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Metal Ion-catalyzed Glycolysis of Terephthalonitrile

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The effects of various metal compounds on the glycolysis of terephthalonitrile were studied in the presence of water at 185°C. The catalytically-active species were found to be metal ions. Their catalytic activities were correlated with the acid ionization constants, $\mathrm{p}K_a$, of metal ions. The active catalysts were limited to the metal ions with $\mathrm{p}K_a$ values larger than 7. The study of the reaction mechanism suggests that, while one group of metal ions accelerates the formation of glycol and hydroxyl anions, the other involves catalytic acceleration through the coordination of metal ions. The metal ions with $\mathrm{p}K_a$ values of less than 7 showed no catalytic activities. These results were interpreted in terms of the tendency of the metal ions to form too stable coordination intermediates. Most of these metal compounds also served to inhibit the reactions. For a series of salts derived from a given metal, the catalytic activities were found to decrease with a decrease in their solubilities in water. On the other hand, metal oxides and hydroxides had high catalytic activities.

The glycolysis of nitriles to the corresponding esters is known to proceed under non-catalytic conditions. The reaction may also be catalyzed by acids and bases.[1] Recently the glycolysis of aromatic nitriles has been reported to be promoted by heavy metal salts and by oxides.[2,3] On the other hand, the metal ions are known to promote the hydrolyses of esters,[4] of amides,[5] and of Schiff bases,[6] and the glycolysis of esters.[7]

A basic study of the metal ion-catalyzed glycolysis of nitriles was, therefore, of interest in order to get a better understanding of the role of the metal ions in the metal-ion catalysis.

We will attempt in this paper to clarify the catalytic effects of metal compounds in the glycolysis of terephthalonitrile.

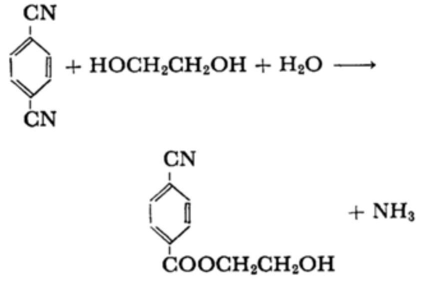
Experimental

Experimental Apparatus and Procedure. The reaction was carried out in a 100-m*l* three-necked glass flask equipped with a reflux condenser, a thermometer, and a nitrogen gas inlet; the flask was immersed in an oil bath with an electric heating system. During the reaction the reactants in this flask and an ammonia-absorbing solution prepared in another flask were stirred by the magnetic stirring device.

A typical example of the determination of reaction rate follows: 6.4 g of terephthalonitrile (0.05 mol), 93.0 g of ethylene glycol (1.5 mol), 1.8 g of water (0.1 mol), and 2.5×10^{-4} mol (as metal) of catalyst were added to the reaction vessel, which was then set in the oil bath preheated at 185°C. Nitrogen gas was bubbled into the reaction mixture at a rate of 40 m*l*/min. The nitrogen flux was introduced through a reflux condenser to the ammonia-absorbing solution kept at 25°C. The reaction was then carried out at 185°C.

The resulting ammonia, carried with the nitrogen flux, was absorbed into the sulfuric acid solution. The rate of the formation of ammonia was followed by the titration of a sulfuric acid solution at given intervals.

As the main reaction products, β-hydroxyethyl *p*-cyanobenzoate, and bis-β-hydroxyethyl terephthalate were obtained by the following reaction sequence:



(1)

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1) Distiller's Co., Brit. Pat. 800875 (1958).

2) Toyo Rayon K. K., Brit. Pat. 981703 (1965).

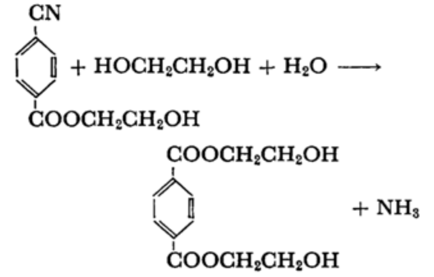
3) Showa Denko K.K., German Pat. to be published.

4) a) H. Kroll, *J. Am. Chem. Soc.*, **74**, 2036 (1952); b) M. L. Bender and B. W. Turnquest, *ibid.*, **79**, 1889 (1957); c) H. L. Conley, Jr., and R. B. Martin, *J. Phys. Chem.*, **69**, 2914, 2923 (1965); d) M. D. Alexander and D. H. Busch, *J. Am. Chem. Soc.*, **88**, 1130 (1966).

5) a) L. Meriwether and F. H. Westheimer, *J. Am. Chem. Soc.*, **178**, 5119 (1956); b) H. L. Conley, Jr., and R. B. Martin, *J. Phys. Chem.*, **69**, 2914 (1965).

6) a) G. L. Eichhorn and J. C. Bailar, *J. Am. Chem. Soc.*, **75**, 2905 (1953); b) G. L. Eichhorn and I. M. Trachtenberg, *ibid.*, **76**, 5183 (1954); c) G. L. Eichhorn and N. D. Marchand, *ibid.*, **78**, 2688 (1956).

7) a) W. Griel and G. Schnock, *J. Polymer Sci.*, **30**, 412 (1958); b) R. E. Wilfong, *ibid.*, **54**, 385 (1961); c) M. Sumoto, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **66**, 1663 (1963); d) K. Yoda, K. Kimoto and T. Toda, *ibid.*, **67**, 909 (1964); e) M. Sumoto and A. Kito, *Ohsaka Kogyo Gijutsushikenjo Kiho* (*Reports of the Government Chemical Industrial Research Institute, Osaka*), **12**, 214 (1961).


(2)

These products were analyzed by gas-liquid chromatography (column: 25 wt% of Apiezon L on Chromosorb W) for β-hydroxyethyl p-cyanobenzoate, and by fractionation and ultraviolet spectroscopy for bis β-hydroxyethyl terephthalate.

Materials. Terephthalonitrile (mp 224°C) was prepared by the ammoxidation of p-xylene and was purified by recrystallization from dioxane. Ethylene glycol (bp 197°C) used was of the reagent grade. The metal compounds were all extra pure, commercially-available products, with the exception of lead glyceroxide, which was prepared according to the procedure proposed by Nitschman.8)

Results and Discussion

According to the kinetics of this reaction, which will be reported in a separate paper, the rate of the reaction of terephthalonitrile is not necessarily equal to the rate of the formation of ammonia, but the conversion of terephthalonitrile is parallel to the formation of ammonia. The catalytic activities of metal compounds can be correlated with the rate of the formation of ammonia.

The rates of formation of ammonia are shown in Fig. 1 for the different initial nitrile concentration; they are independent of the concentration of terephthalonitrile in the initial stage of the reaction, up to a 30% conversion to ammonia. This fact indicates that the rate of the formation of ammonia follows the first-order rate law with respect to the terephthalonitrile at a low range of conversion.

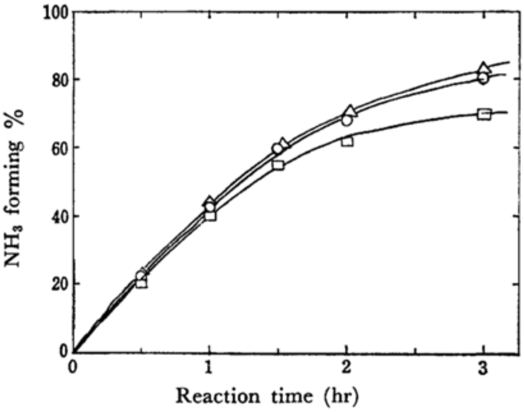


Fig. 1. Glycolysis of terephthalonitrile in the presence of lead acetate at various initial terephthalonitrile concentrations at 185°C.
Initial concentration of terephthalonitrile:
-△-; 0.0125 mol, -○-; 0.025 mol,
-□-; 0.05 mol,
Ethylene glycol 93.0 g; Water 1.8 g;
Lead acetate 0.47 g

TABLE 1. RATE CONSTANTS FOR THE GLYCOLYSIS OF TEREPHTHALONITRILE IN THE PRESENCE OF VARIOUS CATALYSTS AT 185°C

Ethylene glycol 93.0 g; Terephthalonitrile 6.4 g; Water 1.8 g; Catalyst 2.5×10^{-4} atomic equivalent on the basis of metal

Periodic Chart	Catalyst	K	$K-K_0$
	none	0.36	0
Ia	LiOAc	0.50	0.14
	NaOAc	0.50	0.14
	KOAc	0.47	0.11
IIa	$Mg(OAc)_2$	0.45	0.09
	$Ca(OAc)_2$	0.51	0.15
	$Sr(OAc)_2$	0.51	0.15
	$Ba(OAc)_2$	0.44	0.08
IIb	$LaCl_3$	0.21	−0.15
	La_2O_3	0.36	0.00
	$Ce(HCO_3)_3$	0.29	−0.07
	Ce_2O_3	0.36	0.00
	$Th(NO_3)_4$	0.14	−0.22
	$UO_2(OAc)_2$	0.24	−0.12
IVb	$TiOSO_4$	0.19	−0.17
	$ZrOCl_2$	0.17	−0.19
Vb	$VOSO_4$	0.21	−0.15
VIb	$Cr(OAc)_3$	0.29	−0.07
VIIb	$Mn(OAc)_2$	0.59	0.23
VIII	$Fe^{(III)}(OH)(OAc)_2$	0.36	0.00
	$Fe^{(II)}$-oxalate	0.47	0.11
	$Co(OAc)_2$	0.89	0.53
	$Ni(OAc)_2$	0.72	0.36
	$PdCl_2$	0.00	−0.36
Ib	$Cu(OAc)_2$	1.04	0.68
	Ag(OAc)	0.36	0.00
IIb	$Zn(OAc)_2$	0.61	0.25
	Zn(metal)	0.49	0.13
	$Cd(OAc)_2$	0.79	0.43
	HgOAc	0.21	−0.15
	$Hg(OAc)_2$	0.31	−0.05
IIIa	$Al_2O(OAc)_4$	0.40	0.04
	$Al(OC_3H_7)_3$	0.46	0.10
	$InCl_3$	0.29	−0.07
	Tl(OAc)	0.48	0.12
IVa	$Sn(OAc)_2$	0.26	−0.10
	$Pb(OAc)_2$	0.70	0.34
Va	$BiO(NO_3)$	0.33	−0.03
	Sb_2O_3	0.33	−0.03
	H_3PO_4	0.26	−0.10
VIIa	HCl	0.00	−0.36
IIIa	H_3BO_3	0.36	0.00

On the other hand, the reaction proceeds considerably in the absence of any catalyst under the

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8) H. Nitschman, *Helv. Chim. Acta*, **66**, 759 (1935).

above conditions. The catalytic activities, therefore, have to be compared with the specific rate constants, $K-K_0$, adjusted by substracting the specific rate constants in the absence of any catalyst, K_0, from those in the presence of catalysts, K.

Table 1 lists the first-order specific rate constants obtained after the first 30% of the reaction for the glycolysis of terephthalonitrile in the presence of various catalysts.

The metal compounds with catalytic activities were those derived from metals which belong to the Ia, IIa, IIIa, VIIb, VIII, Ib, IIb, and IVa groups in the periodic charts of the elements.[9] Considering the reaction conditions and the results, it appears that the active species of the catalysts may be ascribed to the metal ions. Even the zinc metal itself showed catalytic activity, as Table 1 shows. From this fact, it appears that the effectiveness in this glycolysis can be ascribed to the metal ions in the final reaction state.

The catalytic activities in the glycolysis were found, with a few exceptions, to have a good correlation with the stability constants[10] of the oxine complex of metal ions. These correlations are shown in Fig. 2. From these facts, the coordinations of the reagent to metal ions may be considered to play an important role.

Accordingly, the electron affinity of the metal ions, which determines the coordinating tendency, may be closely related to the catalytic activity. By adopting the acid ionization constants[11,12] of the metal ions as a measure of the electron affinity of the metal ions,[13] the aforementioned relationship may be illustrated as in Fig. 3. The catalytic activities as given by $K-K_0$ are distributed on volcano-type plots. The catalytically-active metal ions are limited to those having acid ionization constants, pK_a, larger than 7. They may be divided into two groups; one comprises alkali, alkaline earth, and thallium(1) metal ions derived from Ia, IIa, and IIIa, while the other includes the metal ions derived from VIIb, VIII, Ib, IIb, and IVa in the periodic chart of the elements.[9]

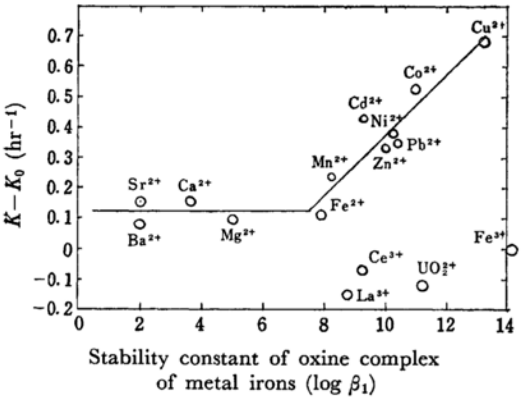


Fig. 2. Correlation between catalytic activities and stability constants of oxine complex of metal ions.

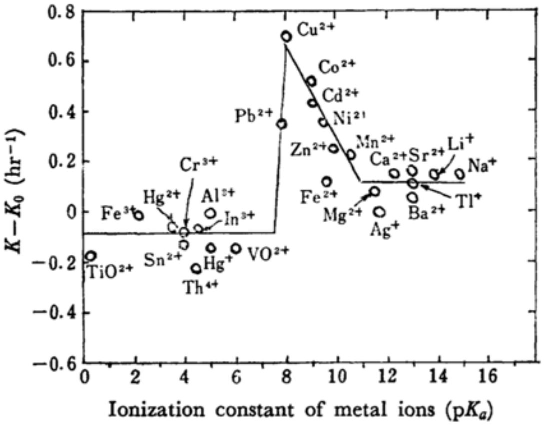
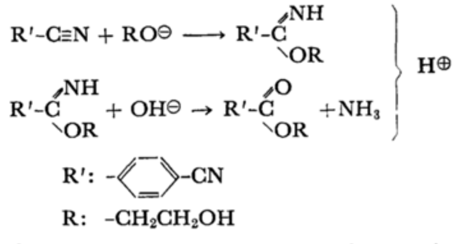


Fig. 3. Correlation between acid ionization constants (pK_a) and rate of the glycolysis of terephthalonitrile.

Metal ions of either group promote the reaction of glycolysis, but possibly by different reaction mechanisms. The former group seems to promote the reaction by accelerating the formation of glycol and hydroxyl anions, which promote the imidate formation and the imidate hydrolysis, as illustrated as follows:

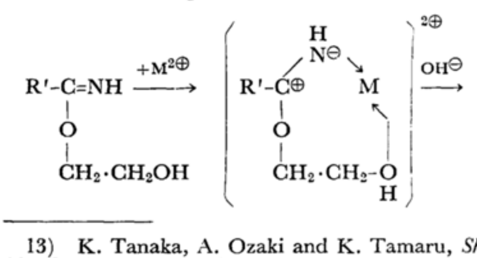


$$\left.\begin{array}{l} R'\text{-}C{\equiv}N + RO^{\ominus} \longrightarrow R'\text{-}C\begin{smallmatrix}{\nearrow}NH\\ \searrow OR\end{smallmatrix} \\ R'\text{-}C\begin{smallmatrix}{\nearrow}NH\\ \searrow OR\end{smallmatrix} + OH^{\ominus} \rightarrow R'\text{-}C\begin{smallmatrix}{\nearrow}O\\ \searrow OR\end{smallmatrix} + NH_3 \end{array}\right\} H^{\oplus}$$

R′: –C$_6$H$_4$–CN

R: $-CH_2CH_2OH$

The latter group seems to promote the reaction by accelerating the formation of carbonium cations of the imidate through the coordination of metal ions:



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[9] "The Merck Index of Chemicals and Drugs," 7th ed., Merck and Co., Inc., Rahway, New Jersey (1960).

[10] K. Yamasaki and T. Inoue, "Sakuen" (Metal Complexes), Maruzen Publishing Co., Tokyo (1959), p. 434.

[11] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., London (1958), p. 387.

[12] A. Ringbom, "Complexation in Analytical Chemistry," Interscience Publishers, London (1963), p. 298.

[13] K. Tanaka, A. Ozaki and K. Tamaru, *Shokubai (Catalysis)*, **6**, 262 (1964).

claimed that an excited singlet state is an only reactive state in the photoreduction of acridine in *isopropanol*.

According to our present results, however, four alcohols behave more or less in different manner and in particular, isopropanol and methanol show distinctly different features in the effect of biacetyl on the photoreduction, which lead to the conclusion that the reactive states is in the former case only singlet excited state in agreement with Porter's conclusion, whereas in the latter case, are singlet and T(n–π*) state as Kellmann and Dubois proposed. Hence it seems timely to report the details of our experiments although we have not yet succeeded in interpreting the unexpected differences found in four kinds of alcohols.

Since Dubois and Kellmann's conclusion was based on the assumption that inhibiting action of biacetyl is due to the energy transfer according to $A^{T(n-\pi^*)}+B\rightarrow A+B^T$ (where A is acridine and B is biacetyl), it is desirable to examine whether biacetyl does not affect the lowest T(π–π*) of acridine by a different mechanism than energy transfer and further to examine whether it does not react with the half reduced acridine. Therefore we have investigated at first by the flash technique using methanol and ethanol as solvents, the effect of the addition of biacetyl on the decays of T(π–π*) of acridine and of the half reduced acridine. In addition, we have made investigations on the effect of the addition of biacetyl on the yield of T(π–π*), AH and AH_2, the results of which have supported the view of Kellmann and Dubois to some extent. These experiments are described in Part I. In Part II, the steady illumination experiments are described. The data, being more accurate than those from flash experiments, are analysed and interpreted on the basis of four alternative processes, and the quantum yields Φ_M^S, Φ_R^S, Φ_M^T and Φ_R^T (where S and T denote singlet excited state and T(n–π*) state and where M and R denote respectively molecular and radical) are separately decided.

Part I.*[1] Flash Photolysis Studies

Experimental

Apparatus, procedures and samples are essentially similar as in the previous papers.[8,10] The decays and yields of T(π–π*) of acridine and of the half-reduced form of acridine were examined respectively at 440 and at 278 mμ (or in some cases as 520 mμ). The yield of acridan was investigated from the increase of optical density at 290 mμ. The concentration of acridine was always 4.8×10^{-5} M and the concentration of biacetyl was changed from zero to 1.1×10^{-2} M. By using a suitable filter only acridine was excited.

Results and Discussion

T-T Absorption Spectra of Biacetyl. Transient absorption spectra of biacetyl in methanol are shown in Fig. 1.

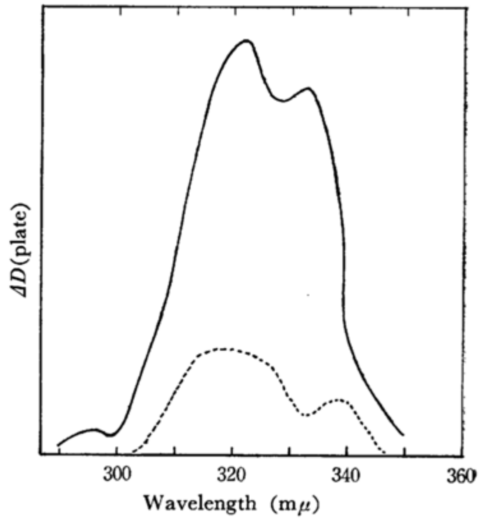

Fig. 1. Transient absorption spectra of biacetyl.
—— after 93 μsec, - - - after 360 μsec

The decay at 320 mμ is of the first order with a rate constant $k\simeq4\times10^3$sec^{-1}. The comparison with the data in literatures[9,12,13] confirms that this species is the triplet state of biacetyl.

The Effect of the Addition of Biacetyl on the Decay of T(π–π*) of Acridine. The decay was not essentially affected by the addition of biacetyl up to 1.1×10^{-2}M. Some of the values of the first order rate constants are given in Table 1.

The Effect of the Addition of Biacetyl on the Decay of Half Reduced Acridine. The decay of half reduced acridine is second order and the rate

TABLE 1. RATE CONSTANT OF THE DECAY OF T(π–π*), $k\times10^{-4}$(sec^{-1})

$[B]_M$	0	1.1×10^{-4}	1.1×10^{-3}	5×10^{-3}	1.1×10^{-2}
Methanl	1.1	1.1	1.1	1.1	1.1
	1.2	1.1	1.2	1.1	1.1
Ethanol	0.8	0.8	0.6	0.7	0.7
	0.9	0.8	0.7	0.7	0.8

[*1] Experiments were made by Yamashita.

12) G. Porter and M. W. Windsor, *Proc. Roy. Soc.*, **A245**, 238 (1958).

13) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958).

metal are quite applicable to that of the glycolysis of dimethyl terephthalate,[7c] it seems that the catalytic reaction mechanisms for this reaction are similar to those for the glycolysis of dimethyl terephthalate.

The reaction mechanisms and kinetics of the metal ion-catalyzed glycolysis of benzonitrile will be discussed in a succeeding paper.

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