$$\int_0^\Theta \frac{dN}{d\Theta}\, d\Theta = \int_0^\Theta k_1 x d\Theta \qquad (6)$$

Transform Equation 4 to the form

$$\frac{(y+\beta)y_\infty}{(y_\infty - y)\beta} = e^{(\beta + y_\infty)k_2\Theta} \qquad (7)$$

in which the constants β, y_∞ and k_2 are all known, and which will be simplified by the substitution of the numerical values. Then solve (7) for y and substitute for y, $x_0 + y_0 + x$, giving the relation between x and Θ, which when substituted in Equations 5 and 6 will give Equation 6 with two variables only, N and Θ.

Equation 6, simplified by the introduction of numerical values, may now be integrated between any two limits of Θ, the amount of nitrate decomposed being most readily calculated by evaluating the integral by the graphical method.

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RECEIVED APRIL 26, 1924
PUBLISHED AUGUST 5, 1924

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

CATALYTIC ALKYLATION OF ANILINE

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RECEIVED JULY 25, 1922 PUBLISHED AUGUST 5, 1924

Introduction

The efficiency of the high grade silica gel prepared in this Laboratory as a catalyst for the amination of alcohols[1] made desirable a study of its effectiveness as a catalyst in the N-alkylation of aniline. Mailhe and de Godon have shown that thoria[2] and zirconia are effective in methylating aniline, and that alumina[3] is exceptionally suitable for methylating aniline, *o*-, *m*- and *p*-toluidine.

The present investigation has for its purpose the quantitative study of the extent of N-alkylation of aniline by methyl, ethyl, *n*-propyl and *n*-butyl alcohols with silica gel as catalyst over the temperature range 300–500°.

Apparatus

The apparatus and method of operating were the same as used for the study of the alkylation of ammonia.[1]

Reactants

The aniline was fractioned through a 60cm. Vigreaux column from a commercial C. P. sample, and the portion boiling constantly within 0.2° taken.

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[1] Articles to appear in *J. Phys. Chem.*

[2] Mailhe and de Godon, *Compt. rend.*, **166**, 467 (1918).

[3] *Ibid.*, **166**, 564 (1918).

Methyl and ethyl alcohols were dried by 2 treatments with lime in the usual manner, while *n*-propyl and *n*-butyl alcohols were freed from the small amounts of water present by fractionating the constant-boiling water-alcohol mixture. All the alcohols were fractionated through a 90cm. Vigreaux column, the portions used being of constant boiling point.

The reactants for the individual runs were mixed in the proper proportions by weight.

Catalyst

The catalyst in every run was a fresh 75g. sample of special silica gel prepared as described in a previous article[1] in fragments of 2 to 4 mm. diameter packed in a 50cc. section of the catalytic tube. Activation was effected by slowly heating to 400° in a current of air.

Reaction Products

The condensate consisted of a water layer and a main product layer of a solution of N-alkylated aniline in unchanged reactants. The water was present as a suspension of small droplets; with the lower alcohols especially, the condensate was homogeneous when the conversion was small.

In addition to the liquid condensate, permanent gases, increasing in amount with increasing temperature, were formed. The greater percentage of the gas mixture was C_nH_{2n} hydrocarbons determined by absorption in fuming sulfuric acid. The residue was considered as hydrogen due to the dehydrogenating tendency of silica gel towards the excess of alcohol present. Only negligible amounts of ammonia were detected.

Analysis

All the methods for the analysis of a mixture of aniline with its mono- and disubstituted N-alkylation products most practicable from the standpoints of speed and accuracy depend upon acetylation as the means of estimating the monosubstituted derivative. This necessitates removal of water and alcohol from the analysis sample. Fractional distillation was the only method found suitable. Consequently the reaction product from about 50 g. of aniline was fractionated through a 90cm. Vigreaux column. To prevent violent bumping following upon the separation of the aniline-water mixture after removal of the alcohol, sufficient propyl alcohol was added to the sample, when necessary, to give a constant-boiling alcohol-water mixture that distills smoothly. After removal of the low-boiling components, the aniline mixture was refluxed up to within 7.5 cm. of the outlet tube for several minutes to ensure removal of the last traces of alcohol and water. Such a fractionation entailed the loss of about 0.1% of the aniline present. The aniline passing over was determined in the distillate.

The anhydrous alcohol-free residue was divided into aliquots for analysis.[4] Aniline, after diazotization, was titrated with standard R-salt solution, using H-acid as indicator; monosubstituted aniline and aniline were determined together by acetylation at 76° with known amounts of analyzed acetic anhydride, followed by titration of the hydrolyzed product of the acetic acid against 0.1 *N* sodium hydroxide solution, using phenolphthalein as indicator. The difference between the acetylation and R-salt values gave monosubstituted aniline, and the difference between the sum of free aniline and monosubstituted aniline and the total gave the disubstituted aniline.

Experimental Part

Each alcohol was mixed with aniline in 2 proportions: 1.05 and 2.05 molecules of alcohol to 1 of aniline. With each of these mixtures a preliminary

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[4] The method and necessary R-salt and H-salt were courteously supplied by E. I. du Pont de Nemours and Co.

run was made taking samples at higher and higher temperatures. The unchanged aniline was determined in these and the results plotted on a curve. From this the temperature of maximum conversion was estimated and the furnace regulated to this optimum temperature at which the desired mixture was run through for about four hours. The large sample thus obtained was used for the complete analysis.

In the case of ethyl alcohol, which was the first one tried, the preliminary and final runs were on subsequent days, but with the other alcohols both were on the same day without letting the furnace cool down. At the start of each run, the mixture was passed through for half an hour to insure constant conditions.

Table I gives the results of the final runs and shows the percentages of mono- and di-alkyl anilines obtained, as well as of unchanged aniline, all figured on the amount of aniline admitted to the furnace. Each run was made at the optimum temperature for that mixture as determined above.

TABLE I

PERCENTAGE OF ANILINE REMAINING AND OF ALKYL ANILINES FORMED BY THE PASSAGE OF ANILINE AND ALCOHOLS OVER SILICA GEL

Run	Temp. °C.	Alc.	Ratio	$PhNH_2$ %	PhNHR %	$PhNR_2$ %
1	365	Methyl	1.05	62.2	25.9	10.9
2	375	Methyl	2.05	63.2	19.0	12.8
3	370	Methyl	2.05	58.0	22.7	13.7
4	362	Methyl	2.05	50.3	19.7	24.9
5	385	Ethyl	1.05	58.5	33.4	6.8
6	385	Ethyl	2.05	40.0	46.6	13.3
7	385	Propyl	1.05	61.2	28.0	6.0
8	385	Propyl	2.05	45.2	37.1	12.0
9	385	Butyl	1.05	68.0	24.1	7.9
10	400	Butyl	2.05	59.7	26.5	8.5

In addition to reacting with the aniline the alcohol is dehydrated and also dehydrogenated. To determine the extent of these side reactions samples of the gases evolved were taken at the middle of the long runs

TABLE II

PERCENTAGES OF ALCOHOLS DEHYDRATED, DEHYDROGENATED AND USED IN ALKYLATION OF ANILINE

Run	Temp. °C.	Alc.	Gas Cc. per min.	C_nH_{2n} %	H_2 %	Used %
1	365	Methyl	1.16	0.06 (?)	1.84	45.4
2	370	Methyl	2.33	0.10 (?)	1.94	21.7
5	385	Ethyl	4.81	3.90	4.92	44.8
6	385	Ethyl	10.69	4.61	5.56	35.7
7	385	Propyl	12.50	16.18	7.68	38.1
8	385	Propyl	19.19	15.12	5.14	29.8
9	385	Butyl	9.41	10.53	4.63	38.0
10	400	Butyl	22.30	16.53	6.27	21.2

given in Table I. The unsaturated hydrocarbon was determined by absorption in fuming sulfuric acid. The small absorption found in the case of methyl alcohol may have been due to methyl ether. In all cases the residual gas was practically pure hydrogen. The results are given in Table II and show the fate of the alcohols. The numbers of the runs refer to those in Table I.

Discussion

Silica gel has proved itself to be an efficient catalyst for the alkylation of aniline as well as of ammonia but its effectiveness falls off rapidly in the first hour or so of use and then declines slowly. Thus with samples taken in the course of Run 3, Table I, the times and percentages were: 1 hour, 62.0%; 4 hours, 45.3%; 5.75 hours, 41.1%; 7.25 hours, 35.5%; the product collected over the whole period showed 42.0%.

This falling off in the activity of the catalyst was more marked with methyl alcohol than with the others. If the catalyst is never raised to a high temperature in the presence of the reactants, the decrease in reactivity is less pronounced, as was shown by samples taken during Run 4, Table I. In this case the temperature had never been raised above 370° and the alkylation was 50.4% after 1.25 hours and 50.7% after 3.5 hours. The relative amount of dimethylaniline was greater than with the weakened catalyst.

Since it appears from Table II that considerable amounts of the aldehydes are produced and since these combine readily with aniline to form bodies which polymerize easily, the fouling of the catalyst is to be expected.

Summary

The alkylation of aniline by passing its vapors with those of methyl, ethyl, *n*-propyl and *n*-butyl alcohol over silica gel has been studied quantitatively. The percentages of alkyl anilines found with ratios of mono-alkyl to di-alkyl at approximately optimum temperatures are as follows. Series 1 for reactants of molal composition: $C_6H_5NH_2$:ROH = 1:1.05; and Series 2 for $C_6H_5NH_2$:ROH = 1:2.05.

Methyl (1) 37.8%, 5:2, at 365°, (2) 52.0%, 5:3, at 370°; ethyl (1) 41.5%, 5:1, at 385°, (2) 60.0%, 7:2, at 385°; *n*-propyl (1) 38.8%, 14:3, at 385°, (2) 54.8%, 3:1, at 385°; *n*-butyl (1) 32.0%, 31:10, at 385°, (2) 40.3%, 33:10, at 400°.

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