

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PYROLYSIS OF BENZALDEHYDE AND OF BENZYL BENZOATE

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The pyrolysis of benzaldehyde appears to proceed essentially in one of two directions depending on the conditions of heating. At moderately high temperatures it changes slowly into benzyl benzoate by a polymerization process which involves the double bond of the carbonyl group. At elevated temperatures benzaldehyde rapidly decomposes into carbon monoxide and benzene. These primary effects were reported, respectively, by Lachman¹ and by Peytral,² and both appear to be well substantiated. However, certain secondary details in each case seemed open to question, and consequently it appeared expedient to give this subject further study.

A brief summary of the features of our work which contrast with the earlier results follows. Mlle. Peytral passed benzaldehyde vapors rapidly through a short platinum tube at 1150°. We obtained a decomposition similar to hers by using a pyrex combustion tube at 680°. She reported the formation not only of benzene, but also of diphenyl and of a solid, m. p. 213°, stated to be anthracene. Actually, we proved this to be 1,4-diphenylbenzene or "terphenyl," and not anthracene. Its formation is the result of continued pyrolysis of the benzene and diphenyl.

With two hours of heating in a sealed tube at 300°, our results showed much less decomposition of benzaldehyde than Lachman reported. In five such experiments our recovery of unchanged aldehyde was 88–95% as contrasted with 70%. The anticipated pyrolysis occurred, however, at 350–370°. For purposes of comparison, our results obtained at 350–370° are listed in Table I with Lachman's 300° data. Both sets of experi-

TABLE I
PYROLYSIS OF BENZALDEHYDE IN A SEALED TUBE

Products formed	Weight of benzaldehyde taken, Lachman, 50 g.		This investigation, 62.5 g.	
	Moles	Equiv. moles of benzalde- hyde consumed	Moles	Equiv. moles of benzalde- hyde consumed
Benzyl benzoate	0.01 ± 0.002	0.02	0.073	0.146
Toluene	0.022	0.022	None	None
Benzene	None	None	0.025	0.025
Benzoic acid	0.033	0.033	0.004	0.004
Dibenzyl ether	0.015	0.03	None	None
Total		0.105	0.175
Original unrecovered benzaldehyde		0.14	0.18
Difference		0.035	0.005

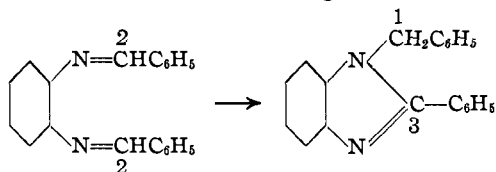
¹ Lachman, *THIS JOURNAL*, **46**, 720 (1924).

² Peytral, *Bull. soc. chim.*, [4] **29**, 44 (1921).

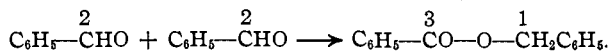
ments were of two hours' duration and in both the recovery of undecomposed aldehyde was about 70%. We found no evidence for toluene or dibenzyl ether as reaction products and only slight evidence for benzoic acid.

From the present data it appears that the essential change at 350–370° is of the Cannizzaro type, giving rise to benzyl benzoate. A minor concurrent reaction, which becomes the major one at higher temperatures, is the pyrolysis into benzene and carbon monoxide.

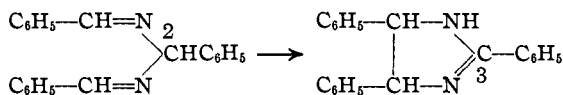
Ammonobenzaldehyde.—Hydrobenzamide and dibenzylidene-*o*-phenylenediamine may be regarded as analogs of benzaldehyde in the ammonia system. Just as with benzaldehyde, these substances undergo a Cannizzaro type of oxidation and reduction by moderate heating. Dibenzylidene-*o*-phenylenediamine³ rearranges into benzaldehyde at 106°.



Atoms numbered (1), (2) and (3) in the equation represent, respectively, carbon atoms in the state of oxidation of alcohol, aldehyde and acid. With benzaldehyde the comparable reaction has been shown to be



Hydrobenzamide undergoes rearrangement⁴ into amarine⁵ by heating at 130° for three to four hours



Since the high-temperature decomposition of benzaldehyde leads to benzene and carbon monoxide instead of benzyl benzoate, it may be inferred that the high-temperature decomposition of "ammonobenzaldehyde" may also follow quite a different course from that which has just been outlined.

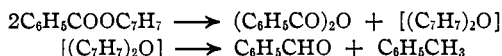
Benzyl Benzoate.—Since benzyl benzoate is a pyrolytic product from benzaldehyde at 350°, it was of interest to study the behavior of benzyl benzoate under similar conditions. The results show that about half of the ester is recoverable after two hours of heating. The products formed

³ Hinsberg and Koller, *Ber.*, **29**, 1497 (1896).

⁴ Bertagnini, *Ann.*, **88**, 127 (1853); Bahrmann, *J. prakt. Chem.*, **27**, 296 (1883).

⁵ Strain, *THIS JOURNAL*, **49**, 1565 (1927), regarded this change as analogous to the benzoin condensation. That it cannot be analogous is evident from structural difficulties (noted by Strain), and also from the fact that benzoin is not a pyrolytic product of benzaldehyde.

are best explained by assuming an initial disproportionation into benzoic anhydride and dibenzyl ether, the former appearing as such and the latter decomposing⁶ further into toluene and benzaldehyde. The reaction mixture was carefully searched for stilbene, phenanthrene, benzene, diphenyl and dibenzyl ether but none of these substances could be identified. The equation, therefore, which best represents the pyrolysis of benzyl benzoate is



A small amount of benzoic acid, in addition to the benzoic anhydride, was also formed. It may have been produced as a primary product, or it may have been produced secondarily from the benzoic anhydride or the benzaldehyde. At least, the absence of stilbene may be taken as evidence that phenylmethylene, $[\text{C}_6\text{H}_5\text{CH}=\text{C}]$, did not appear even momentarily. Phenylmethylene is the residue obtained by detaching the elements of benzoic acid from benzyl benzoate. Possibly some of the benzaldehyde may have arisen by reversal of the Cannizzaro reaction, but the fact that toluene and benzaldehyde were isolated in roughly equivalent quantities is contra-evidence.

Esters with β -hydrogens in the alcohol part of the molecule, such as $\text{RCO}_2\text{CR}_2\text{CHR}_2$, are known to pyrolyze readily into acid, RCO_2H , and olefin, $\text{R}_2\text{C}=\text{CR}_2$. Benzyl benzoate has no such β -hydrogens and in this respect it is similar to methyl benzoate and benzohydril benzoate. The former⁷ of these is stable to 400° , but the latter⁸ gives benzoic anhydride (among other things) on distillation. Presumably the primary effect is one of disproportionation.



Experimental Part

Benzaldehyde at $300\text{--}310^\circ$.—Benzaldehyde was freshly distilled *in vacuo* and was collected over a 2° range. About 50-g. portions were placed in pyrex bomb tubes. Air was excluded with benzaldehyde vapors by boiling prior to sealing. The tube was heated in a bomb furnace for two hours at $300\text{--}310^\circ$ and left overnight to cool. Five such runs were made and the greatest non-recovery of benzaldehyde was 7 g. from 62 g. The percentage of recovery varied between 88–95%. Benzyl benzoate was the major product in the non-benzaldehyde portion, but there was always a small amount of benzoic acid. In no case was any other product isolated.

Pyrolysis of Benzaldehyde at $350\text{--}370^\circ$.—The details of a characteristic experiment will be related. A sample of benzaldehyde weighing 62.5 g. (freshly vacuum distilled)

⁶ Benzoic anhydride is known to be stable at least to 400° [Anschütz, *Ber.*, 10, 1883 (1877); *Ann.*, 226, 15 (1884); Deninger, *J. prakt. Chem.*, 50, 480 (1894); Staudinger, *Ber.*, 44, 544, footnote (1911)], whereas dibenzyl ether decomposes rapidly at its boiling point, 295° , and slowly at $210\text{--}215^\circ$ [Cannizzaro, *Ann.*, 92, 113 (1854); Lowe, *ibid.*, 241, 374 (1887); Lachman, *THIS JOURNAL*, 45, 2358 (1923)].

⁷ Engler and Löw, *Ber.*, 26, 1441 (1893).

⁸ Linneman, *Ann.*, 133, 23 (1865); Anschütz, *ibid.*, 235, 220 (1886).

was heated for two hours in a sealed tube at 350–370°. After cooling overnight and opening, considerable pressure of an inflammable gas was noted. On distillation of the red liquid, 30 g. was obtained from 110–176°, which, on redistillation, yielded 2 g. of a mobile liquid between 70 and 120°. This was chiefly benzene, as shown by nitration to dinitrobenzene (m. p. 88–89°) and confirmation by a mixed melting point determination with a known sample of dinitrobenzene. The mixture melted also at 88–89°. From this first fraction, and from that boiling from 176–196°, 43 g. of benzaldehyde was recovered. Half a gram of benzoic acid was extracted from the residue, thereby leaving 15.5 g. of a benzyl benzoate portion, b. p. 130–190° (6 mm.), and 1 g. of brown residue.

Fifteen g. of the 15.5 g. of liquid just mentioned, on hydrolysis with alcoholic potassium hydroxide (reflux one hour), gave 7 g. of benzyl alcohol, b. p. 75–80° (6 mm.) and 8.4 g. of benzoic acid. The theoretical yields for 15 g. of benzyl benzoate would be 7.6 g. of the alcohol and 8.6 g. of the acid. There was no high boiling residue and no indication of dibenzyl ether.

Pyrolysis of Benzaldehyde at 680–690°.—Forty-one g. of benzaldehyde was dropped from a stoppered-in dropping funnel into an upturned elbow of a nitrogen-filled pyrex combustion tube. The tube was about a meter long and was maintained at 680–690° (thermocouple measurement) by an electric furnace. The effluent end of the tube was connected to a smaller tube which led through a condenser into a receiving flask. The outlet of the flask was connected so that the gas formed could be collected over a saturated sodium chloride solution. After four hours all the benzaldehyde was added. Therefore, the rate of entry was $\frac{1}{6}$ g. per minute. The distillate weighed 31 g. and the volume of the gas was 5.8 liters (standard conditions).

The 31 g. of liquid, on fractionation, gave 11 g. of benzene, 13.5 g. of benzaldehyde and 2.5 g. of diphenyl. Diphenyl (m. p. 65°) was positively identified by chemical and physical properties. From the fraction boiling at 150–200° at 18 mm. about 0.3–0.5 g. of a white crystalline solid (m. p. 213°, corr.) was obtained after two crystallizations from alcohol. It was easily sublimed when distilled in a vacuum and was practically insoluble in cold alcohol or ether. It appeared to be the "anthracene" which Peytral found at 1150°, but no anthraquinone could be isolated from a chromic acid oxidation of a portion, nor could a picrate be made. A mixed melting point determination with anthracene (m. p. 210°) gave a melting point at 170°. Thus the substance was not anthracene. These properties are all those of "terphenyl" or 1,4-diphenylbenzene. In confirmation, a mixed melting point with a known sample of the latter showed no depression of the melting point; mixed m. p. 213° (corr.). Also, it dissolved characteristically in sulfuric acid with a green-blue color which changed to purple on boiling. Finally, a small amount of white powder which did not melt below 295° (terephthalic acid) was obtained from the chromic acid oxidation mixture.

The gas (5.8 liters, corrected volume) contained no methane or unsaturated hydrocarbons. By volume it analyzed as follows: carbon monoxide, 86.7%; hydrogen, 12.9%; carbon dioxide, 0.32%. This is calculated to a nitrogen-free basis.

Benzyl Benzoate, Preparation.—Benzyl benzoate was prepared by refluxing benzoyl chloride and benzyl alcohol for three hours by the method of Cannizzaro.⁹ The yield of ester (alkali washed, and b. p. (23 mm.) 198–203°) was found to be 44.5%.

Pyrolysis of Benzyl Benzoate at 350°.—A sample of the ester weighing 42.5 g. (b. p. (21 mm.) 193–198°) was sealed in an evacuated tube and kept at 340–350° for two hours. After cooling overnight, the tube was opened and found to contain an apparently non-combustible gas under high pressure. The contents were black and the volatile portions were distilled off. Three g. of toluene and 2 g. of benzaldehyde

⁹ Cannizzaro, *Ann.*, 90, 254 (1854).

were isolated. The toluene was identified as dinitrotoluene, which melted at 68–70° after two recrystallizations from alcohol. The same derivative similarly prepared from pure toluene melted at 69–70°, and a mixed melting point was 68–70°. The less volatile material was distilled under diminished pressure, thereby yielding 31.5 g. of distillate. It was dissolved in ether and extracted with alkaline solution, thereby removing 2 g. of benzoic acid. Test portions of the mixture absorbed bromine without the evolution of hydrogen bromide. Although indicative of unsaturated hydrocarbons such as stilbene, no such dibromide could be found. Actually the bromine absorption was caused by benzoic anhydride.¹⁰ A known sample of benzoic anhydride behaved identically. The unused portion weighed 24.5 g. and 20 g. of this was saponified by refluxing with alcoholic potassium hydroxide for an hour and a half. This produced 7.5 g. of benzyl alcohol, b. p. (6 mm.) 75–80°. The equivalent quantity of benzoic acid would be 8.5 g. but actually 12 g. (m. p. 120–122°) was isolated. The excess was produced from benzoic anhydride. These data indicate at least 15 g. of benzyl benzoate and about 3 g. of benzoic anhydride in the original 20 g. which was saponified. In terms of the 31.5 g. of distillate, this extrapolates to 23.6 g. of benzyl benzoate and 4.7 g. of benzoic anhydride.

Summary

The decomposition of benzaldehyde is very slow at 300°, but about one-third of it decomposes, largely into benzyl benzoate, in two hours at 350°. A concurrent reaction of much less importance gives rise to carbon monoxide and benzene. No evidence could be obtained for toluene or dibenzyl ether as reaction products and benzoic acid is formed in negligible amounts.

By passing benzaldehyde through a pyrex tube at 700° at a rate of one-sixth g. per minute, it was about two-thirds decomposed. The major reaction was the formation of benzene by loss of carbon monoxide. Side reactions gave rise to diphenyl and 1,4-diphenylbenzene. Anthracene was definitely absent.

At 350° benzyl benzoate undergoes a reaction of disproportionation. After two hours' heating, the major products of change are benzoic anhydride, toluene and benzaldehyde. Smaller amounts of benzoic acid were also identified. Negative searches were made for stilbene, phenanthrene, benzene, diphenyl and dibenzyl ether in the products of reaction.

EVANSTON, ILLINOIS

¹⁰ Gal, *Compt. rend.*, 54, 1228 (1862).