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**Chemistry.** — "*The bromination of toluene*". By Prof. A. F. HOLLEMAN and Dr. F. H. VAN DER LAAN.

(Communicated in the meeting of October 28, 1905).

In the reaction between toluene and bromine we have a striking example of the influence exerted on the nature of the product of reaction by experimental conditions. About this the following is known:

1. *Influence of temperature.* In the dark and at a low temperature there is formed a mixture of bromotoluenes; on the other hand benzyl bromide is formed at the boiling point of toluene.

2. *Influence of light.* At a low temperature benzyl bromide is exclusively formed; the same takes place at the boiling temperature.

3. *Influence of catalyzers.* Through their action the bromination takes place exclusively in the core, even in full daylight and at an elevated temperature.

If we make a closer study of the papers which have appeared as to this reaction it strikes us, as in so many other cases, that the virtually known suffers from much uncertainty owing to an insufficient observance of the quantitative proportions. When, for instance, SCHRAMM states that on bromination in sunlight benzyl bromide is exclusively formed, a doubt arises as to the correctness of this view, as the only proof he adduces is that the boiling point of his product lies at  $195^{\circ}$ — $205^{\circ}$ ; his boiling point limits are therefore so wide apart that they suggest rather the presence than the total absence of isomers. As regards the bromotoluenes formed in the reaction, it was known that these are *ortho*- and *para*-bromotoluene. But the question, in what proportion those are formed under the influence of the three above factors, has only been made the subject of greatly varying conjectures and rough estimates. Nothing was known also as to the nature of the products of reaction which are formed in the dark at temperatures between the ordinary and the boiling point of toluene ( $110^{\circ}$ ).

There was, therefore, every reason to again study this interesting reaction and to try to solve the following questions:

In how far is the composition of the reaction-mixture dependent 1. on the temperature; 2. on the action of light; 3. on the presence of catalyzers.

In my laboratory, first at Groningen, afterwards at Amsterdam, Dr. VAN DER LAAN has made a contribution to the resolution of these questions by means of a careful experimental research; he commenced

by making sure of the absolute purity of his toluene and bromine by means of special methods of purifying; for details his dissertation and his paper in the "Recueil" (next appearing) should be consulted.

As the composition of the reaction mixture consisting of *ortho*-*parabromotoluene* and benzyl bromide had to be determined, but as no method for this was available, it was necessary to work out a suitable process; in order to do this it was necessary to first possess the three said substances in a chemically pure state so as to be able to make artificial mixtures for testing the analytical methods.

The preparation of *parabromotoluene* and of benzyl chloride presented no difficulties. The first substance was obtained from *paratoluidine* by diazotation, and as this is a solid it could be readily freed from any adhering traces of its isomers by recrystallisation from ligroin and thus yield a *parabromotoluene* also free from its isomers. Benzyl bromide was made from benzyl alcohol and hydrobromic acid. On the other hand the preparation of pure *orthobromotoluene* was not so easy. This was also prepared from the corresponding *toluidine*, but the difficulty was to obtain the latter in a pure condition. This was overcome in the manner previously communicated (These Proc. VII p. 395).

In the actual investigation a large excess of toluene was always taken (8 mols. toluene to 1 mol. of bromine) so as to avoid for certain the formation of higher substitution products. Besides the three above mentioned substances the reaction mixture contains, therefore, a large quantity of toluene: hydrogen bromide is also present and often also a small quantity of free bromine, especially in the reactions which were executed in the dark. This reaction product was now analysed quantitatively as follows: A slow current of air removed almost quantitatively the hydrogen bromide, which was absorbed in water and titrated: the quantity thus found is equivalent to and serves as a measure for the brominated products. In order to free the liquid from any free bromine, and to determine the amount of the same, it is poured into a solution of potassium iodide and the liberated iodine titrated with thiosulphate. The liquid is now washed with water, dried, and the toluene is distilled off in an airbath heated by boiling amyl alcohol. On taking the sp. gr. of the distilled toluene it appeared that this had not carried over any brominated products to speak of.

After these operations the liquid now only consisted of the bromotoluenes and benzyl bromide besides also a small quantity of toluene. In this mixture the benzyl bromide can be estimated by means of alcoholic silver nitrate which yields silver bromide quantitatively.

In order to determine in what proportion *ortho*- and *para*bromotoluene are present, it was necessary to remove the benzyl bromide from the mixture. This was done by bringing it into contact with dimethylaniline. There is then formed quantitatively an ammonium bromide, the bulk of which is deposited as a crystalline mass. By washing the residual liquid with very dilute nitric acid the excess of dimethyl aniline and the still dissolved ammonium bromide are removed so that we obtain finally a liquid consisting merely of the bromotoluenes. When dried and distilled in vacuo it is ready for the determination of the isomers. This was done by determining the solidifying point of this purified liquid. By means of the solidifying point curve previously constructed by Dr. VAN DER LAAN, the composition of the mixture could be at once ascertained from the said point. By the analysis of a series of made up mixtures he was satisfied that this method of analysis gives results accurate within about 1 percent and is therefore sufficiently accurate for the purpose intended.

With the aid of the method described Dr. VAN DER LAAN obtained the following results.

1. *Influence of temperature.* The flask containing the mixture of bromine and toluene was kept carefully in the dark. Observations were made at 25°, 50°, 75° and 100°. At 25° the reaction took place very slowly and even after a week the bromine had not altogether disappeared. At 50° this was already the case in 3 days. The subjoined table contains the analyses of the reaction mixtures. The figures given are each the mean of 3 or 4 concordant determinations.

From this it appears that in the dark a regular increase of the benzyl bromide content takes place with a rising temperature. From a graphical extrapolation it appears that benzyl bromide is no longer formed below 17°, but, on the other hand, above 83° it is the sole reaction product. These conclusions, however, must still be confirmed experimentally. The proportion in which *ortho*- and *para*bromotoluene are formed also alters somewhat in favour of the first-named isomer. A determination of the sp. gr. of the mixture showed that this does not contain any of the higher brominated substances. The mixture obtained at 25° had a sp. gr. of 1.3598 at 64°.6 whilst a mixture of the two isomers in the same proportion shows a sp. gr. of 1.3598 at 64°.

2. *Influence of light.* As already observed, SCHRAMM claims to have obtained exclusively benzylbromide when brominating at low temperature in full sunlight, although his experimental data create

T A B L E I.

Temp.	Composition of the brominating product			Composition of the mixture	
	ortho bromotoluene	para	benzyl bromide	ortho + para bromotoluene	
25	35.5	53.9	10.6	39.7	60.3
50	23.5	32.8	43.7	41.8	58.2
75	6.2	7.5	86.3	45.3	54.7
100	—	—	100	—	—

some doubt about this. In diffuse daylight *ortho*- and *para*-bromotoluene are also formed according to him; ERDMANN, on the other hand, stated that benzylbromide is the sole product. The observations of Dr. VAN DER LAAN confirm those of ERDMANN. In diffuse daylight the bromination proceeds very rapidly at 25°; in about 10 minutes all the bromine has disappeared. The analysis of the product gave 99% of benzylbromide. From this it follows that pure benzylbromide can be readily prepared in this manner. BEILSTEIN, who attempted this previously, arrived at the opposite result. This, however, was caused by the fact that he exposed to the light a mixture of bromine and toluene in equivalent proportions at the temperature of boiling toluene. Operating in this manner we obtain indeed a product without a constant boiling point which on fractionation appears to contain products boiling at higher temperatures. If, however, working in the light and at 100°, only one mol. of bromine is used for 10 mols. of toluene, the formation of these higher boiling substances is prevented. The excess of toluene is readily removed by distillation. After a distillation in vacuo Dr. VAN DER LAAN obtained a product solidifying at -4°.3 of a sp. gr. 1.3887 at 65°.5 whilst these constants, according to his observations, are -3°.9 and 1.3858 at 65°.5 for pure benzylbromide from benzylalcohol. The benzylbromide thus prepared contains, therefore, less than 0.5% of impurities.

3. *Influence of Catalysts.* As the influence of light is, as we have seen, very great, all the experiments with catalysts were made in complete darkness. Of these were tested: antimonytribromide, aluminiumbromide, ferricbromide and phosphorustribromide. Of the first three it is stated that they favour the bromination in the core, of the latter that it accelerates the formation of benzylbromide. The observations of Dr. VAN DER LAAN are in harmony with this. The

temperature at which the reaction was tried was 50°, and the action of the catalyzers was determined in such a manner that increasing quantities of them were added and the composition of the reaction product determined each time.

A feeble catalyzer was found in antimony tribromide as shown in the subjoined table.

T A B L E II.

Temp. 50°; 50 cM.<sup>3</sup> toluene + 3 cM.<sup>3</sup> bromine. Dark.

Mol SbBr <sub>3</sub> on 1 mol Br <sub>2</sub>	Composition of the mixture ortho-para bromotoluene		Composition of the brominating product		
	ortho	para	ortho	para	benzyl bromide
0 00	41 8	58.2	23.5	32.8	43.7
0.0017	40.1	59 9	22 4	33.4	44 2
0.0084	38 9	61 1	24 0	37.8	38 2
0.016	38 3	61.7	26.0	42 0	32.0
0.034	38 9	61.1	28 0	44 1	27.9
0 089	—	—	—	—	18.7

The quantity of benzylbromide diminishes with increasing quantities of the catalyzer but is not inversely proportional; the decrease is much less. The proportion of *ortho*- and *para*bromotoluene undergoes but a slight modification.

*Aluminiumbromide*, however, acts very energetically, as very small quantities prevent the formation of benzylbromide. The experiments were conducted by adding a little aluminium powder to the mixture of toluene and bromine, thereby converting it rapidly into the bromide. The following figures were obtained :

T A B L E III.

Temp. 50°; 50 cM.<sup>3</sup> toluene + 2.5 cM.<sup>3</sup> bromine. Dark.

Mol AlBr <sub>3</sub> on 1 mol Br <sub>2</sub>	Benzyl- bromide	Composition of the mixture.	
		ortho	para bromotoluene
0	43 7	41 8	58.2
0.002	43.1	43.9	56.1
0.004	0.5 (?)	44.6	55.4
0.006	0	44 3	55.7
0.017	0	49.2	50.1

Whereas  $\text{SbBr}_3$  modifies the proportion of *ortho-para* slightly in favour of the *para* there is present here a much stronger influence of  $\text{AlBr}_3$  in favour of the *ortho*.

Particularly interesting here is the influence on the amount of benzyl bromide. Although with only 0.002 mol. no modification of those proportions is perceptible, this becomes so pronounced with double the quantity that practically no more benzyl bromide is formed. This result is very striking and deserves a closer study.

With ferric bromide this phenomenon was repeated; this appeared to be a still more powerful catalyzer than aluminium bromide, as the limit of its activity is situated still considerably lower as may be seen from the subjoined table:

T A B L E IV.

Temp.  $50^\circ$ ; 50 cM.<sup>3</sup> toluene + 2.5 cM.<sup>3</sup> bromine. Dark.

Mol Fe Br <sub>3</sub> on 1 mol Br <sub>2</sub>	Benzyl- bromide	Composition of the mixture.	
		ortho	para
		bromotoluene	
0	43.7	41.8	58.2
0.0007	40.8	36.9	63.1
0.001	7.8	—	—
0.002	0	36.0	64.0
0.006	0	37.9	62.1
0.01	0	37.0	63.0

Here, the quantity of *ortho* is again depressed by the catalyzer.

With *phosphorus trichloride* as catalyzer Dr. VAN DER LAAN has only made one experiment which, in accordance with ERDMANN's investigation, gave an increase in the amount of benzyl bromide.

T A B L E V.

Temp.  $51^\circ$ ; 50 cM.<sup>3</sup> toluene + 3 cM.<sup>3</sup> bromine. Dark.

Mol P Br <sub>3</sub> on 1 mol Br <sub>2</sub>	Benzyl- bromide	Bromotoluenes	
		ortho	para
0	45.4	41.8	58.2
0.02	54.7	41.4	58.6

The quantity of benzyl bromide has therefore, much increased but the proportion *ortho-para* has kept fairly well unaltered.

For further particulars as to these researches VAN DER LAAN'S original dissertation should be consulted. An article by him on this subject will also appear, shortly, in the "Recueil".

Amsterdam, Sept. '05. Chemical Laboratory of the University.

**Geology.** — "*On fragments of rocks from the Ardennes found in the Diluvium of the Netherlands North of the Rhine.*" By Prof. A. WICHMANN.

(Communicated in the meeting of November 25, 1905).

Ever since the 18<sup>th</sup> Century, the attention of geologists has been drawn to the boulders scattered about our heathgrounds and in opposition to the various and oftentimes curious theories started to account for their presence there, A. VOSMAER then already expressed the opinion that they had been transported from elsewhere by "A Mighty Flood".<sup>1)</sup> A little later, A. BRUGMANS<sup>2)</sup> and after him S. J. BRUGMANS<sup>3)</sup> pointed to Scandinavia as the original home of these erratics; but this view, though shared by a few other scientists, was not generally adopted until after the publication of J. F. L. HAUSMANN'S treatise<sup>4)</sup>. It seemed then as if the only question still remaining to be solved, was in what way and by what road this transport had been affected. Little or no thought was given to the possibility that other countries might be also accountable for their origin.

It was not until 1844 that W. C. H. STARING, whilst investigating the nature of these boulders, discovered that at least those composed of sandstone and quartzite, were found as well in the Ardennes, in the districts of Berg and Mark, at the foot of the Harz Mountains

<sup>1)</sup> JOHANNES VAN LIER. Oudheidkundige brieven, bevattende eene verhandeling over de manier van Begraven, en over de Lijkbussen, Wapenen, Veld- en Eere-teekens der oude Germanen. Uitgegeven . . . door A. VOSMAER. 's-Gravenhage 1760, p. XV, 10, 11, 103.

<sup>2)</sup> Sermo publicus, de monumentis variarum mutatarum, quas Belgii foederati solum aliquando passum fuit. Verhandelingen ter nasporing van de Wetten en Gesteldheid onzes Vaderlands. I. Groningen 1773, p. 504, 508.

<sup>3)</sup> Lithologia Groningana. Groningae 1781. Preface p. 2, 3.

<sup>4)</sup> Verhandelingen over den oorsprong der Graniet en andere primitieve Rotsblokken, die over de vlakten der Nederlanden en van het Noordelijk Duitschland verspreid liggen. Natuurk. Verhandelingen der Hollandsche Maatsch. van Wetensch. XIX. Haarlem 1831, p. 341—349.