

SIDE-CHAIN CHLORINATION OF TOLUENE.

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ABSTRACT

When chlorine is bubbled into boiling toluene the amount of chlorine used may be gauged by the temperature (thermometer in liquid). This method is more convenient than previous methods such as the increase in weight of the reaction mixture, loss of weight of the chlorine cylinder, or increase in specific gravity. The boiling point curve of toluene-benzyl chloride mixtures is plotted. In the chlorinations described, when the temperature has reached 145°C., the composition is 21% toluene, 70% benzyl chloride and 9% benzal chloride. At 155°C. the composition is 12% toluene, 70% benzyl chloride and 13% benzal chloride. These values were obtained by fractionally distilling the products and determining the weight and refractive index of each fraction. The relation between refractive index and composition of benzyl chloride-benzal chloride mixtures is linear. The following refractive indices were determined with an Abbé refractometer: toluene $n_D^{20} = 1.4971$, benzyl chloride $n_D^{20} = 1.5391$ and benzal chloride $n_D^{20} = 1.5502$.

In these studies on the chlorination of toluene we have investigated certain modifications of technic which have wide application to chlorinations in general. A new method for the control of the amount of chlorine used has been devised and, as a suitable method of analyzing the product of chlorination, it has been found satisfactory to fractionate the product and determine the composition of each fraction from its refractive index.

Various methods have been proposed for controlling the amount of chlorine used in chlorinations. The earliest method, before the advent of cheap liquid chlorine, was to bubble chlorine, prepared usually from pyrolusite and hydrochloric acid, into the reaction flask until a definite gain in weight had been attained. The gain in weight does not correspond exactly with the amount of chlorine used in the case of the chlorination of toluene because weight is lost in the evolution of hydrogen chloride. The true weight of chlorine may be calculated from the increase in weight by the following formula (after a correction has been made for toluene vapour carried over to the absorbers by the hydrogen chloride):

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$$\text{Wt. Cl}_2 = \frac{\text{Increase in weight}}{1 - \frac{\text{Mol. wt. HCl}}{\text{Mol. wt. Cl}_2}} = 2.058 \times \text{Increase in weight.}$$

With cheap liquid chlorine available, it is possible to determine the amount used from the loss of weight of the chlorine cylinder. These tanks are usually heavy, making accurate weighing difficult, and the cylinder must be on the scale at the time of chlorination, which is often inconvenient.

To avoid these difficulties, it is stated¹ that in the manufacture of benzyl chloride dry chlorine is passed into boiling toluene until it has attained the requisite specific gravity.

Perhaps the simplest check on the amount of chlorine is that employed by the senior author some years ago in the manufacture of benzyl chloride, namely the temperature of the boiling reaction mixture. During the introduction of chlorine the boiling point of the liquid gradually rises and the chlorine is shut off when the temperature has reached the requisite point.

To obtain a rough idea of the composition of the reaction mixture when the chlorination is carried to certain temperatures (thermometer in liquid), the boiling points of various mixtures of toluene and benzyl chloride were determined in an apparatus somewhat similar to that used in the chlorinations, but holding only 100 c.c. of liquid. One glass bead was added to cut down superheating. The results are given in Fig. I. It is to be expected that this curve will give only an approximation to the composition of the product of chlorination because of the following factors: (1) production of benzal chloride, (2) superheating, (3) presence of HCl and Cl₂. To test the effect of HCl, dry HCl was bubbled into the boiling-point apparatus containing a sample (20% C₆H₅CH₃ and 80% C₆H₅CH₂Cl). The boiling point was reduced slightly. Whether this depression was due to the cooling effect of the gas,

¹Cohen, "Theoretical Organic Chemistry," Macmillan and Co., London, 1928, p. 406. Kyrides, U. S. Patent, 1,345,373.

to cutting down superheating, or to solution was not determined.

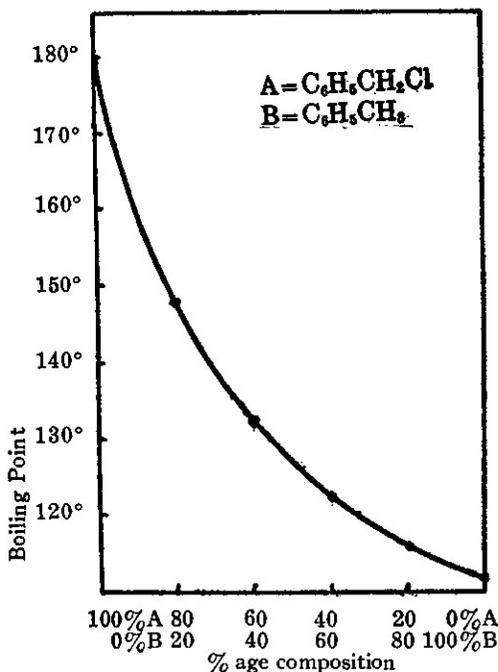


Fig. I.

nation. This was done by boiling the toluene in the apparatus before the introduction of chlorine until all the water had distilled off through the uncooled condenser. Under these conditions—all glass apparatus and absence of water—the product was practically colorless; otherwise it is often nearly black with a pronounced fluorescence. The amount of toluene condensed in the absorbers was measured at the end of the chlorination and deducted from the weight of toluene used.

²The efficacy of light as a catalyst has been questioned by Book and Eggert (*Z. Elektrochem.* **29**, 521 (1923)) but Bergel (*Ber.* **59B**, 153 (1926)) found that light does accelerate the side-chain chlorination of toluene. We did not study this point in detail. In our experiments we noticed that no chlorine passed on to the absorbers and the product contained no detectable amount of the chlorotoluenes.

From this curve two values, 145° and 155°, were chosen for checking by chlorinations on a moderate scale. Dry chlorine from a tank was bubbled into boiling toluene in a Pyrex flask fitted with a reflux condenser and containing a thermometer with the bulb immersed in the liquid. All glass connections were used. The apparatus was illuminated by a 100 watt, nitrogen-filled bulb². It was found essential that every trace of water be removed before chlori-

	145°	155°
Wt. C ₈ H ₈ CH ₂ Cl (crude)	578.6 gms.	583.4 gms.
Wt. C ₈ H ₈ CH ₃ (corrected)	444.5 gms.	434.3 gms.
Increase in weight	134.1 gms.	149.1 gms.
Wt. Cl, used in chlorination	276.0 gms.	307.0 gms.
(Calc. from increase in wt.)		

In order to analyze these products, they were fractionated in a partial vacuum ($p = 10$ cm.).

The distilling flask was heated by a metal bath resting on an electric hot-plate, the temperature of which was controlled by a rheostat. To prevent bumping one glass bead was added. During the distillation this bead danced up and down against the flask, giving off a stream of bubbles each time it touched the bottom. This method of cutting down superheating and inducing even distillation has been found to be effective in distillations generally.

Fitting into the distilling flask by a ground-glass joint was a fractionating column, 90 cm. long and 8 mm. internal diameter. In order to bring about more efficient interchange between the descending liquid and the ascending vapour, an even spiral was pressed into the tube. This column was wound with resistance wire and well insulated with asbestos paper. The temperature was regulated by a rheostat. The upper end of the fractionating column was cooled with water, the height of which was adjustable. Above the cooler, the column was bent through 180° and a condenser attached to the downward portion. This led to a receiver from which samples could be drawn without destroying the vacuum.

Three hundred grams of the sample were placed in the distilling flask. The hot-plate was heated until the reflux from the fractionating column was dripping at just a countable rate. The fractionating column was then heated until refluxing was visible in the water cooler. The level of the water was then lowered until the ratio of the drops in the reflux to those delivered to the receiver was about 10 to 1. When all the toluene had distilled over, the rate of distillation diminished and more heat had to be applied to the distilling flask and to the fractionating column to reestablish the former rate.

The course of distillation was followed by removing the distillate at intervals, weighing, and determining the refractive index by an Abbé refractometer. This refractometer was loaned to us by Mr. C. C. Forward, Dominion Government Analyst. We take this opportunity of thanking him for his kindness.

In preliminary experiments in distilling chlorinated toluene (c. p. toluene being used), the following refractive indices were measured with this instrument:

	n_D^{20}
Toluene	1.4971
Benzyl chloride	1.5391
Benzal chloride	1.5502

From these values it is possible to calculate the composition of each sample, if one assumes that the relation between percentage composition and refractive index is linear. In the case of the fractions intermediate between pure toluene and pure benzyl chloride, this assumption was made, since these fractions were so small that no significant error is introduced. The fractions between pure benzyl chloride and pure benzal chloride were larger, and it was thought best to test our assumption in this case. The linear relation between percentage composition and refractive index was found to hold. The weight of one constituent in a sample (x) is then calculated from the following formula:

$$x = \frac{ab}{c}$$

where

a = wt. of fraction, and,

in the case of $C_6H_5CH_3$ and $C_6H_5CH_2Cl$ mixtures,

b = n_D of sample — n_D of $C_6H_5CH_3$

c = n_D of $C_6H_5CH_2Cl$ — n_D of $C_6H_5CH_3$ = 0.0420

and, in the case of $C_6H_5CH_2Cl$ and $C_6H_5CHCl_2$ mixtures,

b = n_D of sample — n_D of $C_6H_5CH_2Cl$

c = n_D of $C_6H_5CHCl_2$ — n_D of $C_6H_5CH_2Cl$ = 0.0111.

Using the technic described the following results were obtained:

Chlorination of Toluene to 145°C.

Fraction	Wt. gms.	n_D^{20}	Wt. $C_6H_5CH_3$ gms.	Wt. $C_6H_4CH_2Cl$ gms.	Wt. $C_6H_3CHCl_2$ gms.
Loss in fraction.	4.89		4.89		
1	4.18	1.4971	4.18		
2	1.87	1.4971	1.87		
3	14.56	1.4971	14.56		
4	4.84	1.4971	4.84		
5	19.20	1.4971	19.20		
6	3.09	1.4971	3.09		
7	4.53	1.4971	4.53		
8	4.26	1.4971	4.26		
9	1.15	1.4971	1.15		
10	0.43	1.5111		0.14	
11	1.13	1.5339	0.01	1.17	
12	1.73	1.5391		1.73	
13	7.02	1.5391		7.02	
14	46.22	1.5391		46.22	
15	5.81	1.5391		5.81	
16	45.93	1.5391		45.93	
17	6.85	1.5391		6.85	
18	4.78	1.5391		4.78	
19	7.78	1.5391		7.78	
20	7.29	1.5391		7.29	
21	7.24	1.5391		7.24	
22	8.17	1.5393		8.02	0.15
23	7.69	1.5393		7.55	0.14
24	9.09	1.5394		8.84	0.25
25	9.21	1.5394		8.96	0.25
26	8.67	1.5397		8.20	0.47
27	9.95	1.5398		9.32	0.63
28	8.79	1.5401		8.00	0.79
29	8.49	1.5418		6.42	2.07
30	9.72	1.5462		3.50	6.22
31	7.79	1.5502			7.79
Residue	7.6				7.6
			62.87	210.77	26.36

Chlorination of Toluene to 155°C.

Fraction	Wt. gms.	n_D^{20}	Wt. $C_6H_5CH_3$ gms.	Wt. $C_6H_5CH_2Cl$ gms.	Wt. $C_6H_5CHCl_2$ gms.
Loss in fraction.	4.10		4.10		
1	1.58	1.4971	1.58		
2	2.11	1.4971	2.11		
3	28.49	1.4971	28.49		
4	0.74	1.4971	0.74		
5	0.65	1.5351	0.06	0.59	
6	1.93	1.5383	0.04	1.89	
7	1.90	1.5391		1.90	
8	3.73	1.5391		3.73	
9	50.28	1.5391		50.28	
10	7.12	1.5391		7.12	
11	49.83	1.5391		49.83	
12	7.87	1.5391		7.87	
13	45.82	1.5391		45.82	
14	8.46	1.5391		8.46	
15	8.75	1.5393		8.59	0.16
16	8.05	1.5394		7.83	0.22
17	7.76	1.5397		7.34	0.42
18	8.63	1.5401		7.85	0.78
19	7.50	1.5409		6.28	1.22
20	8.41	1.5428		5.61	2.80
21	7.07	1.5458		2.80	4.27
22	7.43	1.5497		0.33	7.10
23	6.20	1.5504			6.20
24	7.59	1.5504			7.59
Residue	8.0				8.0
			37.12	224.12	38.76

We assume that the weight of material unaccounted for by the summed weights of the fractions is toluene, the most volatile constituent. The residue is assumed to be benzal chloride, though it must have contained some benzotrichloride. These fractions are so small that no significant error is introduced in making these approximations.

The accompanying graphs, Figs. II and III, summarize the results of these analyses.

In the case of the chlorination to 145°, the combined fractions, 11 to 28 inclusive, are considered to be the yield of benzyl chloride; in the case of the chlorination to 155°, the fractions 5 to 18 inclusive. The yield of benzyl chloride in the 145°

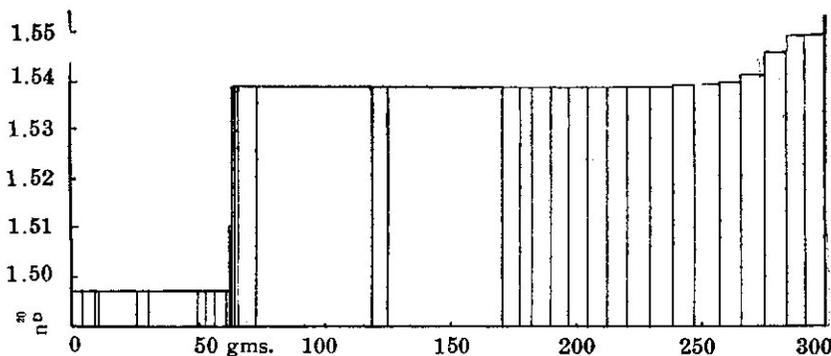


Fig. II. Fractional Distillation Graph. Chlorination to 145°C.

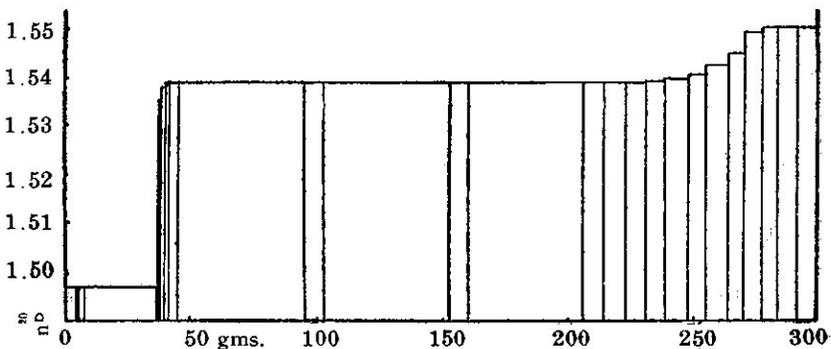


Fig. III. Fractional Distillation Graph. Chlorination to 155°C.

chlorination is calculated to be 79% and, in the 155° chlorination, 74%, based on the chlorine calculated from the increase in weight. These percentage yields are significant only in the comparison of the two runs which were as nearly identical as possible in all respects save that of the final boiling temperatures. If the ratio of chlorine to toluene vapour be increased, of course the yield of benzyl chloride will be decreased due to increased production of benzal chloride. Therefore for maximum production of benzyl chloride, it is preferable to conduct the experiment so that the benzyl chloride can be removed from the chlorination chamber as soon as formed.

In order to check the analyses of the chlorinated mixtures, the following calculations are made:

	145°	155°
Wt. $C_6H_5CH_2$ (in 300 gm. sample)	62.87 gms.	37.12 gms.
Wt. $C_6H_5CH_2Cl$ (in 300 gm. sample)	210.77 gms.	224.12 gms.
Wt. $C_6H_5CHCl_2$ (in 300 gm. sample)	26.36 gms.	33.76 gms.
$C_6H_5CH_2$	21%	12%
$C_6H_5CH_2Cl$	70%	75%
$C_6H_5CHCl_2$	9%	13%
Total wt. $C_6H_5CH_2Cl$ in whole batch	406.5 gms.	435.8 gms.
Total wt. $C_6H_5CHCl_2$ in whole batch	50.8 gms.	75.4 gms.
Cl in total $C_6H_5CH_2Cl$	113.9 gms.	122.1 gms.
Cl in total $C_6H_5CHCl_2$	22.4 gms.	33.2 gms.
Total Cl in product	136.3 gms.	155.3 gms.
Wt. Cl ₂ used in chlorination (Calc. from Cl in fractionated product)	272.6 gms.	310.6 gms.

The weight of chlorine calculated from the chlorine found in the product agrees satisfactorily with that calculated from the increase in weight, namely 276.0 gms. and 307.0 gms. respectively.

In order to determine how accurate a guide the graph on p. 206 is, the composition actually resulting from each of these chlorinations is compared with that predicted by the curve. Assuming that benzal chloride has approximately the same effect in raising the temperature of boiling as has benzyl chloride, the chlorination boiling at 145° contained 79% combined benzyl chloride and benzal chloride, while that boiling at 155° contained 88%. From the curve, it is predicted that at 145° the reaction mixture should contain 77% $C_6H_5CH_2Cl$ and, at 155°, 86% $C_6H_5CH_2Cl$, a difference of 2% in each case.