has been devised for determining the atomic mass of tungsten, it will perhaps be better to accept the result 184, as the most probable value of this constant.

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ON β-HEPTYLAMINE.[1, 2]

[FIRST PAPER.]

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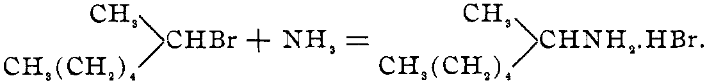
Received August 2, 1899.

ALTHOUGH β-heptylamine has been prepared by Cahours and Pelouse[3] and later by Schorlemmer,[4] the description of it was so meager, that it was considered worth while to study this base more thoroughly.

β-Heptyl bromide, prepared according to the method of Venable[5] from heptane of the *Pinus sabiniana*, was heated in a sealed tube at 100° with an excess of an alcoholic solution of ammonia. The resulting products were primary β-heptylamine hydrobromide, ammonium bromide, heptylene, and unchanged β-heptyl bromide. There was no evidence of the formation of a base other than primary β-heptylamine, which accords with the observations of Jahn,[6] that by the action of ammonia on isopropyl iodide, β-hexyl iodide or β-octyl iodide, only amide bases are formed. The formation of unsaturated hydrocarbons of the series C_nH_{2n} was observed by Jahn,[7] in the action of ammonia on isopropyl iodide and β-hexyl iodide.

The results show that, similar to the examples cited from Jahn, two separate reactions take place in the action of ammonia on β-heptyl bromide. One is the condensation of the ammonia with the bromide to form the primary amine hydrobromide as shown in the following equation:



$$\left.\begin{array}{r}CH_3\\CH_3(CH_2)_4\end{array}\right\rangle CHBr + NH_3 = \left.\begin{array}{r}CH_3\\CH_3(CH_2)_4\end{array}\right\rangle CHNH_2.HBr.$$

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[1] I name those compounds which have the group or element characterizing them attached to the second carbon atom in the normal hydrocarbon chain, β-derivatives; thus $CH_3CH_2CH_2CH_2CH_2CHNH_2CH_3$ is called β-heptylamine.

[2] Read at the Columbus meeting of the American Association for the Advancement of Science.

[3] *Jsb. d. Chem.* (1863), 528.

[4] *Ann. Chem.* (Liebig), **127**, 318.

[5] *Ber. d. chem. Ges.*, **13**, 1650.

[6] *Monatsh. Chem.*, **3**, 165.

[7] *Ibid.*, **3**, 166 and 170.

The other is the splitting off of hydrogen bromide by the ammonia with the formation of heptylene and ammonium bromide as follows:

$$CH_3(CH_2)_4CHBrCH_3 + NH_3 = CH_3(CH_2)_4CH{=}CH_2 + NH_4Br.$$

Preparation of β-Heptylamine, $CH_3(CH_2)_4CHNH_2CH_3$.—β-Heptyl bromide, boiling-point 164°–168°, was sealed in a tube with an excess of an alcoholic solution of ammonia and heated in a water-bath for forty-eight to seventy-two hours; at the end of this time the reaction was apparently complete. The contents of the tube were filtered to remove ammonium bromide, which had formed in some quantity. The alcohol was then distilled off and the residue heated for some time in a partial vacuum at about 125° in order to free it from unchanged β-heptyl bromide or other impurities volatile at that temperature and pressure. The crude β-heptylamine hydrobromide, obtained in this manner, was dissolved in a small quantity of warm benzene and petroleum ether added until the clear liquid was slightly turbid.

After warming on a water-bath until clear and allowing to stand for some hours, fairly pure β-heptylamine hydrobromide crystallized out. The purified hydrobromide was dissolved in a small quantity of water and an excess of potassium hydroxide solution (1 : 1) added. Although there was evolution of heat and the separation of the amine seemed complete, the mixture was heated fifteen minutes on a water-bath to be sure that all the base had been liberated. The free β-heptylamine, floating on the potash solution, was separated and the solution extracted with ether. After drying the ethereal solution with solid potassium hydroxide and distilling off the ether, a slightly brown colored liquid was obtained, which was distilled in a partial vacuum from anhydrous barium oxide, over which it had stood for five days. When carefully fractioned at ordinary pressures, the greater portion distilled at 142°–144° (most at 143°). The density of this fraction at 24° compared with water at the same temperature is 0.7667.

On diluting the alcohol which was distilled from the crude hydrobromide, an oil separated. This was roughly divided by distillation into two fractions, the lower boiling being heptylene, as it had the characteristic odor, and absorbed bromine; the higher boiling fraction was unchanged β-heptyl bromide as was shown by its boiling-point and the presence of bromine.

β-Heptylamine is a colorless liquid with a very characteristic amine-like odor and bitter, burning taste. It is soluble in alcohol, ether, or petroleum ether; slightly soluble in water. It takes up some water, from which it is freed with the greatest difficulty. It is strongly alkaline, combining with acids with evolution of much heat. If left in the air, it absorbs water and carbon dioxide.

I. 0.2317 gram of the amine gave 0.6166 gram carbon dioxide and 0.3140 gram water.

II. 0.1353 gram of the amine gave 15.5 cc. nitrogen at 28° and under a pressure of 752 mm.

III. 0.2844 gram of the amine gave 33 cc. nitrogen at 29° and under a pressure of 752 mm.

	Calculated for $C_7H_{17}N$.	Found. I.	II.	III.
Carbon	73.05	72.58		
Hydrogen	14.78	15.06		
Nitrogen	12.16		12.43	12.52

β-Heptylamine Hydrobromide, $CH_3(CH_2)_4CHNH_2CH_3.HBr$.—The fairly pure β-heptylamine hydrobromide as obtained in the preparation of β-heptylamine was recrystallized from a mixture of benzene and petroleum ether until the melting-point was constant.

β-Heptylamine hydrobromide crystallizes in exceedingly fine, white, silky needles, which are two to three cm. in length and melt at 163°. It is very soluble in alcohol, benzene, and water; soluble in a large volume of dry ether, practically insoluble in petroleum ether.

I. 0.3125 gram of the substance gave 0.2980 gram silver bromide.

II. 0.3988 gram of the substance gave 0. 3836 gram of silver bromide.

	Calculated for $C_7H_{18}NBr$.	Found. I.	II.
Bromine	40.81	40.57	40.93

β-Heptylamine Hydrochloride, $CH_3(CH_2)_4CHNH_2CH_3.HCl$.—This salt was prepared by passing hydrochloric acid gas into an ethereal solution of β-heptylamine. As the ether was not completely dry, it did not all precipitate as was expected, therefore the ether was allowed to evaporate. The slightly colored residue, obtained in this manner, was dissolved in warm benzene, petroleum ether added until slightly turbid, and set aside to crystallize. Crystallization was repeated until the melting-point was constant.

β-Heptylamine hydrochloride crystallizes in beautiful, white, silky, slightly deliquescent needles, which melt at 133°. It is readily soluble in water, alcohol, and benzene; insoluble in petroleum ether and sparingly soluble in ether.

I. 0.2198 gram of the substance gave 0.4460 gram carbon dioxide and 0.2322 gram water.

II. 0.1928 gram of the substance gave 15.4 cc. nitrogen at 19° and under a pressure of 753 mm.

III. 0.2029 gram of the substance gave 18 cc. nitrogen at 19° and under a pressure of 753 mm.

IV. 0.3345 gram of the substance gave 0.3140 gram silver chloride.

V. 0.3618 gram of the substance gave 0.3370 gram silver chloride.

	Calculated for $C_7H_{18}NCl$.	Found.				
		I.	II.	III.	IV.	V.
Carbon	55.45	55.35				
Hydrogen	11.88	11.74				
Nitrogen	9.24		8.88	9.87		
Chlorine	23.43				23.21	23.09

β-Heptylamine Chlorplatinate, $(C_7H_{15}NH_2.HCl)_2PtCl_4$, was prepared from the amine hydrochloride by dissolving it in a small amount of water and adding an excess of chlorplatinic acid. The salt separates in fine plates which are sparingly soluble in cold, easily in warm water. It crystallizes from the latter on cooling, in large yellow plates. It is readily soluble in alcohol. On heating to 195° it decomposes.

0.2164 gram of the salt gave 0.0653 gram platinum.

	Calculated for $C_{14}H_{34}NCl_6Pt$.	Found.
Platinum	38.23	37.98

β-Heptylamine Chloraurate, $C_7H_{15}NH_2.HClAuCl_3$, was prepared by adding chlorauric acid to a concentrated solution of the amine hydrochloride in water. It separates in light yellow crystals which melt at 63°–64°. In cold water it is sparingly soluble; readily soluble in warm water from which it may be crystallized in large yellow plates.

0.1805 gram of the salt gave 0.0778 gram gold.

	Calculated for $C_7H_{17}NCl_4Au$.	Found.
Gold	43.30	43.10

β-Heptylamine Oxalate, $(C_7H_{15}NH_2)_2C_2H_2O_4$, was prepared by adding the amine in slight excess to an alcoholic solution of oxalic acid, precipitating with ether, and recrystallizing from alcohol. It crystallizes in beautiful, white plates, which melt at 204°–205° with decomposition. In cold water or alcohol it is moderately soluble; in the warm solvents it is readily soluble. It is insoluble in ether and petroleum ether. On boiling it with water it is completely decomposed, the oxalic acid remaining and the β-heptylamine passing off with the steam.

I. 0.2545 gram of the substance gave 0.5626 gram carbon dioxide and 0.2605 gram water.

II. 0.1873 gram of the substance gave 0.4122 gram carbon dioxide and 0.1882 gram water.

III. 0.2900 gram of the substance gave 24.8 cc. nitrogen at 18° and under a pressure of 753 mm.

IV. 0.2658 gram substance gave 20.7 cc. nitrogen at 18° and under a pressure of 753 mm.

	Calculated for $C_{16}H_{36}O_4N_2$.	Found.			
		I.	II.	III.	IV.
Carbon	60.00	60.30	60.03		
Hydrogen	11.25	11.37	11.17		
Nitrogen	8.75			8.35	8.90

At the time I made the nitrogen determinations given in this paper, the apparatus was inadequate, which will, in part, account for the poor results obtained.

The study of β-heptylamine is being continued in this laboratory.

I wish to express my sincere thanks to Dr. F. P. Venable for his advice and interest in the prosecution of this task.

CHEMICAL LABORATORY OF THE
UNIVERSITY OF NORTH CAROLINA, July 28, 1899.