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New Haven, Connecticut

[Contribution from the Chemical Laboratory of Washington University]

THE DECOMPOSITION OF THE AMINOBENZOIC ACIDS BY BOILING WATER

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The decomposition of anthranilic acid, when heated above its melting point, into carbon dioxide and aniline is well known. Fritzsche[1] identified the gas evolved as carbon dioxide and Liebig[2] showed that the oily distillate obtained was aniline. Powlewski[3] studied this decomposition and found it to be complete when the acid was heated for 1 hour at 205–210°.

The *m*-aminobenzoic acid yields carbon dioxide, aniline and ammonia on treatment with caustic potash[4] and the *p*-aminobenzoic acid gives aniline and carbon dioxide when treated with conc. hydrochloric acid.[5] However, no mention is made of the effect of heating aqueous solutions of these acids.

The object of this investigation was to study not only the decomposition of the aminobenzoic acids by boiling water but also to determine the rate of decomposition and the volatility of the acids with steam.

Experimental Part

Products of Decomposition.—The presence or absence of aniline and carbon dioxide as products of the decomposition was ascertained by boiling 5g. samples of the pure acids[6] with water under a short reflux condenser for 3 hours, the gases evolved being led into a tube of lime-water protected by a tube of soda lime. The solutions were then neutralized with sodium hydroxide, extracted with ether, and the ether extracts tested for aniline. It was found that the *ortho* and *para* acids gave aniline and carbon dioxide while the *meta* acid did not.

Rate of Decomposition.—Weighed samples of the acids were placed in Erlenmeyer flasks and distilled water was added. The flasks were heated just to boiling over the Bunsen flame, and then transferred to an electric hot plate, where gentle boiling was maintained for the desired length of time. During this period the carbon dioxide and aniline escaped from the

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[1] Fritzsche, *Ann.*, **39**, 86 (1841).

[2] Liebig, *ibid.*, **39**, 94 (1841).

[3] Powlewski, *Ber.*, **37**, 592 (1904).

[4] Beilstein, "Handbuch der Organischen Chemie," Voss **1896**, II, 1256.

[5] Weith, *Ber.*, **1**, 105 (1879).

[6] We wish to thank the Monsanto Chemical Works of St. Louis for the anthranilic acid which was prepared and purified by them for us.

flasks along with the steam. The quantity of solution was kept constant by the frequent addition of hot water during the boiling period. The flasks were then removed from the hot plate and the undecomposed acid determined by titration with standard sodium hydroxide, using phenolphthalein as indicator. The amount of acid decomposed was obtained by subtracting this value from the weight of the sample. Since the amount obtained by this method would also include the acid volatilized with the steam, a correction was made in order to obtain the true decomposition. The average rate of evaporation of water from the flasks was found to be 100 cc. per hour; so for each hour of boiling the amount of acid per 100 cc. of water, as determined by the distillation with steam, was subtracted from the total weight of the acid lost.

The steam distillations were carried out in the usual manner using a Claisen flask. The weight of the acid per 100 cc. of distillate was determined by titration with standard alkali. It was found that 100 cc. of the distillate contained 0.016 g. of the *ortho* acid and 0.0056 g. of the *para* acid. The *meta* acid is not volatile with steam.

The following data were obtained.

TABLE I

ANTHRANILIC ACID

	2 g. in 150 cc. water				3 g. in 200 cc. water			
Boiling time Hours	Acid decomp. G.	Acid decomp. Apparent %	True %	K	Acid decomp. G.	Acid decomp. Apparent %	True %	K
1	0.0672	3.36	2.56	0.027	0.0921	3.07	2.54	0.028
2	0.1429	7.15	5.55	0.029	0.1857	6.19	5.13	0.028
3	0.1870	9.35	6.95	0.025	0.3132	10.44	8.84	0.031
4	0.3072	15.36	11.66	0.031	0.4446	14.82	12.69	0.033
5	0.3422	17.11	13.11	0.027	0.5592	18.64	15.97	0.033
6	0.3768	18.84	14.04	0.025	0.6006	20.02	16.82	0.030
7	0.4052	20.26	15.46	0.025	0.6948	23.16	19.43	0.028

TABLE II

PARA-AMINOBENZOIC ACID

2 g. in 200 cc. water

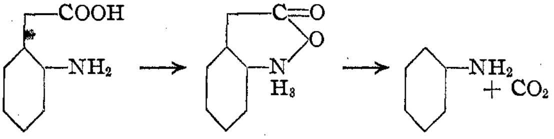
Boiling time Hours	Acid decomp. G.	Acid decomp. Apparent %	True %	K
1	0.0370	1.85	1.57	0.015
2	0.0640	3.20	2.64	0.014
3	0.0852	4.26	3.52	0.013
4	0.1326	6.63	5.51	0.014
5	0.1754	8.77	7.37	0.015
6	0.2025	10.13	9.55	0.017

Discussion

By substituting the decomposition values in the expression for a unimolecular reaction, $K = \frac{1}{0.4343\,t} \log \frac{a}{a-x}$, where a is the initial concentration, x the amount of acid decomposed, and t the time in hours, the values for the velocity constants were obtained.

In the case of anthranilic acid the values of K for the initial concentration of 3 g. are greater than in the case of the 2g. sample, apparently indicating an increase in decomposition with increasing size of sample. However, the increase is comparatively small and is due partly to the fact that the correction for volatility with steam and the error due to mechanical losses during boiling form a smaller percentage of the acid in the case of the 3g. sample than in the case of the 2g. sample.

It is interesting to note that only the *o*- and *p*-aminobenzoic acids decompose into aniline and carbon dioxide and that the *para* acid decomposes only half as fast as does the *ortho*. A possible explanation of these facts may be due to the formation of the inner salt and the subsequent decomposition of this salt as shown by the following reaction.



The *para* acid also forms this inner salt but to a much less extent than anthranilic acid, while the *m*-aminobenzoic acid does not form such a salt at all, and hence does not give aniline and carbon dioxide.

Summary

1. The anthranilic acid and *p*-aminobenzoic acid are decomposed by boiling water into aniline and carbon dioxide but the *m*-aminobenzoic acid is not.

2. Both anthranilic acid and *p*-aminobenzoic acid are slightly volatile with steam, while *m*-aminobenzoic acid is not.

3. The rate of these decompositions has been studied and the reaction found to be monomolecular. The *para* acid decomposes $^1/_2$ as fast as does the *ortho*.

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