

[CONTRIBUTION NO. 37 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

THE EQUILIBRIUM $C_6H_6 + CO_2 \rightleftharpoons C_6H_5COOH^1$

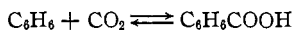
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The decomposition of organic acids into carbon dioxide has been studied extensively, as has the decomposition of malonic acid and derivatives into carbon dioxide and monobasic acids; but we are not aware of any attempt to determine whether the reaction is reversible and if so whether the reaction proceeds sufficiently far to be of practical value.² With these points in view several investigations have been started.

The reaction of benzene with carbon dioxide was chosen for the first study because of the adaptability of the substances involved. An approximate calculation of the free energy of the reaction



showed that the position of equilibrium would be far to the left, but that provided an equilibrium could be established, a small amount of benzoic acid would be produced.

The search for an appropriate catalyst was made by studying the rate of decomposition of benzoic acid in contact with various catalytic mixtures at various temperatures, assuming that an active catalyst for the reverse reaction would catalyze the forward reaction as well. The percentage decomposition at various time intervals and temperatures for some of the better catalysts are listed in the experimental part. The most effective were of the Zn-Cu-Cr oxide type used in methanol synthesis. Such catalysts produced considerable decomposition of benzoic acid at temperatures as low as 250°, the boiling point of the acid. This temperature is much lower than any recorded previously. The rate of decomposition at 300° is shown in the accompanying diagram. The shape of the curve indicates that after about five days of heating, an equilibrium was being approached.

The forward reaction was studied by heating benzene and carbon dioxide in glass bomb tubes containing the catalyst to pressures between 17 and 35 atmospheres. At 300° and about 35 atmospheres' pressure the crude yield of acid products amounted to 0.13% based on the weight of benzene

¹ Presented at the Cincinnati meeting of the American Chemical Society, September, 1930.

² Two patents on the reaction of methane with carbon dioxide are of interest in this connection. Plauson and Vielle, Brit. Pat. 156,148 (1920); *Chem. Abstracts*, 15, 1726 (1921), and H. Dreyfus, Brit. Pat. 226,248 (1923); *Chem. Abstracts*, 19, 2057 (1925). Friedel and Crafts [*Ann. chim. phys.*, [6] 14, 1441 (1887)] found that benzoic acid was produced in traces by the action of aluminum chloride on benzene and carbon dioxide. An attempt to use the method commercially was unsuccessful [Frydlender, *Revue des Produits Chimiques*, 21, 24 (1918)].

used. When the crude acid product was heated, benzoic acid sublimed, giving a yield of 0.08%.

Since benzoic acid has been obtained from benzene and carbon dioxide, and benzoic acid is decomposed by heat into those substance, it should be possible to establish an equilibrium. The determination of the position of equilibrium under various conditions has not been attempted, because, unfortunately, catalysts sufficiently active for a rapid attainment of equilibrium have not been found.

The search for more active catalysts is being continued, as well as the extension of the method to the formation of other acids.

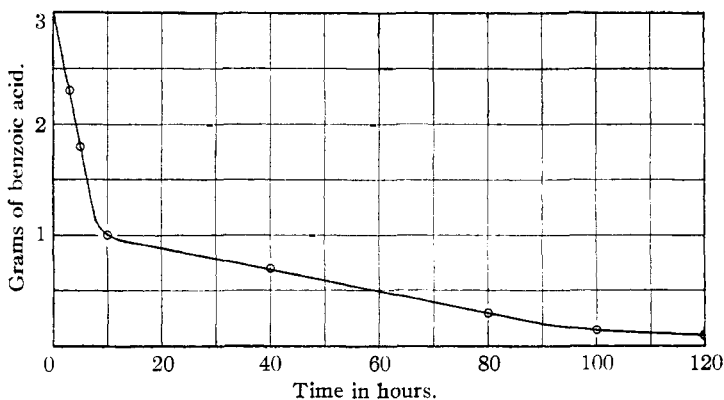


Fig. 1.—Rate of decomposition of benzoic acid at 300° in contact with a Zn-Cu-Cr oxide catalyst.

Experimental Part

After a number of preliminary experiments, the two reactions were studied by heating pairs of bomb tubes, both of which contained a given catalyst, together with 3 g. of pure benzoic acid in the first tube, and 2 g. of pure benzene and 2.2 g. of carbon dioxide³ (introduced as snow) in the second. The two tubes were then heated in a Carius furnace at as nearly a constant temperature as possible. This seldom varied more than three or four degrees in either direction. After heating, the tubes were opened and the contents digested for several minutes with boiling potassium hydroxide. The solution was cooled, filtered and extracted twice with ether. The potassium hydroxide was neutralized with dilute hydrochloric acid and if there was sufficient benzoic acid present to be precipitated, it was filtered out before extracting the remaining acid with two portions of ether. The ether was evaporated and the weight combined with that of the precipitated acid. In the experiments on the decomposition of benzoic

³ In several experiments 4.4 g. of carbon dioxide was introduced. The pressure in these tubes was calculated to be about 35 atmospheres at 300° and about 17 atmospheres in the tubes containing 2.2 g. of carbon dioxide.

acid an odor of phenol was often pronounced, although the amount actually produced was quite small. The more characteristic of the results obtained are listed in Table I.

TABLE I
CHARACTERISTIC RESULTS

Catalyst	Temp., °C.	Time of heating, hours	Amount of benzoic acid decomposed, %	Amount of benzoic acid produced
3 g. Zn-Cu-Cr oxides ^a	355-360	10	27	Trace
3 g. Zn-Cu-Cr oxides ^b	245-250	10	27	Trace
	273-283	10	47	Trace
	280-290	10	47	Trace
3 g. Zn-Cu-Cr oxides ^c	300	3	13.3	
3 g. Zn-Cu-Cr oxides ^c	300	5	40	
3 g. Zn-Cu-Cr oxides ^c	300	10	67	Trace
3 g. Zn-Cu-Cr oxides ^c	300	40	77	Trace
3 g. Zn-Cu-Cr oxides ^c	300	80	90	Trace
3 g. Zn-Cu-Cr oxides ^c	300	100	95	Trace ³
3 g. Zn-Cu-Cr oxides ^c	300	120	96.6	Trace
3 g. manganous oxide ^d	290-300	10	3	None
3 g. Zn-Cu-Cr, oxides ^c mixed with 1 g. of manganous oxide ^d	290-300	10	85	Trace
3 g. Zn-Cu-Cr, oxides ^c mixed with 1 g. of manganous oxide ^e	270	10	33	None ³
3 g. Zn-Cu-Cr, oxides ^c mixed with 1 g. of ferric oxide ^e	290-300	10	70	Trace
3 g. Zn-Cu-Cr, oxides ^c mixed with 1 g. of nickel oxide ^e	290-300	10	60	Trace
3 g. Zn-Cu-Cr, oxide ^c mixed with 1 g. of cadmium oxide ^e	300	10	67	Trace ³
3 g. of manganous oxide ^d mixed with 1 g. of ferric oxide ^e	270-280	10	23	None ³

^a Prepared by the method of Fenske and Frolich, *Ind. Eng. Chem.*, 21, 1052 (1929), except that the oxides were reduced by heating them with benzoic acid. ^b Same as ^a except that the oxides were reduced with benzoic acid in a stream of carbon dioxide. ^c Same as ^a except that the oxides were not reduced, but were heated in air until the mixture turned black. ^d Made by heating the carbonate in a stream of hydrogen. ^e Made by heating the nitrate in an open crucible until all of the nitrogen oxides were driven off.

In order to determine the yield of benzoic acid from benzene and carbon dioxide, six tubes, each containing 2 g. of benzene and 4.4 g. of carbon dioxide, were heated with catalyst (c) for ten hours at 300°. The pressure was calculated to be about 35 atmospheres. Upon opening the tubes, the acid produced in four of them was extracted with hot sodium hydroxide, the solution cooled, filtered, acidified, and extracted four times with ether. The ether was evaporated and the weight of the brown crystalline mass remaining was 0.0165 g. The ether extract from the last two tubes was extracted four times with dilute sodium carbonate, the sodium carbonate solution acidified and extracted four times with ether. Upon removing the ether, the residue was no purer than that obtained by extracting with dilute sodium hydroxide. There was no odor of phenol. The crude acid weighed 0.0080 g. and was sublimed onto a cold watch crystal. The

weight was 0.0050 g. and the melting point 103–108°. Mixed with pure benzoic acid, the melting point was raised to 110–114°. A second sublimation did not raise the melting point.

Summary

Catalysts have been found which initiate the decomposition of benzoic acid into benzene and carbon dioxide at temperatures as low as 245–250°. The reaction was found to be slightly reversible, benzoic acid being produced by the reaction of benzene on carbon dioxide in small amounts.

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SOME SUBSTITUTED DI-(BETA-PHENYLETHYL)-AMINES AND BENZYL-BETA-PHENYLETHYLAMINES

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A great deal of attention has been given to derivatives of β -phenylethylamine, particularly to their physiological action. This group contains compounds such as epinine, hordenine, tyramine, etc., and may also be considered as related to the hydrastinines (for example, Lodal), so that it is of great importance.

Much less work appears to have been done on secondary amines containing more than one benzene nucleus, of the type of di-(β -phenylethyl)-amine and benzyl- β -phenylethylamine, although a small number of these compounds is described in the literature and in some cases their pharmacological action has been examined. Di-(β -phenylethyl)-amine has been described by many workers; benzyl- β -phenylethylamine, *p*-methoxy-benzyl- β -phenylethylamine, *p*-hydroxybenzyl- β -phenylethylamine, *o*-hydroxybenzyl- β -phenylethylamine, and 3-methoxy-4-hydroxybenzyl- β -phenylethylamine, by Shepard and Ticknor;¹ *o*-veratrylhomopiperonylamine by Kaufmann and Müller;² benzyl-*p*-hydroxy- β -phenylethylamine, piperonyl-*p*-hydroxy- β -phenylethylamine, veratryl-*p*-hydroxy- β -phenylethylamine, and *o*-hydroxybenzyl-*p*-hydroxy- β -phenylethylamine, by Hoffmann and La Roche;³ and *p,p'*-diamino-di-(β -phenylethyl)-amine and *p,p'*-dihydroxy-di-(β -phenylethyl)-amine by von Braun and Blessing.⁴ The last authors also prepared cyclohexyl-*p*-hydroxy- β -phenylethylamine and cyclohexyl-*p*-amino- β -phenylethylamine. No compound containing the physiologically important catechol group (adjacent hydroxyl groups, usually in the 3,4-positions) appears to have been described. It was with the idea of prepar-

¹ Shepard and Ticknor, *THIS JOURNAL*, **38**, 381 (1916).

² Kaufmann and Müller, *Ber.*, **51**, 126 (1918).

³ Hoffmann and La Roche, German Patent 259,874.

⁴ Von Braun and Blessing, *Ber.*, **56**, 2153 (1923).