ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. I. THE ACTION ON A MIXTURE OF ANILINE AND METHYL ALCOHOL.

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It has already been shown by Mailhe and Godon,(1) and Brown and Emmet(2) that silica and alumina which are the principal components of Japanese acid earth, promote the dehydration of alcohols and also the condensation of alcohols and amines. On repeating these experiments with alumina prepared from ammonium alum obtained from Potter's clay by heating at 700–800° and then treated with concentrated sulphuric acid and ammonium sulphate successively, the same experimental result as obtained by other chemists, was obtained.

When, however, silica, prepared from natural pumice by treating with concentrated nitric acid for several days, and composed of 98.30 percent of

(1) Mailhe and Godon, *Compt. rend.* **160** (1918), 467 & 564.
(2) Brown and Emmet, *J. Am. Chem. Soc.*, **46** (1924), 1836.

SiO_2 and 1.67 percent of Fe_2O_3, was used as catalyst, a result was obtained which differed from others in detail. A mixture of 46 grams of aniline and 18 grams of methyl alcohol was passed over the catalyst heated at 350°, 47.1 grams of reaction product was obtained, which after examination of the physical constants and the melting point of the acetates of fractions yielded by fractional distillation, as will be seen in Table 1, was confirmed as composed of p-toluidine and methylaniline.

TABLE 1.

No.	Fraction	Yield (gr.)	Sp.gr.(d_2^{20})	M.p. of acetate	Principal product
1	90–100°	0.9	—	—	—
2	185–190°	2.9	0.9937	107–111°	Aniline & Methylaniline
3	190–195°	18.1	0.9910	120–122°	Methylaniline & p-toluidine
4	195–198°	6.2	0.9865	124.5–126.5°	Methylaniline & p-toluidine
5	198–202°	4.0	0.9809	132.5–133.8°	p-Toluidine
6	202–210°	2.6	—	129–132°	—
7	210–215°	1.5	—	—	—

p-Toluidine was isolated in the pure form of the acetate (m. p. 146°–147°), from the fifth fraction, b. p. 198–202° shown in Table 1.

The author has, therefore, studied the action of Japanese acid earth on a mixture of methyl alcohol and aniline, and has observed that the condensation of these substances, and the contact isomerisation of the condensed substance have occurred simultaneously.

The catalyst used in the experiment was obtained from crude Japanese acid earth, washed with water, and dried, which gave on analysis the following chemical compositions:

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Moisture dried at 110°	Ignition loss	Total
61.67%	12.28%	1.87%	0.16%	3.44%	15.66%	4.64%	99.72%

The earth was filled in a glass tube of 1 metre in length, and 2 cm. in diameter, heated to 350°, and a mixture of methyl alcohol and aniline was passed on it.

p-Toluidine.

From the reaction product of 22 grams methyl alcohol and 55 grams aniline, 50.4 grams of an oily substance and 17.5 grams of water were obtained, and the oily substance was divided into the following 7 fractions by fractional distillation, and the density of each fraction was determined and

the melting-point of the acetates obtained by treating the oil with acetic anhydride was also determined.

TABLE 2.

No.	Fraction	Yield (gr.)	Sp. gr. (d_{20}^{20})	M.p. of acetate	
				1	2
1	to 180°	2.9	—	—	—
2	189–193°	7.4	0.9977	120–121°	about 125°
3	193–197°	13.4	0.9947	139–143°	140–143°
4	197–200°	11.2	0.9904	140–143°	140–143°
5	200–205°	5.0	0.9858	140–143°	103–106°
6	205–207°	3.3	0.9814	114–116.5°	105–106°
7	Residue	2.8	—	—	—

In the table, acetate 1 and acetate 2 respectively show the melting-point of the first and second crops of crystals, separated from solutions.

The third and fourth fractions which composed the main part of the reaction product, from the melting-point of the acetates, were noticed to be composed principally of p-toluidine. Higher fractions boiling above 200°, should contain, by refering to their physical and chemical properties, some homologous substances of aniline, and other secondary and tertiary amines.

Methylaniline.

When, however, a mixture of 50 grams methyl alcohol and 120 grams aniline was passed in an interval of 8 hours on the catalyst heated to 250°, 106 grams of an oily reaction product and 26 grams of water were obtained, and the reaction product was divided into the following 6 fractions by fractional distillation.

TABLE 3.

No.	Fraction	Yield (gr.)	Sp. gr. (d_{20}^{20})
1	75–100°	—	—
2	180–187°	21.7	1.0051
3	187–190°	25.8	1.0028
4	190–197°	37.8	0.9949
5	197–200°	6.1	0.9852
6	Residue	—	—

The fourth fraction, b. p. 190–197°, was confirmed as consisting of methylaniline, since its density and the melting-point of the acetate agree with those of methylaniline.

To our interest, when an equimolecular mixture of methyl alcohol and aniline was passed on Japanese acid earth heated at 250°, methylaniline was obtained as a main reaction product, while the same mixture by the contact action of the same catalyst at higher temperature such as 350°, was noticed to be transformed into p-toluidine which was usually regarded as resulting from methylaniline by Hofmann reaction, and such transformation could not be observed to occur previously when alumina was used as the catalyst. In order to test whether the Hofmann reaction would occur actually by passing a mixture of aniline and methyl alcohol on the heated acid earth, 50 grams of the fourth fraction, b.p. 190–197°, shown in Table 3, which was composed of methylaniline, were passed again on the catalyst heated at 350°, and the reaction product was divided into the following 7 fractions, and the density of each fraction and the melting-point of the acetate, were studied, and also the primary amine-content by means of benzene sulphonylchloride.

TABLE 4.

No.	Fraction	Yield (gr.)	d_{20}^{20}	M.p. of acetate			RNH_2 %	N %
				1	2	3		
1	185–187°	5.5	0.9800	113–116°	96°	96–98°	—	9.50
2	187–190°	9.0	1.0050	119–122°	107–111°	96–98°	88.94	9.44
3	190–193°	2.3	1.0050	117–119°	96–98°	83–86°	96.04	9.21
4	193–198°	7.2	1.0023	119–121°	98–100°	70–72°	92.94	9.24
5	198–202°	10.4	1.0000	121.5–124°	101–103°	99–101°	86.90	9.56
6	202–208°	3.0	0.9951	126–129°	115–118°	83–86°	87.30	9.48
7	about 208°	—	—	128–131°	120–122°	91–94.5°	—	—
	p-toluidine	—	—	—	—	—	—	9.39
	aniline	—	—	—	—	—	—	10.37

The fractions 2, 3, 4, 5, and 6 were confirmed from their physical and chemical properties, as consisting mainly of p-toluidine, and the writer has succeeded in obtaining it in pure state as an acetate (m.p. 147°; N=9.40%) from the fifth fraction by fractional crystallisation. And analogously, the first and last two fractions were confirmed to contain chiefly of aniline and dimethylaniline respectively.

The writer, thus, has proved experimentally the assumption that methylaniline formed by the direct condensation of methyl alcohol and aniline, was transformed into p-toluidine by contact action of the acid

earth at higher temperature, with the formation of aniline and dimethylaniline.

The mechanism of the reaction for the formation of p-toluidine and dimethylaniline by the interaction of methyl alcohol and aniline in presence of the catalyst will be explained by the following scheme :

$$CH_3OH + C_6H_5NH_2 \longrightarrow C_6H_5NHCH_3 \longrightarrow CH_3C_6H_4NH_2 \cdots\cdots(1)$$

$$C_6H_5NH(CH_3) \longrightarrow C_6H_5NH_2 + C_6H_3N(CH_3)_2 \cdots\cdots(2)$$

Dimethylaniline which occurs in the reaction product of methylaniline by the contact action, and of aniline and methyl alcohol in presence of the acid earth, should behave in an analogous way yielding methyl-p-toluidine, methylaniline and xylidines, with methylaniline, by the contact action of the catalyst at high temperature.

70 grams of dimethylaniline which contains 4.7% of methylaniline as an impurity, were passed on the catalyst heated at 350°, and a reaction product composed of 35% of primary amines, 28% of secondary amines, and 37% of tertiary amines, was obtained which was divided into 9 fractions by distillation. Of each fraction, the density, content of primary amines, melting point of acetates and content of nitrogen were determined, and the results are shown in the following table.

TABLE 5.

No.	Fraction	Yield (gr.)	d_{20}^{20}	R—NH_2 %	M.p. of acetate		Content of N %	
					1	2	1	2
1	140-195°	1.0	—	—	—	—	—	—
2	195-198°	7.0	0.9765	42.70	—	122-124°	9.05	—
3	198-201°	10.0	0.9749	40.98	130-131°	125-128°	9.14	—
4	201-203°	11.0	0.9746	39.42	138-141°	124-127°	9.29	8.77
5	203-205°	17.0	0.9734	37.84	134-135°	130-133°	9.29	8.11
6	205-207°	12.0	0.9704	31.43	139-142°	129-130°	9.16	8.27
7	208-210°	4.0	0.9686	27.26	138-141.5°	129-134°	9.28	7.90
8	211-215°	2.0	0.9686	—	94-96°	—	7.59	—
9	215-225°	2.0	—	—	103-105°	—	—	—

Content of nitrogen in the acetate of C_7H_9N 9.39%

" " " " " $C_8H_{11}N$ 8.58%

As will be seen in the experimental results shown in the table above, p-toluidine and methyl-p-toluidine composed chiefly the reaction product, and the chemical reactions for the formation of these compounds from dimethylaniline will be shown in an analogous manner to the transformation of methylaniline into p-toluidine and other amines.

The migration of the methyl radical in both the methyl- and dimethyl-anilines, from the nitrogen atom to the carbon atom, forming p-toluidine and methyl-p-toluidine, was effected by the contact action of Japanese acid earth, and such chemical change was found with silica but not with alumina, the both were considered to be principal constituents of Japanese acid earth.

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