

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

THE EQUILIBRIUM BETWEEN BENZALDEHYDE AND BENZOIN

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Introduction

In 1832, Wöhler and Liebig first prepared benzoin by mixing a concentrated solution of potassium carbonate with oil of bitter almonds and allowing the mixture to stand for several weeks.¹ After purifying the compound these investigators attempted to convert it into benzaldehyde but were unsuccessful. In 1840, Zinin² prepared benzoin by the action of potassium carbonate in alcohol solution on benzaldehyde containing hydrocyanic acid. Zinin treated the benzoin thus obtained with hydrocyanic acid, apparently with the purpose of reversing the reaction. This, however, did not take place. Since this early work, chemists have generally regarded the benzoin condensation as non-reversible.

Certain facts indicate the possibility of the existence of an equilibrium between benzaldehyde and benzoin. In the first place, the best method of preparing benzoin³ gives a yield of not over 92% thus leaving 8% of the materials unaccounted for. Furthermore, there is always a noticeable odor of benzaldehyde at the close of the preparation. Finally, by adding more potassium cyanide to the filtrate from the first crop of benzoin and heating again, a second crop of benzoin can be obtained. A careful study by the authors has shown that such an equilibrium does exist and that the benzoin condensation can be readily reversed.

Experimental Part

Isolation of Uncondensed Benzaldehyde.—To a solution of 77.53 g. of benzaldehyde in 500 cc. of 95% alcohol, 17 g. of finely divided sodium cyanide was added. The mixture was heated on the boiling water-bath for 1 hour under a reflux condenser in an atmosphere of nitrogen. The reaction mixture was poured into an equal volume of water, cooled, and the benzoin collected and washed with 250 cc. of 50% alcohol. The weight of the benzoin obtained was 56.1 g. Solubility determinations showed that 300 cc. of 50% alcohol dissolved 0.250 g. of benzoin at approximately 20°. The amount of benzoin in the 1250 cc. of filtrate was, therefore, 1.04 g., and the total weight of benzoin in the reaction mixture was 57.14 g. or 73.7% of the original weight of benzaldehyde.

In order to isolate the benzaldehyde, the 1250 cc. of alcoholic filtrate from the benzoin was diluted to 2500 cc. with distilled water and the benzaldehyde extracted with ether. The ether extract was dried over calcium chloride, the ether distilled and the remaining liquid fractionally distilled. The greater part, 10.79 g., came over between 175° and 190°. The temperature then rose rapidly to 250° where a few drops distilled, and finally to 340° where a small amount of benzoin came over. There was no

¹ Wöhler and Liebig, *Ann.*, **3**, 276 (1832).

² Zinin, *Ann.*, **34**, 186 (1840).

³ Adams, "Organic Syntheses," John Wiley and Sons, 1921. Zincke, *Ber.*, **9**, 1772 (1876); *Ann.*, **198**, 150 (1879).

indication of the presence of benzyl alcohol, b. p. 212°. The 10.79 g. on redistillation gave 8.2 g. of pure benzaldehyde, boiling at 178–179°. This was still further identified by conversion, practically quantitatively, into benzalphenylhydrazone and benzoic acid, both with the correct melting points. Because of the rapidity of oxidation of the benzaldehyde and the large volume of the solution it was difficult to recover all of the benzaldehyde.

Reversal of the Benzoin Condensation.—Seventy g. of pure benzoin was dissolved in 500 cc. of boiling 95% alcohol, 17 g. of powdered sodium cyanide added and the whole heated for 1 hour under a reflux condenser in an atmosphere of nitrogen. This converted a portion of the benzoin into benzaldehyde, showing that the reaction is reversible. The benzoin and benzaldehyde were separated from the reaction mixture as described above. The total weight of benzoin recovered was 51.04 g. or 74.2% of the benzoin used. The benzaldehyde obtained weighed 10.93 g. This on redistillation gave 9.01 g. of pure benzaldehyde boiling at 178–179°. This was still further identified as described above.

These two experiments prove conclusively that the benzoin condensation is a reversible process.

Determination of the Equilibrium Constant.—In determining the equilibrium constant an accurately weighed amount of either pure benzoin or benzaldehyde was placed in sufficient hot 95% alcohol to dissolve all the benzoin present at equilibrium. Finely powdered sodium cyanide to the extent of approximately 2.5% of the weight of the solution was added, and the volume of the solution accurately measured. The solution was heated to 79° for 1 hour under a reflux condenser in an atmosphere of nitrogen on a boiling water-bath. An equal volume of water was added, the solution quickly cooled, the benzoin collected and washed with a small volume of cold 50% alcohol previously saturated with benzoin. The product was dried, weighed and the weight of benzoin corrected for that which remained in solution. The weight of benzaldehyde present at equilibrium was the difference between the weight of benzaldehyde or benzoin used and the benzoin found.

Tables I and II give the equilibrium constant between benzaldehyde and benzoin determined as described above. The results in Table I

TABLE I
THE EQUILIBRIUM CONSTANT BETWEEN BENZALDEHYDE AND BENZOIN AT 79° STARTING WITH BENZALDEHYDE

Volume Cc.	Benzaldehyde used G.	Benzoin found G.	Benzaldehyde found G.	K
918	19.43	9.65	9.78	0.20
168	19.36	13.74	5.62	0.26
168	19.93	14.01	5.92	0.28
168	19.86	14.20	5.66	0.25
168	19.40	14.28	5.12	0.21
483	19.55	10.98	8.57	0.26
168	20.04	14.13	5.91	0.28
168	20.03	14.11	5.92	0.28
570	77.53	57.14	20.39	0.24

Av. 0.25

TABLE II
THE EQUILIBRIUM CONSTANT BETWEEN BENZALDEHYDE AND BENZOIN AT 79° STARTING
WITH BENZOIN

Volume Cc.	Benzoin used G.	Benzoin found G.	Benzaldehyde found G.	K
84	10	7.115	2.885	0.26
168	20	14.25	5.75	0.26
168	20	14.1	5.9	0.28
168	20	14.44	5.56	0.24
563	70	51.00	19.00	0.24
168	20	14.56	5.44	0.23
168	20	14.76	5.24	0.21
483	20	11.92	8.08	0.21
168	20	14.47	5.53	0.24
168	20	14.54	5.47	0.23

Av. 0.24

were obtained by starting with benzaldehyde, while those in Table II were obtained by starting with benzoïn. The equilibrium constant, K , was calculated by the regular equilibrium constant formula for a reaction of the type, $2A = B$, that is, $K = A^2/B$, where A and B are measured in gram moles per liter of solution. The average value of K from Tables I and II is 0.245. This is certainly very near the correct value of the equilibrium constant.

Discussion of Results.—Along with the benzoïn condensation there is another reaction proceeding very slowly. This uses up small amounts of the materials. For this reason the solution should be heated only sufficiently long to reach equilibrium. When benzaldehyde is the starting material, 1 hour at 79° is the correct length of time. If it is heated for a shorter or longer length of time the apparent value of K will be greater than it actually is. This is because when heating is for a shorter time than 1 hour equilibrium has not been reached and the amount of benzaldehyde present is larger than at equilibrium; when heating is for longer than 1 hour the side reaction is using up some of the materials and the apparent amount of benzaldehyde is greater than the actual amount. When benzoïn is the starting material, 1.5 hours is the correct length of time to heat the solution.

The higher values given in Tables I and II were obtained by heating slightly longer than the specified time, or in a few cases by not having an atmosphere of nitrogen present. Where slightly impure materials are used, or the heating is continued for longer periods of time, or in the absence of an atmosphere of nitrogen the constant found immediately increases. This is because some of the material calculated as benzaldehyde is not that substance.

The amount of benzaldehyde in the filtrate from the benzoïn was usually checked up by precipitation with phenylhydrazine but this method did

not give concordant results, especially when the volumes of the solution and the amounts of sodium cyanide were large.

Pure benzaldehyde must be used as a starting material and the weight must be corrected for the small amount of benzoic acid present or the value of K will appear larger than it actually is.

The solvent used in the most satisfactory method for preparing benzoin is 50% alcohol. The larger yield obtained when this solvent is used is due to the benzoin precipitating out of solution, thus allowing the reaction to go nearer to completion.

The senior author is investigating the equilibrium reached in the reversal of other similar reactions, the temperature coefficients, and the velocities of some of these reactions.

The authors desire to thank Dr. H. G. Deming for helpful suggestions made during the course of the investigation.

Summary

1. The benzoin condensation is a reversible process.
2. The equilibrium constant between benzaldehyde and benzoin at 79° is very nearly 0.245.

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A NEW TYPE OF SYNTHESIS. I. THE REACTION BETWEEN HALOGEN-ALKYL SULFONATES AND ORGANOMAGNESIUM HALIDES

Preliminary Note

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Introduction

There are but few reactive substances which exceed in importance the alkyl and aryl halides. This is particularly true from the viewpoint of synthetic chemistry because of the many classes of compounds prepared either directly or indirectly from such halogen-containing substances. The methods available to organic chemists for the introduction of halogens into compounds removed from the simpler types are very few in number and generally unsatisfactory in the sense that the yields are poor, the technique is involved, and the reactions are sometimes "unreliable" in the determination of molecular structures.

The present work is a preliminary account of a method which obviates to some extent these difficulties. It has been found that when organomagnesium halides are treated in ethereal solution with halogen-alkyl esters of aromatic sulfonic acids a smooth reaction takes place at the boil-