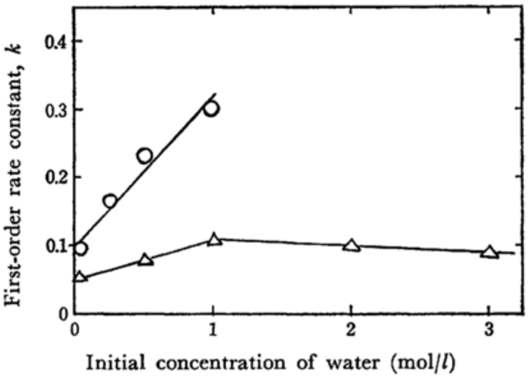

Fig. 4. The influence of the initial concentration of water in the glycolysis of benzonitrile.
○ Reaction temperature 170°C
△ Reaction temperature 150°C

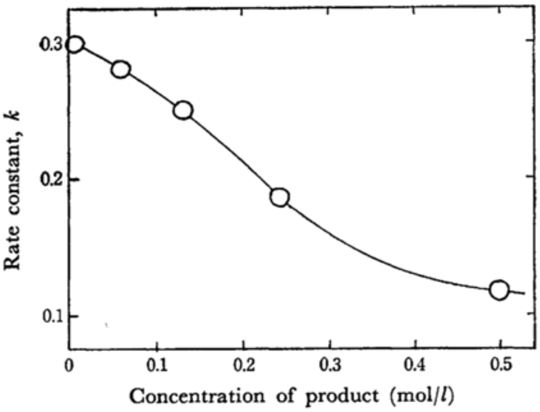

Fig. 5. The effect of the product in the glycolysis of benzonitrile.

In order to ascertain the inhibiting effect exerted by the product, $\beta$-hydroxyethyl benzoate, the glycolysis of benzonitrile was carried out in the presence of extra $\beta$-hydroxyethyl benzoate at 170°C. The results obtained are shown in Fig. 5. The initial rate constant decreases from 0.3 to 0.12 as the concentration of $\beta$-hydroxyethyl benzoate varies over the range from 0 to 0.5 mol/$l$. It is evident here that the product tends to inhibit the glycolysis reaction

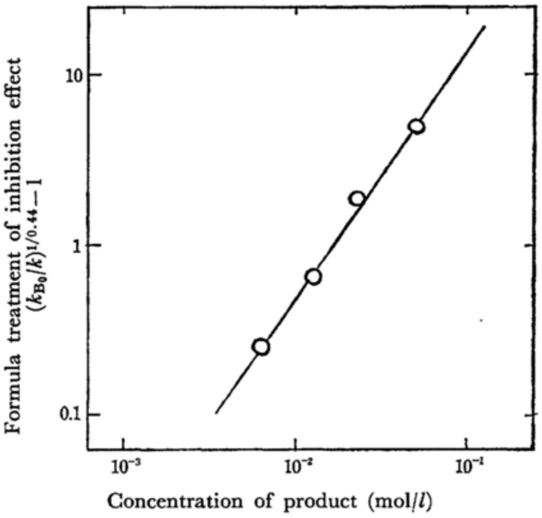

Fig. 6. The graphical analysis of the inhibiting effect of the product in the glycolysis of benzonitrile.

The rate of the formation of ammonia can be presented as follows:

$$k = k_{B_0}/(1 + C[\text{product}]^n)^{0.44} \qquad (2)$$

where $k_{B_0}$ represents the rate constant when no product is added, and where $C$ and $n$ are the constants.

Moreover, by treating the rate data as shown in Fig. 6, the inhibiting effect of the product in the glycolysis of benzonitrile is found to fit the above formula and may be represented as Eq. (2′) for the rate of the formation of ammonia:

$$k = k_{B_0}/(1 + 330[\text{product}]^{1.50})^{0.44} \qquad (2')$$

where $k_{B_0}$ represents the above-described rate constant.

The Arrhenius plots of the first-order rate constant in the glycolysis of benzonitrile at a given concentration of the reactant are shown in Fig. 7. The apparent activation energy for the formation of ammonia in the temperature range of 150—170°C was 18.0 kcal/mol.

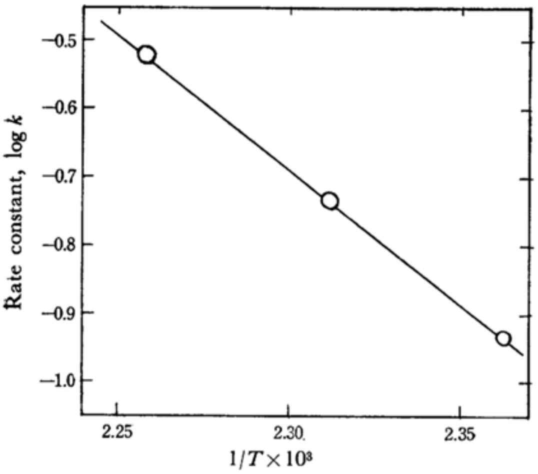

Fig. 7. Arrhenius plot of the first-order rate constant in the glycolysis of benzonitrile.

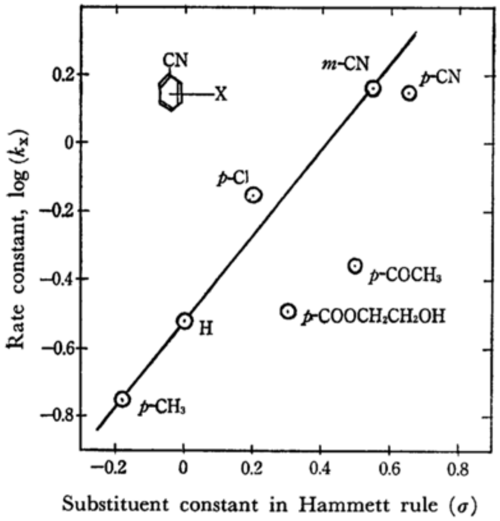

Fig. 8. Hammett correlation of $\log k_X$ *vs.* $\sigma$ in the glycolysis of substituted benzonitrile.

The glycolysis reactions were also carried out with various substituted benzonitriles. The reaction rate constant is plotted against the Hammett constant, $\sigma$,[4] in Fig. 8.

The Hammett correlation gives a straight line except for substituted benzonitriles with the carbonyl group, such as $\beta$-hydroxyethyl *p*-cyanobenzoate and *p*-cyanoacetophenone. The Hammett reaction constant, $\rho$, calculated from the slope in Fig. 8 is 1.2.

The effects of the types of glycol on the glycolysis of benzonitrile at 150°C may be seen in Table 1. Here the rate of reaction decreases rapidly with an increase in the number of the carbon atoms between the two hydroxy groups.[5] The rate also decreases as the order of hydroxy group involved becomes higher. Thus, primary>secondary>tertiary.

**Glycolysis of Benzamide.** In order to examine to what extent the reaction proceeds through another path where benzamide is known to participate as an intermediates, we studied the reaction of benzamide with glycols under catalytic conditions. Here the benzamide may be formed through the hydrolysis of benzonitrile. The apparent first-oder rate constants in the glycolysis of benzamide are listed in Table 2. With ethylene glycol, the rate of reaction in the glycolysis of benzamide is about one-third that observed in the glycolysis of benzonitrile. The rate of the reaction in the glycolysis of benzamide with tetramethylene glycol is, however, in the same range as that with ethylene glycol.

Thus, with tetramethylene glycol, the rate of reaction in the glycolysis of benzamide is much greater than that in the glycolysis of benzonitrile. These results suggest that the glycolysis of nitrile may be different in mechanism from that of amide.

**Reaction of *m*-Nitrobenzonitrile with Glycols.** Since the rate of the glycolysis of benzonitrile was found to be remarkably affected by the type of glycol used (Table 1), we studied the kinetics of the formation of imidate from nitrile and alcohol.

The results of the kinetic investigation of the formation of imidate from *m*-nitrobenzonitrile with ethylene glycol under various conditions are summarized in Table 3. The equilibrium constants for the reaction with a series of butanols are also indicated. The equilibrium constant, $K$, between benzonitrile and imidate in the presence of ethylene glycol under the reaction conditions described in the Experimental Section is not different from that for *n*-butanol. With secondary or tertiary butanol, however, the reaction to imidate hardly proceeded at all.

The temperature dependence of the equilibrium

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[4] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[5] B. Robinson, *J. Chem. Soc.*, **1963**, 2417.

TABLE 1. THE EFFECTS OF THE VARIOUS TYPES OF GLYCOLS IN THE GLYCOLYSIS OF BENZONITRILE
Reaction conditions, glycols: 93 g each, benzonitrile: 10.4 g (0.1 mol), $Pb(OAc)_2 \cdot 3H_2O$: 0.38 g (0.001 mol), $H_2O$: 1.8 g (0.1 mol), reaction temperature: 150°C

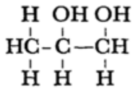
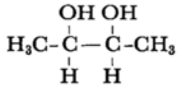
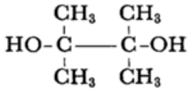
| Kind of glycol used | Structural formula of glycol | First-order rate constant $k$ ($hr^{-1}$) |
|---|---|---|
| Ethylene glycol | $HOCH_2CH_2OH$ | 0.101 |
| Trimethylene glycol | $HOCH_2CH_2CH_2OH$ | 0.041 |
| Tetramethylene glycol | $HOCH_2CH_2CH_2CH_2OH$ | 0.0048 |
| Pentamethylene glycol | $HOCH_2CH_2CH_2CH_2CH_2OH$ | 0.0036 |
| Propylene glycol |  $\mathrm{H\overset{H}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}H}$ | 0.062 |
| 2, 3-Butandiol |  $\mathrm{H_3C-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-CH_3}$ | 0.039 |
| Pinacol |  $\mathrm{HO-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-OH}$ | 0.000 |

TABLE 2. THE FIRST-ORDER RATE CONSTANTS IN THE GLYCOLYSIS OF BENZAMIDE
Reaction conditions, benzamide: 12.1 g (0.1 mol), glycol: 93 g each, reaction temperature: 170°C

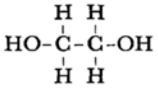
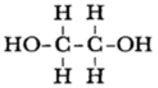
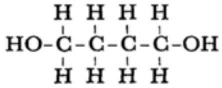
| Glycol | Structural formula of glycol | $Pb(OAc)_2$ catalyst | First-order rate constant $k$ ($hr^{-1}$) |
|---|---|---|---|
| Ethylene glycol |  $\mathrm{HO-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH}$ | 0.001 mol | 0.088 |
| Ethylene glycol |  $\mathrm{HO-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH}$ | none | 0.000 |
| Tetramethylene glycol |  $\mathrm{HO-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH}$ | 0.001 mol | 0.067 |

TABLE 3. THE EFFECTS OF THE KIND OF ALCOHOLS IN THE IMIDATE FORMATION OF *m*-NITROBENZONITRILE AND ALCOHOLS AT VARIOUS REACTION TEMPERATURE
Reaction conditions, alcohol: 124 g each, sodium metal: 0.014 g ($0.25 \times 10^{-4}$ g atom), *m*-NBN: 0.0125 mol

| Kind of alcohol | Additives | Reaction temperature | Time to reach equilibrium state | Equilibrium constant $K$ ($l$/mol) |
|---|---|---|---|---|
| Ethylene glycol | — | 25°C | 24 hr | 0.107 |
| Ethylene glycol | — | 60°C | 1.5 hr | 0.054 |
| Ethylene glycol | — | 100°C | 15 min | 0.024 |
| Ethylene glycol | $H_2O$*1 | 100°C | 10 min | 0.025 |
| Ethylene glycol | BHT*2 | 100°C | — | 0.031 |
| Ethylene glycol | $PbCl_2$*4 | 100°C | none*3 | 0 |
| *n*-Butanol | — | 60°C | 1 hr | 0.063 |
| *n*-Butanol | — | 100°C | 10 min | 0.030 |
| *sec*-Butanol | — | 60°C | — | 0.000 |
| *t*-Butanol | — | 60°C | — | 0.000 |

*1: 0.0125 mol *2: 0.0125 mol of bis-β-hydroxyethyl terephthalate
*3: none reaction *4: 6.25 mmol of $PbCl_2$ instead of Na

constant is presented in Fig. 9. The heat of reaction for the imidate formation was found to be −5.9 kcal/mol. By extrapolation from these results, the equilibrium constant for the imidate formation at 170°C was estimated to be *ca.* 0.01 $(mol/l)^{-1}$. The data listed in Table 3 also indicate that the rates of the

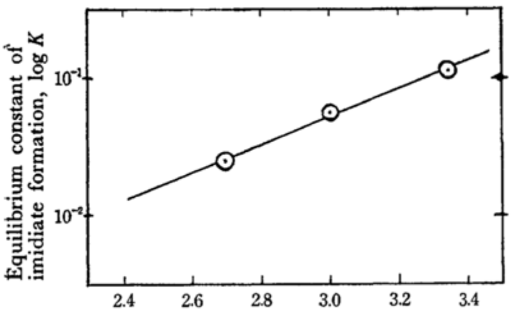


Fig. 9. Correlation of equilibrium constant log $K$ *vs.* the reciprocal of reaction temperatures in the imidate formation reaction of benzonitrile. Reaction condition: *m*-NBN: 0.0125 mol, E.G: 2 mol, Na: 0.625 mg atom

formation of imidate in the presence of sodium metal are very fast at 170°C.

The data of Tabe 3 suggest that the formation of imidate can not be catalyzed by lead chloride, though it is known to promote the reaction of glycolysis.[1] The formation of imidate is not influenced by the presence of water or of bis-$\beta$-hydroxyethyl terephthalate, which inhibited the glycolysis reaction. The rates of the lead-ion catalyzed glycolysis of benzonitrile at 170°C were not affected by the addition of sodium metal ($2.5\times10^{-4}$ g atom) and were about five times faster than that of the sodium-catalyzed glycolysis of benzonitrile ($2.5\times10^{-4}$ g atom sodium).

## Discussion

The experimental results presented above suggest that the rate-controlling step in the glycolysis reaction is the chemical reaction in the reaction mixture, while the rates of the desorption of ammonia are rapid. An analysis of the reaction rate data suggests that the formation of $\beta$-hydroxyethyl benzoate is accompanied by the formation of ammonia and that the rates of reaction may be inhibited by the presence of the product, $\beta$-hydroxyethyl benzoate. These may be the reasons why the rate of ammonia formation tends to deviate from the first-order reaction scheme at higher conversions and at different initial concentrations of benzonitrile, as is shown in Fig. 2. From the fact that *p*-cyanoacetophenone also inhibits the reaction, as is shown in Fig. 8, the inhibiting effect may be ascribed to the carbonyl group. Since the reaction was promoted by the metal ions, such as cupric, lead, and zinc ions, with a coordination tendency, as has been presented in the previous report,[1] the inhibition by the ester might be caused by the coordination of the carbonyl groups of the product to the lead ion, thus forming a more stable complex than the reaction intermediates. The deviation at the Hammett plots illustrated at Fig. 8 may be caused by the same factor.

The Hammett reaction constant for the glycolysis of variously substituted benzonitriles ($\rho=1.2$) is of the same magnitude as those for the alkaline hydrolysis of substituted benzonitriles ($\rho=1.5$) and of benzamides[6] ($\rho=1.75$) and that for the formation of imidate from benzonitrile[2] ($\rho=1.9$). This may suggest that the nucleophilic attack on benzonitrile is involved in the reaction mechanism.

From the results of the glycolysis of benzamide, the reaction route through the formation of benzamide from nitrile with water seems insignificant.

The addition of nitrile to glycols, the imidate formation, may be suggested to be involved in the reaction mechanism, since the rate of the reaction of glycols with a secondary or tertiary hydroxy group is smaller than that of ethylene glycol, and this tendency is similar to that in imidate formation. The presence of excess glycols, the effect of the type of glycol, and the effect of the substituted group of benzonitrile are other reasons to support the formation of imidate.

The reaction of the imidate formation of benzonitrile with glycol could not be promoted in the presence of a lead catalyst. The lead ion-catalyzed glycolysis of benzonitrile was found not to be promoted especially by the co-presence of alkaline metal and to be considerably faster than that of the sodium ion-catalyzed glycolysis of benzonitrile. Therefore, it seems likely that the reaction of imidate formation proceeds quickly under the given conditions.

Contrary to the lead ion-catalyzed trans-esterification of dimethyl terephthalate, in which the rate of the reaction with ethylene glycol is of a magnitude similar to that with tetramethylene glycol, the effect of the methylene sequence length of the two hydroxy groups is remarkable in the glycolysis of benzonitrile. Taking account of the effect of the neighboring hydroxy group's assistance in the alkaline hydrolysis of the ester,[7] the reaction mechanism may be considered to involve the internal solvation of the critical transition state by the neighboring hydroxy group.

In the basence of water, the rate of ammonia formation was slow and the amount of $\beta$-hydroxyethyl benzoate formed was very little in the glycolysis reaction, while in the presence of water the rate of ammonia formation was remarkably promoted and there was a sizable formation of $\beta$-hydroxyethyl benzoate. These facts obviously suggest the participation of water in the rate-determining step in the ester formation.

In view of the above facts, the following reaction mechanism may be proposed for the lead ion-catalyzed glycolysis of benzonitrile:

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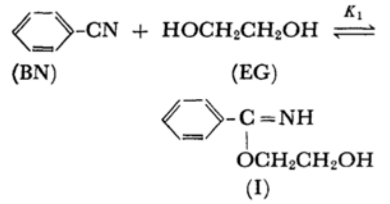
6) L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **84**, 1625 (1962).

7) 1) T. C. Bruice and T. H. Fife, *ibid.*, **84**, 1973 (1962). b) T. C. Bruice and S. J. Benkovic, " Bioorganic Mechanism " Vol. 1, W. A. Benjamines Inc., New York, N.Y. (1966), p. 146. c) T. Yamanaka, A. Ichihara, K. Tabe and T. Matsumoto, *Shokubai* (*Catalysis*), **6**, 304 (1964).



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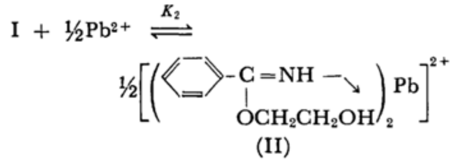

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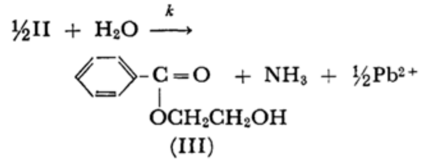

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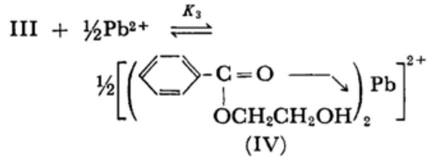

(6)

Here we consider that Eq. (5) represents the rate-determining step, in which the internal solvation of the critical transition state by the neighboring hydroxy group is involved. The above mechanism leads to Eqs. (7)—(11) for the rate of ammonia formation in the lead ion-catalyzed glycolysis of benzonitrile:

$$\frac{d[NH_3]}{dt} = k[II]^{1/2}[H_2O] \tag{7}$$

$$[II]^{1/2} = K_2[I][Pb^{2+}]^{1/2} \tag{8}$$

$$[I] = K_1[BN][EG] \tag{9}$$

$$[IV]^{1/2} = K_3[III][Pb^{2+}]^{1/2} \tag{10}$$

$$[Pb^{2+}] = [Pb^{2+}]_0 - [II] - [IV] \tag{11}$$

As the electronegativity of oxygen is larger than that of nitrogen, it is presumed that $K_3 > K_2$. In addition, as the concentration of [II] is very small under the given reaction conditions, in consideration of the mass balance, Eq. (11) may be simplified to Eq. (12):

$$[Pb^{2+}] \fallingdotseq [Pb^{2+}]_0 - [IV] \tag{12}$$

where $[Pb^{2+}]_0$ is the initial concentration of lead ions.

By combining Eq. (10) with Eq. (12), we have Eq. (13):

$$[Pb^{2+}] = \frac{[Pb^{2+}]_0}{1 + K_3{}^2[III]^2} \tag{13}$$

Thus, Eq. (7), replaced by Eqs. (8), (9), and (13), can be formulated as follows:

$$\frac{d[NH_3]}{dt} = kK_1K_2[BN][EG][H_2O]\left\{\frac{[Pb^{2+}]_0}{1 + K_3{}^2[III]^2}\right\}^{1/2} \tag{14}$$

Therefore, the initial rate of the formation of ammonia in the presence of excess ethylene glycol can be presented as follows:

$$\frac{d[NH_3]}{dt} = k'K_1K_2[BN][H_2O]\left\{\frac{[Pb^{2+}]_0}{1 + K_3{}^2[III]^2}\right\}^{1/2} \tag{15}$$

On the other hand, the observed initial rate of the lead ion-catalyzed glycolysis of benzonitrile, neglecting the reaction in the absence of any catalyst and of water, may be presented as in Eq. (16):

$$\frac{d[NH_3]}{dt} = k''[BN][H_2O]\left\{\frac{[Pb^{2+}]_0}{1 + 330[III]^{1.5}}\right\}^{0.44} \tag{16}$$

This equation agrees satisfactorily with Eq. (15).

Thus, the kinetic studies obviously support the afore-mentioned reaction mechanisms for the metal ion-catalyzed glycolysis of benzonitrile.

The reaction of non-catalytic glycolysis and that in the absence of water occured simultaneously in the above glycolysis of benzonitrile. These reactions are presumed to have more complicated reaction routes than that of the above-mentioned glycolysis; they will be discussed in the succeeding paper.