A STUDY OF THE BENZOIN REACTION—IV.

The Kinetics of the Benzoin Reaction in the Presence of Organic Solvents.

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Introduction.

FOR some time past this laboratory has been engaged on a study of the kinetics of the benzoin reaction between solid potassium cyanide and benzaldehyde.[1] It has been shown that when pure potassium cyanide and pure benzaldehyde react, two concurrent reactions take place : a fast homogeneous autocatalytic reaction, which requires the presence of benzoin, between benzaldehyde and the trace of potassium cyanide dissolved in it ; and a slow heterogeneous reaction between benzaldehyde and the solid potassium cyanide.

The object of the present paper has been to study the reaction between potassium cyanide and benzaldehyde in the presence of inert organic liquids and of hydroxy-compounds.

It has been shown that with inert solvents the heterogeneous reaction is unaffected, but the homogeneous reaction is decelerated ; because, a portion of the dissolved potassium cyanide is precipitated. The action of hydroxy-compounds is complicated, but on the whole, they accelerate the reaction.

Morton and Stevens[2] have previously investigated at room temperatures the course of the reaction in presence of relatively large amounts of various solvents, but owing to the difference between their experimental conditions and ours it is difficult to compare the results.

Materials Employed.

Benzaldehyde.—Merck's purest benzaldehyde, which gave consistent results, was used. It was stored in small quantities in an atmosphere of nitrogen and checked at intervals by standard experiments.

Potassium cyanide.—Kahlbaum's purest cyanide, which had been dried at 110° C. at 2 mm. pressure for 2 hours, was used. It always gave consistent results indicating uniformity of particle size.

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[1] Parts I, II and III, *J. Phys. Chem.*, 1935, **39**, 727, 901, 907; *Curr. Sci.*, 1935, **4**, 94.

[2] *J.A.C.S.*, 1930, **52**, 2031.

Benzene.—Merck's purest thiophene-free benzene was used.

Chlorobenzene.—Merck's pure chlorobenzene, freshly distilled, was used. In a few control experiments Kahlbaum's purest chlorobenzene was found to give similar results.

Toluene.—Merck's purest toluene was used after distilling. Kahlbaum's toluene, "free from sulphur, for the determination of molecular wieghts", gave similar results.

Chlorotoluene.—Kahlbaum's chlorotoluenes (*o*-, *m*- and *p*-) were used after distilling.

Benzyl chloride.—Kahlbaum's purest benzyl chloride was used.

Cyclohexane.—Kahlbaum's cyclohexane was used after distilling.

Pentane.—Kahlbaum's purest pentane reagent was used.

Chloroform and Carbon tetrachloride.—Kahlbaum's purest varieties were employed.

Thiophene.—Kahlbaum's purest thiophene was used.

Acetone.—Kahlbaum's acetone " Pro Analysi" was employed; Kahlbaum's acetone "from bisulphite compound" gave similar results.

Alcohols.—Kahlbaum's " Methanol, Pro Analysi " was used; Merck's absolute alcohol was dehydrated over calcium metal and distilled before use. Kahlbaum's purest ethylene glycol and Merck's extra pure glycerol, freshly distilled under reduced pressure and kept in presence of phosphorous pentoxide, were also employed. Pure samples of erythrite, mannite, dulcite, sorbite and inosite from Kahlbaum were used.

Experimental Results.

Benzene.—Figs. 1, 2 and 3 show the effect of addition of benzene on the rate of the benzoin reaction. It will be seen that the curves obtained with the same quantity of benzene and different amounts of potassium cyanide, are parallel for the autocatalytic portion of the reaction, and that increase in the amount of benzene decreases the rate of reaction. Since the curves are parallel the rate of the autocatalytic reaction is seen to be, as in the experiments without benzene (*loc. cit.*, Part I, p. 733), independent of the total quantity of KCN present, and determined by the quantity of KCN dissolved in the benzene-benzaldehyde-benzoin mixture.

The equation for calculating the course of the reaction curve for the reaction upto the conversion of about half of the benzaldehyde, which was worked out in Part I, can here be applied using the same value for the heterogeneous constant as previously employed and choosing a smaller value for the homogeneous constant, since a portion of the potassium cyanide has been precipitated. The equation is :—

$$t-c' = -1/k_1\left[\frac{-50}{(10+\mathrm{X}')n'} + \frac{(11\cdot51)\ (30+2\mathrm{X}')}{(10+\mathrm{X}')^2}\log n' - \frac{(20+\mathrm{X}')^2}{(10+\mathrm{X}')^2}(1\cdot15)\log(10+\mathrm{X}'-n')\right]$$

or, when X′ is small,

$$t-c' = -1/k_1[-5/n' + 3\cdot45\log n' - 4\cdot60\log(10+\mathrm{X}'-n')],$$

where

n' =gram. benzaldehyde remaining at time t,
k_1 =the value of the homogeneous constant,
$\mathrm{X}' = 2k_2'/k_1$, k_2' being the heterogeneous constant,
and c' is a constant.

k_2' for 1g. effective KCN per 10 g. benzaldehyde =0·185, and k_1 is chosen so that the curve will fit one result. Effective KCN, it may be noted, is the gross quantity of potassium cyanide used less 0·17 g., since it has been found previously (Part I, p. 730) that 0·17 g. KCN is always ineffective in the experiments.

Other Inert Solvents.—The results with chlorobenzene, toluene, chlorotoluene, benzyl chloride, cyclohexane, pentane, chloroform and carbon tetrachloride were of the same type as with benzene. Pentane was found to have a definite inhibiting effect though Morton and Stevens (*loc. cit.*) claim that it accelerates the reaction.

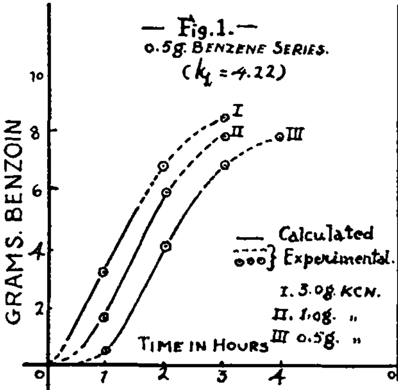
Fig. 4 shows the effect of various solvents on the value of k_1, the homogeneous constant. The action of carbon tetrachloride is greatest. Pentane, cyclohexane and benzene have much the same effect.

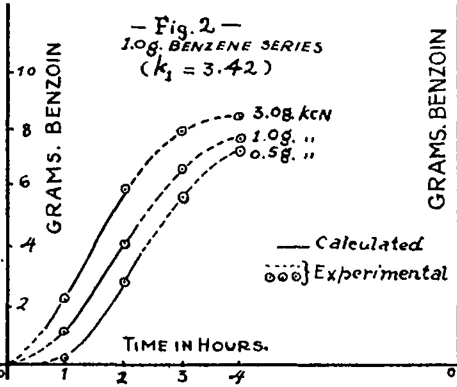
Thiophene.

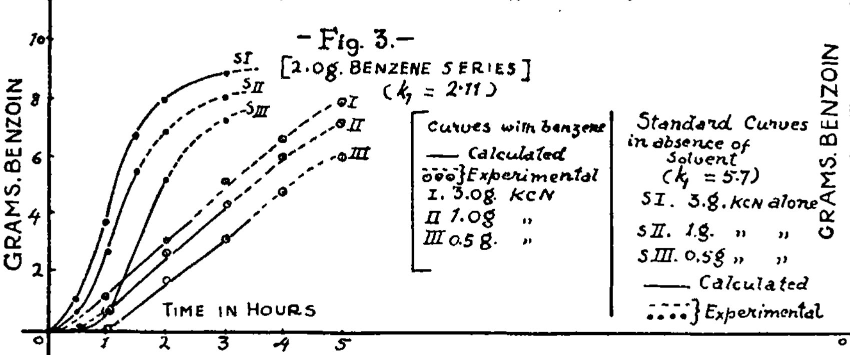
Experiments were made with thiophene as it was found that benzene, not thiophene-free, showed a greater inhibiting action than the pure benzene employed. The results with thiophene show that it is an inhibitor of the type studied in Part II ; very small quantities prove definitely inhibiting.

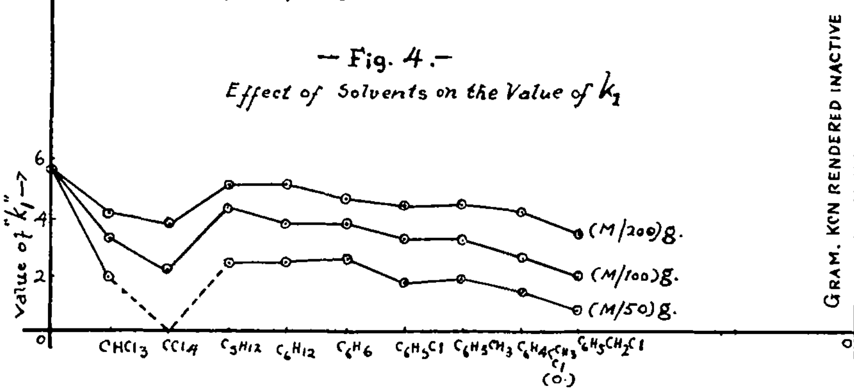
Fig. 5 shows the effect of quantities of up to 0·42 g. on the reaction. Since it acts purely on the heterogeneous reaction and the homogeneous reaction is not affected, it is possible to obtain a coincidence between curves with a smaller amount of pure potassium cyanide and potassium cyanide in presence of thiophene. (See Fig. 6 ; *cf.* Part II, p. 901.)

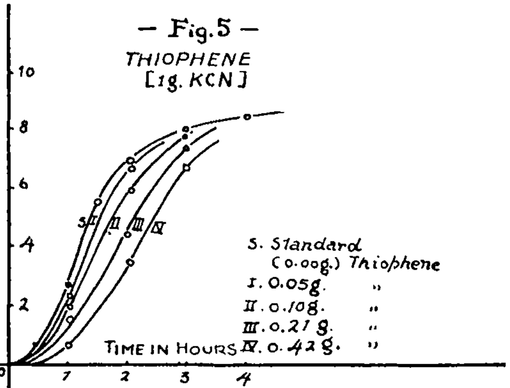
For each of the thiophene curves we can find what was the equivalent amount of pure potassium cyanide that gives the same results, and in this way obtain Fig. 7 which shows the amount of potassium cyanide rendered

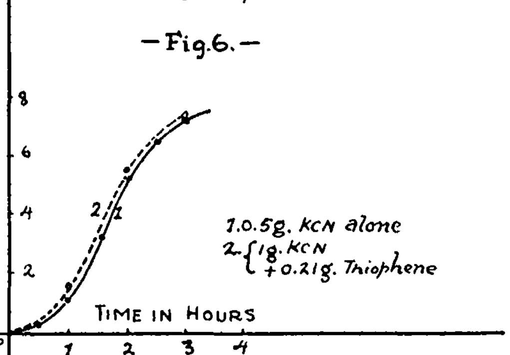

— Fig.1.—
0.5g. BENZENE SERIES. (k_1 = 4.22)

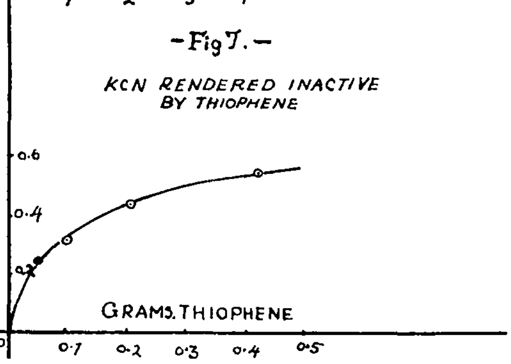

— Fig. 2 —
1.0g. BENZENE SERIES (k_1 = 3.42)


— Fig. 3.—
[2.0g. BENZENE SERIES] (k_1 = 2.11)


— Fig. 4.—
Effect of Solvents on the Value of k_1


— Fig.5 —
THIOPHENE [1g. KCN]


— Fig.6. —


— Fig 7. —
KCN RENDERED INACTIVE BY THIOPHENE

inactive by given amounts of thiophene. It will be seen that the curve is of the adsorption type, the effect of small quantities of thiophene being much greater in proportion.

Acetone.

As benzoin accelerates the reaction, the effect of acetone was studied, and it was found that it also acted as an accelerator as shown in Figs. 8 and 9. The accelerated portions of the curves for the same quantity of acetone are parallel and can be reproduced by the equation :—

$$t-c'=-1/k_1[-5/n'+3\cdot45\ \log n'-4\cdot60\ \log\,(10+X'-n')]$$

by taking the normal value of k_2', the heterogeneous constant, and an increased value of k_1 which is independent of the amount of potassium cyanide present.

Acetone, therefore, would appear to act by increasing the amount of potassium cyanide dissolved in a given mixture of benzaldehyde and benzoin. Fig. 10 shows that the value of k_1 plotted against the amount of acetone gives a straight line.

Methyl and Ethyl Alcohols.

Both alcohols show an accelerating effect on the reaction. The results are, however, complicated (see Figs. 11 and 12). Small quantities accelerate the heterogeneous reaction ; intermediate quantities delay the start of the homogeneous catalytic reaction, while larger amounts accelerate the reaction from the beginning.

Ethylene Glycol.

The results with ethylene glycol (Fig. 13) are of the same type as those obtained with methyl and ethyl alcohols.

Glycerol.

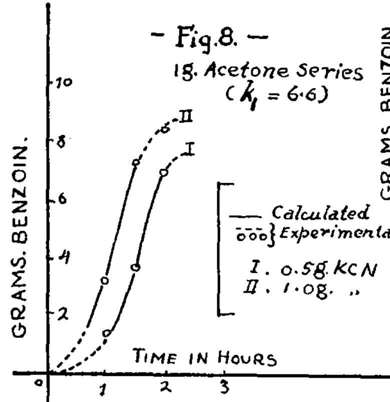
With different amounts of glycerol and the same quantity of KCN the time-yield curves are nearly parallel (see Fig. 14), showing that the rate of the accelerated reaction is independent of the quantity of glycerol used. Owing to the limited solubility of glycerol in benzaldehyde a constant amount of glycerol is dissolved in the benzaldehyde. Glycerol also accelerates the heterogeneous reaction.

Fig. 15 shows that the curves obtained with small quantities of alcohols can be made approximately to coincide with curves obtained in the absence of alcohol and with larger quantities of KCN. Thus we may deduce that alcohols in small quantities do not affect greatly the homogeneous catalytic reaction but accelerate the heterogeneous reaction.

Polyhydric Alcohols.

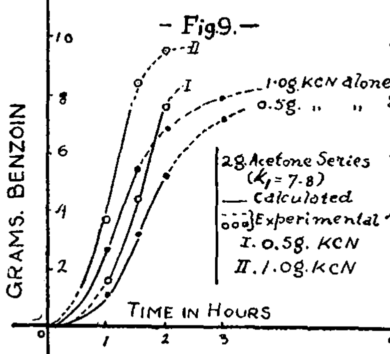
Polyhydric alcohols increase the rate of reaction even in small amounts

- ACETONE -

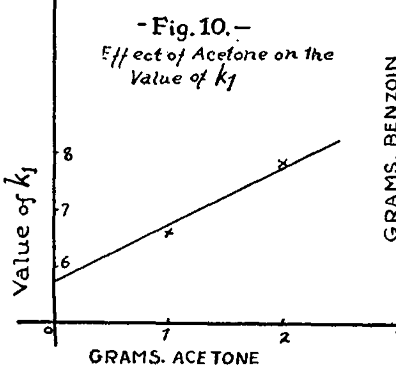


- Fig. 8. -

1g. Acetone Series ($k_1 = 6{\cdot}6$)



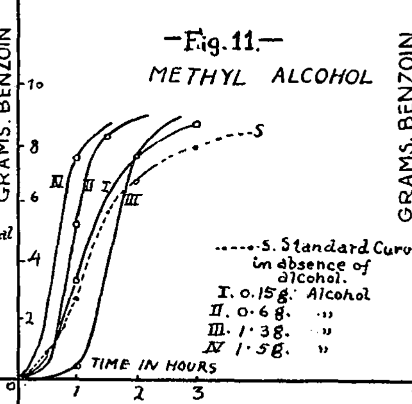
- Fig 9. -



- Fig. 10. -

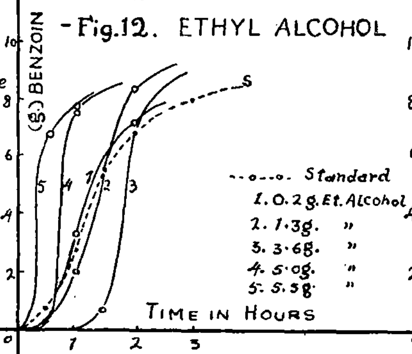
Effect of Acetone on the Value of k_1

HYDROXY COMPOUNDS. [1.0g. KCN]

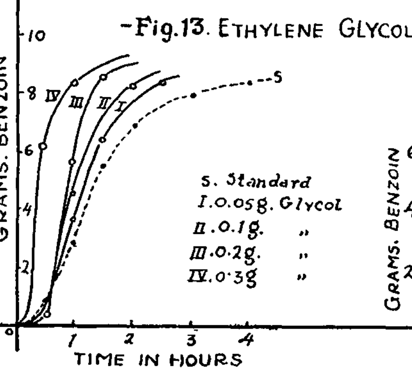


- Fig. 11. -

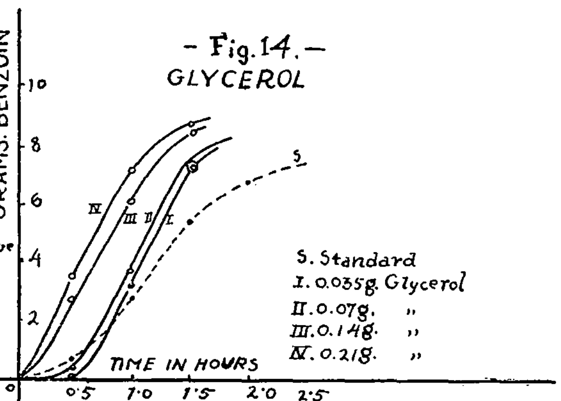
METHYL ALCOHOL



- Fig. 12. ETHYL ALCOHOL

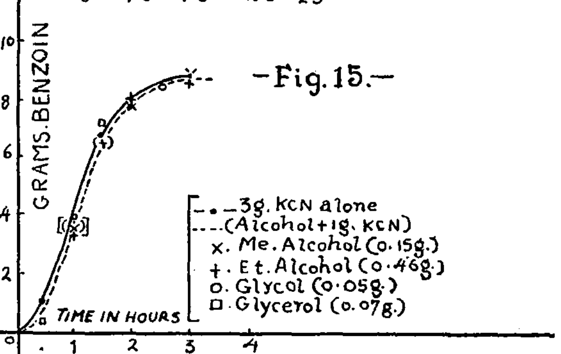


- Fig. 13. ETHYLENE GLYCOL

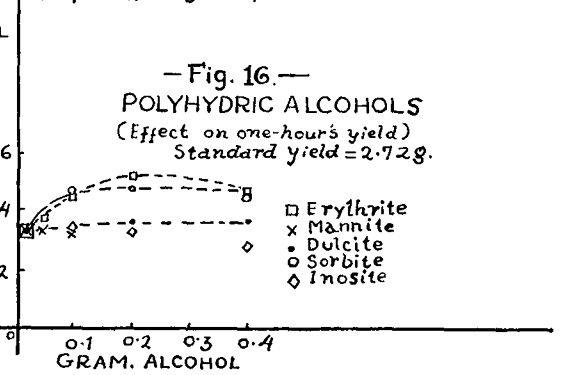


- Fig. 14. -

GLYCEROL



- Fig. 15. -



- Fig. 16. -

POLYHYDRIC ALCOHOLS

(Effect on one-hour's yield)
Standard yield = 2·72g.

(see Fig. 16). The effect, however, does not increase with the amount of the alcohol added, probably because, these alcohols have a very limited solubility in benzaldehyde.

A comparison of the results obtained with the hydroxy-compounds shows that glycol and glycerol are more powerful accelerators than methyl and ethyl alcohols. Thus the accelerating effect appears to increase with the number of hydroxy-groups in the molecule of the compound added. A definite acceleration has been observed with 0·2% of polyhydric alcohols in benzaldehyde, 0·35% of glycerol and 0·5% of glycol.

It will be seen that the results with alcohols are much more complex than with inert solvents and do not admit of mathematical formulation. In all cases they accelerate the reaction, probably by increasing the quantity of potassium cyanide dissolved. But they tend, in certain quantities, to delay the start of the homogeneous reaction. It is this dual effect which makes the results complicated.

It should be remembered when discussing the results with hydroxy-compounds that they may react with benzaldehyde to form acetal derivatives.

Summary.

1. Inert organic solvents, when added to a mixture of solid potassium cyanide and benzaldehyde, precipitate a portion of the small quantity of potassium cyanide dissolved in the benzaldehyde, and thus cause the homogeneous autocatalytic reaction to proceed more slowly. They do not affect the heterogeneous reaction.

2. Hydroxy-compounds accelerate the benzoin reaction and the accelerating effect increases with the number of hydroxy groups.