melts at 191°.) The following simultaneously determined pure and mixed melting points indicated that the product was not identical with that obtained from 4-acetylamino-1 acid: derivative from 4-acetylamino-1 acid, 186–187°; derivative from acetylated Adler acid, 190–191°; mixture of the two derivatives, 173–178°.

Preparation of 1-Acetylamino-2-chloronaphthalene from 1-Acetylamino-2-naphthalenearsonic Acid.—Employing the method of the preceding procedure, 0.45 g. of 1-acetylamino-2 acid was converted into a white solid, m. p. 190–192°, which gave a negative test for the arsonic acid group[11] and a positive Beilstein cupric oxide test for halogen. (Charrier and Ferreri[13] have reported that 1-acetylamino-2-chloronaphthalene melts at 191°.) The following simultaneously determined melting points demonstrated that acetylated Adler acid and 1-acetylamino-2 acid are identical: derivative from 1-acetylamino-2 acid, 191–192°; derivative from acetylated Adler acid, 189–191°; mixture of these two derivatives, 190–192°.

Summary

1. The aminonaphthalenearsonic acid obtained by the direct arsonation of α-naphthylamine by means of the Béchamp reaction has been identified structurally as 1-amino-2-naphthalene-arsonic acid by a series of mixed melting points, the preparation of an acetyl derivative, and the preparation of 1-acetylamino-2-chloronaphthalene from this acetyl derivative.

2. The assignment of this structure instead of that of 4-amino-1-naphthalenearsonic acid as reported in the literature involves a correction of the structure of all naphthalene arsenicals dependent on the Béchamp reaction as a part of their method of preparation, including certain substituted naphthalenearsonic acids, the only known hydroxynaphthalenearsonic acid, and the product at present assigned the structure of the naphthalene analog of arsphenamine.

3. 1-Amino-2-naphthalenearsonic acid was obtained from 4-amino-1-naphthalenearsonic acid by heating the latter in α-naphthylamine, thus demonstrating that in a medium of α-naphthylamine at temperatures above 175°, the former isomer is more stable than the latter.


The Synthesis of Pyrazine by the Catalytic Dehydrogenation of Ethanolamine

BY J. G. ASTON, T. E. PETERSON AND J. HOLOWCHAK

A study of the dehydrogenation of the vapor of ethanolamine has been made using catalysts at temperatures varying from 230 to 300°. The catalysts used were copper, copper and zinc oxide, zinc oxide and sodium carbonate. In each case pyrazine is formed directly, the reactions involved presumably being

$$CH_2(NH_2)CH_2OH \longrightarrow CH_2(NH_2)CHO + H_2 \quad (A)$$
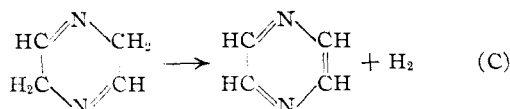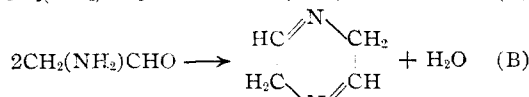
One mole of ethanolamine should thus yield one-half mole of pyrazine and one and one-half moles of hydrogen. The best yields were obtained at 300° using a copper catalyst. The yield was then 5.6% of pyrazine isolated as the mercuric chloride double salt although the hydrogen obtained was 0.54 mole per mole of ethanolamine. It thus appears that most of the amino acetaldehyde dis-

appeared by side reactions producing resins. These resins eventually rendered the catalyst inactive.

Experimental

For each run one mole of redistilled ethanolamine (b. p. 168–170°) was used. This was kindly furnished by the Carbide and Carbon Chemical Corporation.

The catalysts used were A, finely divided copper; B, an equimolecular mixture of finely divided copper and zinc oxides; C, zinc oxide with 4.5% by weight of sodium carbonate. The first two were prepared by the method used by Frolich, Fenske and Quiggle.[1] except that the mixed hydroxides were pasted while wet on rolled copper gauze, and slid into the tube. The catalyst was then dried, heated to 300° to convert into oxides, and reduced in a current of hydrogen, diluted with nitrogen, at about 200°. The third was made by mixing sodium carbonate (4.5% by weight) with zinc oxide which had been prepared from zinc nitrate solution by precipitation with ammonium hydroxide and drying overnight at 120°. It was supported on moistened tile.

The catalyst tube was about 2 cm. inside diameter and 75 cm. long with a small inside tube running from end to end for a thermocouple. It was wrapped with an electrical heater, and surrounded by an air jacket consisting

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(1) Frolich, Fenske and Quiggle, Ind. Eng. Chem., 20. 694 (1928).

of a concentric Pyrex tube packed with asbestos at each end.

Ethanolamine vapor was supplied at a constant rate by dropping the liquid slowly from a dropping funnel into a 100-cc. distilling flask immersed in an oil-bath at 225°. The vapors leaving the catalyst tube were condensed by a water-cooled condenser. The gas was then measured by means of a wet test meter.

The condensate was distilled. Fractions were taken as follows: 95 to 125°, 125 to 170°, residue above 170°. The first fraction was shown to contain all the pyrazine, while the second fraction was largely ethanolamine (75% by weight). The pyrazine was recovered from the first fraction by acidifying with dilute hydrochloric acid and adding excess of a saturated solution of mercuric chloride. The mercury double salt, $C_4H_4N_2 \cdot HgCl_2$ was then filtered off. Experiment showed that all the pyrazine present was separated in this way. Since it was shown, by analysis for mercury, that the uncrystallized double salt was practically pure, the yield of pyrazine was calculated from the weight of dry double salt.

The results of the various experiments are summarized in Table I.

TABLE I

PRODUCTS FROM ONE MOLE OF ETHANOLAMINE

Catalyst	Temp, °C.	Time. hours	Mole of gas	Mole of mercury double salt	Mole of ethanol-amine recov.	% Yield of pyrazine
A 1-1	230	5	0.54	0.01	0.11	2.27
A 1-2	300	4	.62	.023	.17	5.56
A 1-3	230	9	.47	.0057	.18	1.47
A 2-1	230	5	.43	.012	.25	3.34
A 2-2	230	5	.38	.0055	.31	1.62
A 2-3	230	5	.42	.0048	.31	1.42
A 4-1	300	5	.55	.021	.14	5.04
A 4-2	300	4	.27	.009	.28	2.52
B 1-1	240	5	.13	.0024	.31	0.72
B 1-2	300	4	.48	.012	.12	2.75
C 1-1	260	5	.29	.0021	.42	0.72
Tile	300	5	0	0	.61	0

In Column 1 the following notation is used in specifying the catalyst. The letters denote the nature and composition of the catalyst as already specified. The first number denotes the number of the preparation. The second number denotes the number of the run with this particular prepara-

tion, so that examination of the details of previous runs with the same preparation shows completely its history. In Column 7 the percentage yield of pyrazine has been calculated from the weight of double salt, allowing for the ethanolamine recovered. The significance of the other columns is plain. It was shown by analysis that the gas evolved in runs with the copper catalyst was exclusively hydrogen within experimental error. It is to be noted that the copper catalyst deteriorated with time even at 230°. This loss of activity is attributed to the catalyst becoming coated with non-volatile decomposition products.

The last run in Table I was made with the tube filled with tile. It shows that in the absence of catalysts ethanolamine is quite stable at 300°. The poorer yields of pyrazine when the catalyst contained zinc oxide must have been due to the simultaneous dehydrating influence of the latter.

The mercury double salt was recrystallized from dilute hydrochloric acid.

Anal. Calcd. for $C_4H_4N_2Cl_2Hg$: Hg, 57.06. Found: Hg, 56.63, 56.86.

The pyrazine was obtained from the double salt by distillation with concentrated potassium hydroxide and saturation of the distillate with potassium hydroxide. After drying by melting with solid potassium hydroxide, it boiled at 111–114°. The portion of b. p. 112–114° (730 mm.) and m. p. 48.0° was taken for analysis.

Anal. Calcd. for $C_4H_4N_2$: C, 59.97; H, 5.03. Found: C, 59.93, 59.79; H, 5.31, 5.18.

Summary

1. Pyrazine can be prepared by the catalytic dehydration of ethanolamine.

2. The most favorable conditions are a copper catalyst at a temperature of 300°.

3. The copper catalyst loses its activity after a few hours of use.