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The Kinetics of the Metal Ion-catalyzed Glycolysis of Terephthalonitrile

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The kinetics of the lead ion-catalyzed glycolysis of terephthalonitrile have been studied in the absence of and in the presence of water. In the absence of water, scarcely any formation of β-hydroxyethyl *p*-cyanobenzoate is observed, but some orthoesters are formed. The reaction rate data obtained in the absence of water are found to fit a reversible consecutive reaction scheme in which some basic compounds are involved as the intermediates. In proportion to the increase in the concentration of water, such intermediates as the orthoesters and basic compounds are hydrolyzed more rapidly to form β-hydroxyethyl *p*-cyanobenzoate, but simultaneously the hydrolysis of terephthalonitrile and the basic intermediates also takes place in the reaction mixture, thus yielding amide.

The effectiveness of the various kinds of metal compounds on the metal ion-catalyzed glycolysis of terephthalonitrile[1] and the kinetics of the metal ion-catalyzed glycolysis of benzonitrile[2] have been discussed in previous papers.

The heavy metal ions, such as cupric, lead, and zinc ions, have been found to promote the glycolysis of nitriles. Their catalytic activities have been correlated with the coordinating tendency of metal ions.

Benzonitrile first affords imidate upon the addition of glycol, and then two moles of the thus-derived imidates are chelated to a metal ion. The imidates activated by forming the chelate can be easily hydrolyzed by water to form esters and ammonia. However, these esters tend to chelate to the metal ions thus inhibiting the reaction.

The kinetic study of the metal ion-catalyzed glycolysis of terephthalonitrile is, therefore, important in order to have a better understanding of the reaction mechanisms and various reaction routes. No kinetic study of the glycolysis has been found in the literature.

We will attempt here to clarify the reaction routes and mechanisms of the metal ion-catalyzed glycolysis of terephthalonitrile in the absence of and in the presence of water.

Experimental

Kinetic Measurements. The procedure and measurements for the glycolysis of terephthalonitrile were similar to those employed in previous works.[1,2]

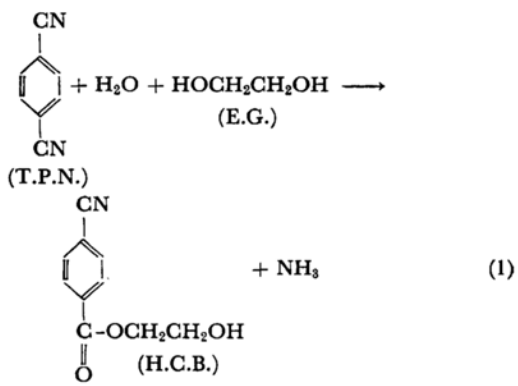
A typical set of reaction conditions employed is as follows: A reaction mixture of 0.05 mol of terephthalonitrile (T.P.N.), 1.5 mol of ethylene glycol (E. G.), 0.1 mol of water, and 0.00025 mol of a catalyst was reacted at the reaction temperature of 170°C. The reaction was carried out under a nitrogen atmosphere, nitrogen being bubbled into the mixture at the rate of 40 ml/min.

A 100-ml three-necked glass flask equipped with a reflux condenser, a thermometer, and a nitrogen gas inlet was used as the reaction vessel. The reaction mixture in the flask was immersed in an electrically-heated oil bath stirred by a magnetic apparatus. The ammonia formed during the reaction was absorbed in a dilute sulfuric acid solution stirred by a magnetic stirrer set in the flask.

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. The rate of the conversion of terephthalonitrile was determined at given intervals by using gas-liquid chromatography. The rates of the formation of both β-hydroxyethyl *p*-cyanobenzoate (H.C.B.) and bis-β-hydroxyethyl terephthalate (B.H.T.) were examined by using gas-liquid chromatography and ultraviolet spectroscopy.

The heated liquid product in the reaction state was quickly sampled with a micro-syringe (50 μl) and analyzed by gas-liquid chromatography on a 2 m×6 mm stainless steel column of 25% Apiezon L on Chromosorb W at 190°C, using helium as a carrier gas and α-naphthol as an internal-standard substance.

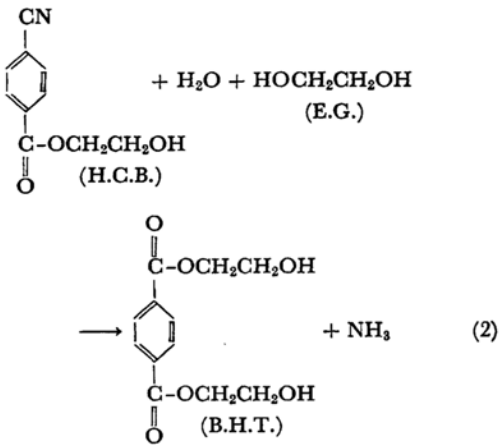
The reaction of the glycolysis of terephthalonitrile proceeds as in the following sequence:



(1)

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

2) T. Ikeda, M. Kitabatake, M. Ito and Y. Noguchi, *ibid.*, **41**, 1158 (1968).



(2)

The reaction routes and the mechanism of the glycolysis of terephthalonitrile discussed here are limited to the first stage of the overall reaction.

Materials. Terephthalonitrile (mp 224°C) was prepared by the ammoxidation of *p*-xylene and was purified by recrystallization from dioxane.

Ethylene glycol (bp 197.2°C) and dipropylene glycol (bp 231.8°C) used were of reagent grades.

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

Results and Discussion

The influence of the concentration of water on the conversion rate of terephthalonitrile was investigated.

Data on the conversion of terephthalonitrile and on the formation of ammonia and β-hydroxyethyl *p*-cyanobenzoate for each concentration of water are shown in Figs. 1 and 2 in relation to the reaction time. The reactions were carried out under the standard reaction conditions described above except for the amount of water. These figures indicate that the conversion rate of terephthalonitrile increases with an increase in the amount of water below a 2-molar ratio of water to terephthalonitrile. The rate of the formation of β-hydroxyethyl *p*-cyanobenzoate has the same tendency, but scarcely any β-hydroxyethyl *p*-cyanobenzoate is formed in the absence of water, though the formation of ammonia is recognized.

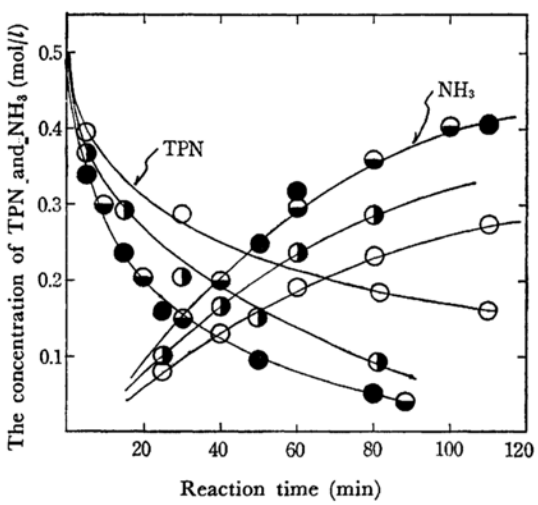


Fig. 1. The influence of concentration of water on the conversion of the concentration of terephthalonitrile and ammonia.
-○-: 0 initial molar ratio of H_2O to TPN
-◑-: 1 initial molar ratio of H_2O to TPN
-◒-: 2 initial molar ratio of H_2O to TPN
-●-: 3 initial molar ratio of H_2O to TPN
Reaction conditions: E.G./TPN=30, $Pb(OAc)_2$/TPN=1/200 at 170°C

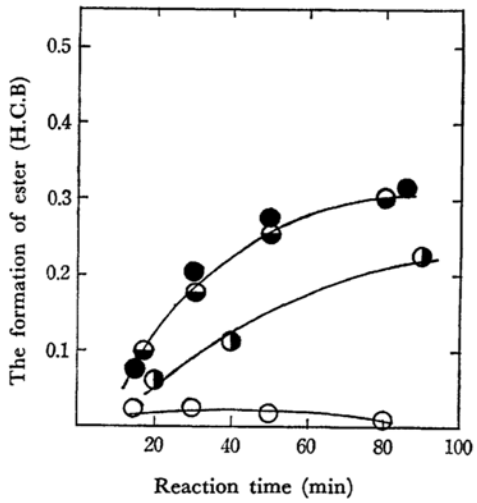


Fig. 2. The influence of the concentration of water on the formation of β-hydroxyethyl *p*-cyanobenzoate (H.C.B.).
-○-: 0 initial molar ratio of water to terephthalonitrile
-◑-: 1 initial molar ratio of water to terephthalonitrile
-◒-: 2 initial molar ratio of water to terephthalonitrile
-●-: 3 initial molar ratio of water to terephthalonitrile
Reaction conditions: E.G./TPN=30, $Pb(OAc)_2$/TPN=1/200 at 170°C

The rate of the conversion of terephthalonitrile is usually greater than that of the formation of ammonia. This fact indicates that nitrogen compounds may be present as intermediates in the routes from nitrile to the ester and/or that a side reaction such as the hydrolysis of nitrile to amide may exist.

The basic compounds which react with sulfuric acid were actually observed in the reaction mixture, as shown in Fig. 3. Since the desorption of ammonia from the reaction mixture was rapid under the given conditions, the amount of ammonia in the reaction mixture was insignificant. These basic compounds in the reaction mixture had a tendency to decrease with an increase in the concentration of water. Besides, at high concentrations of water,

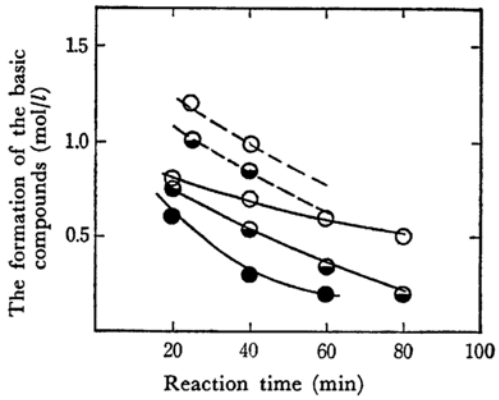


Fig. 3. The influence of the concentration of water and reaction temperature on the formation of basic compounds.
-○-: 0 initial molar ratio of water to terephthalonitrile
-◒-: 2 initial molar ratio of water to terephthalonitrile
-●-: 3 initial molar ratio of water to terephthalonitrile
——: 170°C
- - -: 145°C
Reaction conditions: E.G./TPN=30, $Pb(OAc)_2$/TPN=1/200

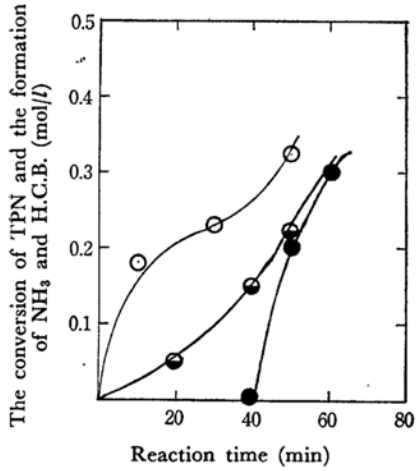


Fig. 4. The conversion of TPN and the formation of ammonia and ester (H.C.B.) by the addition of water to the non-aqueous reaction mixture at the reaction time of 40 min.
-○-: concentration of TPN reacted
-◒-: formation of NH_3
-●-: formation of ester (H.C.B.)
Reaction conditions: E.G/TPN=30, $Pb(OAc)_2$/TPN=1/200 at 170°C

there were quite large differences between the amount of the conversion of terephthalonitrile and that of both β-hydroxyethyl *p*-cyanobenzoate and the basic compounds, suggesting the formation of amide.

It is shown in Fig. 2 that scarcely any β-hydroxyethyl *p*-cyanobenzoate is formed in the absence of water, though the amounts of terephthalonitrile reacted and of ammonia formed increase considerably. However, the ester was observed to be formed, as shown in Fig. 4, when water was added to this non-aqueous reaction mixture in the course of the reaction. This fact indicates that the compounds other than the ester are formed in the absence of water and are susceptible to being hydrolyzed to the ester.

In Fig. 5 the experimental data on the concentration of unchanged terephthalonitrile, the amounts of the basic compounds titrated by sulfuric acid in the reaction mixture, and the formation of orthoester-type compounds are plotted against the reaction time at 170°C in the absence of water.

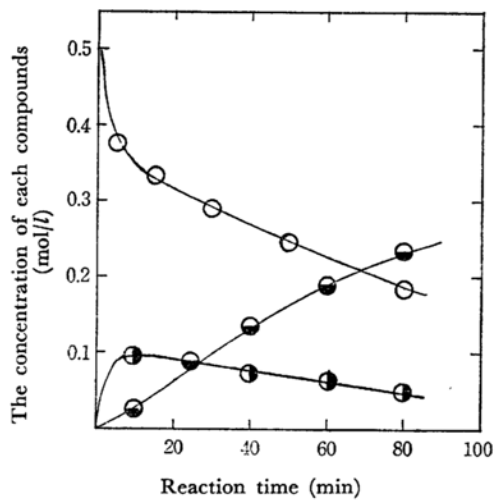


Fig. 5. The experimental data of the concentration of terephthalonitrile, orthoester and basic compound represented by marks and the calculated results with analog computer represented by real curved lines in the absence of water.
-○-: the concentration of terephthalonitrile unchanged
-◒-: the formation of orthoester (ammonia)
-◑-: the formation of basic intermediate compounds
Reaction conditions: E.G/TPN=30, $Pb(OAc)_2$/TPN=1/200, H_2O=0 at 170°C

The total amounts of ammonia formed and of the basic compounds in the reaction mixture in the absence of water correspond to the amounts of terephthalonitrile reacted. On the other hand, the rate of the reaction of terephthalonitrile was found to be first-order for the concentration of terephthalonitrile at a low conversion rate of terephthalonitrile.[1)]

In view of the above facts, the following rate expressions for the reaction scheme (Eq. (3)) were chosen:

$$\text{T.P.N.} \underset{k_2,\ HOCH_2CH_2OH}{\overset{k_1}{\rightleftarrows}} \text{B} \xrightarrow[HOCH_2CH_2OH]{k_3} \text{C} + NH_3 \quad (3)$$

B: basic compounds
C: orthoester-type compounds

The curves calculated by an analog computer according to Eqs. (4), (5) and (6) are presented in Fig. 5 by real curved lines, which are more agreeable to the experimental data.

$$d[TPN]/dt = k_2[B] - k_1[TPN] \quad (4)$$

$$d[B]/dt = k_1[TPN] - k_2[B] - k_3[B] \quad (5)$$

$$d[C]/dt = k_3[B] \quad (6)$$

The rate constants of the three reaction paths, k_1, k_2, and k_3, were 0.129 min^{-1}, 0.343 min^{-1}, and 0.033 min^{-1} respectively.

In order to get information about the C intermediate, initial reaction rates of the terephthalonitrile at different initial concentrations of ethylene glycol were investigated in an inert solvent such as dipropylene glycol; the following rate expression were chosen:

$$\gamma_0 = k_1[TPN]_0[EG]_0^n \quad (7)$$

γ_0: initial reaction rate of terephthalonitrile

Plots of k_1 in relation to the initial concentration of ethylene glycol give a straight line, as shown in Fig. 6, and the reaction order of ethylene glycol is nearly equal to 2. This fact suggests that two moles of ethylene glycol participate in the formation of the intermediate, B, or the product, C.

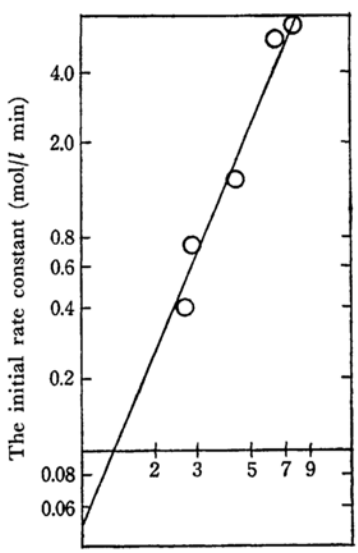
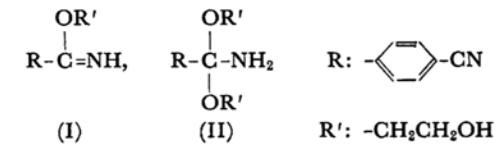


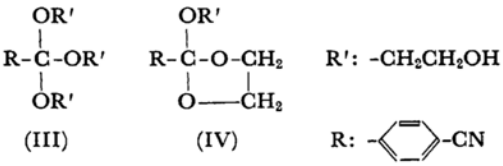
Fig. 6. The correlation between the initial rate constants and the initial concentration of ethylene glycol.
Reaction condition: $Pb(OAc)_2$/TPN=1/200 at 170°C

The reaction intermediate, B, is, in the absence of water, a substance which reacts with sulfuric acid. It may, therefore, be expected to have the following structures:



(I) (II)

The product, C, is presumed to be a orthoester-type compound:

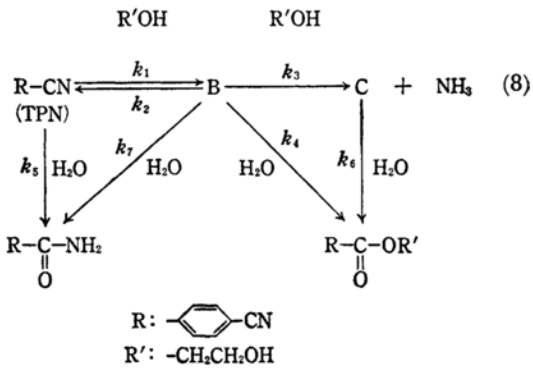


(III) (IV)

In Fig. 6 the straight line intercepts the vertical axis at the value of 0.0055. Using the values of 0.0055 and the initial concentration of terephthalonitrile of 0.448 mol/l, the rate constant, k_1, is calculated to have the value of 0.123 min^{-1}, a value which is almost equal to the above calculated value, k_1= 0.129 min^{-1}. These results indicate that the proposed reaction scheme and kinetics are consistent with all the experimental observations.

Even in the presence of water, the reaction to form B from the nitrile and that to give C from B may take place successively. Water is considered to participate in the reaction steps to form the ester and the amide.

Thus the following reaction scheme and rate equations may be considered for the first step of the glycolysis reaction:



$$\frac{d[TPN]}{dt} = k_2[B] - k_1[TPN] - k_5[TPN][H_2O] \quad (9)$$

$$\frac{d[B]}{dt} = k_1[TPN] - k_2[B] - k_3[B] - k_4[B][H_2O] - k_7[B][B_2O] \quad (10)$$

$$\frac{d[C]}{dt} = k_3[B] - k_6[C][H_2O] \quad (11)$$

$$\frac{d[RCOOR']}{dt} = k_4[B][H_2O] + k_6[C][H_2O] \quad (12)$$

$$\frac{-d[H_2O]}{dt} = k_5[TPN][H_2O] + k_4[B][H_2O] + k_6[C][H_2O] + k_7[B][H_2O] \quad (13)$$

$$\frac{d[NH_3]}{dt} = k_3[B] + k_4[B][H_2O] \quad (14)$$

In Fig. 7 the experimental data of the concentration of unchanged terephthalonitrile, the amounts of basic compounds titrated by sulfuric acid in the reaction mixture, and that of the formation of ammonia and β-hydroxyethyl *p*-cyanobenzoate are plotted against the reaction time at 170°C in the presence of water.

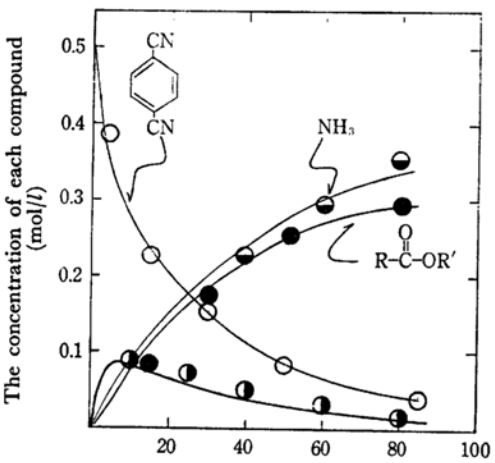


Fig. 7. The experimental data of the concentration of terephthalonitrile, ammonia, basic intermediate compounds and ester (H.C.B.) represented by marks and the calculated results with analog computer represented by real curved lines in the presence of water.
-○-: the concentration of TPN
-◒-: the formation of NH_3
-◑-: the formation of basic intermediate compound
-●-: the formation of ester (H.C.B.)
Reaction conditions: E.G./TPN=30, $Pb(OAc)_2$/TPN=1/200 H_2O/TPN=2, at 170°C

On the basis of the experimental data in Fig. 7, theoretical curves, as calculated by the analog computer, are shown in Fig. 7 by real curved lines using the above equations, (9), (10), (11), (12), (13), and (14). These rate constants at 170°C are obtained as follows:

$k_1 = 0.129\ min^{-1}$
$k_2 = 0.343\ min^{-1}$
$k_3 = 0.033\ min^{-1}$
$k_4 = 0.055\ min^{-1}\ mol^{-1}l$
$k_5 = 0.011\ min^{-1}\ mol^{-1}l$
$k_6 = 0.071\ min^{-1}\ mol^{-1}l$
$k_7 = 0.040\ min^{-1}\ mol^{-1}l$

The above results are also supported by the facts that scarcely any formation of the intermediate, C, is observed in the presence of water and that the rate constant of the direct hydrolysis of terephthalonitrile to amide in dipropylene glycol is very small, even in the presence of water.

It may, therefore, be considered that the glycolysis of terephthalonitrile to form β-hydroxyethyl *p*-cyanobenzoate may proceed *via* the hydrolysis of an ortho-ester-type compound, C, especially at a low concentration of water, and *via* an imidate- or amine-type intermediate, B, at a high concentration of water. Furthermore, at a higher concentration of water the formation of amide becomes a little more significant.

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