XVIII.—*The α - and β -Modifications of Benzene Hexachloride.*

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SOME results obtained by Professor McLeod, by the simultaneous action of chlorine and sodium hydrate on some inorganic substances, led me to investigate the action of these agents on some organic compounds.

The substance chosen for commencing the investigation was benzene, and although the reaction did not proceed in the direction which was expected, yet the results obtained seem of sufficient importance to warrant publication, the more so as the reaction appears to be of general application with respect to a large number of aromatic hydrocarbons and their derivatives.

Some benzene was placed upon the surface of a dilute solution (about 1 per cent.) of sodium hydrate in a flask, and, without any special precautions being taken, a stream of chlorine was passed into the mixture. After the first few bubbles of gas had been passed, the benzene lost its transparency and very soon became bright yellow; on continuing to pass in chlorine for some time, the benzene evidently increased considerably in density, and at length fell to the bottom of the sodium hydrate solution in the form of a heavy, yellow oil. More benzene was then added, and the stream of chlorine continued till the second portion of benzene also sank to the bottom of the flask. It was then corked up and placed outside the laboratory for the night, to see whether any solid would crystallise out on exposure to the low temperature. Next morning about one-half of the oil had been converted into large masses of white crystals, and the oil still remaining had become colourless. The crystals were separated from the oil and the aqueous solution, and, after being well washed with water, were dried upon a porous plate; the oil was again treated with dilute sodium hydrate solution and chlorine, and was finally almost entirely converted into the crystalline solid.

A chlorine determination was made upon the air-dried crystals with the following result:—

0.2035 gram of the substance burnt with ignited Iceland spar gave
0.5773 gram AgCl.

Found,
70.17

Theory for $C_6H_6Cl_6$.
73.19 per cent. chlorine.

This high percentage of chlorine showed almost conclusively that the substance was approximately pure benzene hexachloride, the

more so as the melting point of the crude substance was found to be 148—151° (uncorr.), and the melting point of the α -C₆H₆Cl₆ is given as 157° (corr.).

As these results pointed simply to the formation of an additive compound of benzene, and as there was no apparent reason for the use of the sodium hydrate, the action of chlorine on a mixture of benzene and water was tried. The reaction was found to proceed on the same lines as before, but although considerable quantities of the hexachloride have been made by this method, the results never seemed quite so satisfactory as when sodium hydrate solution was employed, the amount of uncrystallisable oil being greater; the process with water alone has been abandoned, therefore, in favour of that first described.

The following method has been found to be the most convenient for the preparation of crude benzene hexachloride, as it does not depend at all on the temperature of the mixture, and equally good results are obtained either in bright sunlight or in darkness, and further, the rate of formation of the substance practically depends only on the rate at which the chlorine can be generated.

A series of three or four flasks, a convenient size being about 12 ounces, is arranged with the delivery tube from one flask passing to the bottom of the next. The flasks are about half filled with a 1 per cent. solution of caustic soda, and 20 to 40 grams of benzene are added to each flask; the flasks are connected, and a rapid stream of chlorine is passed through the apparatus, when it will be found that absorption is practically complete in the first flask for a considerable time. The temperature rises considerably in the first flask, and at length crystals begin to appear, and the mixture becomes saturated with chlorine. When the flask in which the chlorine is generated becomes exhausted, the flask or flasks which have been saturated should be detached, and allowed to stand for 12 hours in a cool place. The crystals may then be removed from the oily and aqueous portions, most conveniently by means of a coarse muslin filter; fresh benzene, and some more sodium hydrate may then be added to the oily layer, and the saturation continued as before. By this method of working, the amount of substitution products produced seems to be very small, although after the chlorine has been passed through the same portion of benzene several times, it is noticed that the oil does not crystallise so readily, doubtless on account of the formation of substitution compounds.

The crude substance obtained by this process is a colourless, crystalline mass, closely resembling in its properties the benzene hexachloride prepared by other methods. It is soluble in all the ordinary organic solvents, but crystallises best from about 80 per

cent. acetic acid. After several recrystallisations, the melting point is 157° (corr.), and no further alteration takes place even on repeated recrystallisation.

The behaviour, both of the crude substance and of the recrystallised portions, when the melting point is determined, shows that the substance is a mixture; although the melting point, 157° , is perfectly definite, yet the substance, even after repeated recrystallisation from various solvents, always leaves a residue which does not melt, or dissolve in the fused portion, till a much higher temperature is reached. It seemed probable that the difficultly fusible portion was the β -benzene hexachloride described by Meunier (*Bull. Soc. Chim.*, **41**, 530; and *Compt. rend.*, **98**, 436), and by Schüpphaus (*Ber.* **17**, 2256).

Many attempts were made to obtain one of the substances free from the other by fractional crystallisation, but although, as will be seen later, they differ greatly in their solubility in the ordinary solvents, it was not found possible to obtain either of them in a state of purity.

The method of preparing the β -compound described by Meunier was next tried, namely, by boiling the mixture of α - and β -substances with alcoholic potassium cyanide for 30 hours. By this means, the α -substance is entirely decomposed, whilst the more stable β -compound is able to resist the action. It was thus found possible, but only with great difficulty, to obtain the β -substance in a state of purity; the chief difficulty consisting in extracting the undecomposed β -derivative from the large amount of tarry matter produced by the decomposition of the α -compound.* Alcohol was found to be the most suitable solvent, as although the β -compound was not very readily soluble in it on boiling, yet the tarry products dissolved in it much less readily than in any other solvent tried. The crystals deposited by the alcoholic solution were purified by careful sublimation, as described by Meunier. By Meunier's process of separation, it will be seen that the whole of the α -substance, constituting about 70 per cent. of the crude benzene hexachloride, is lost; moreover, the yield of the β -compound is far from satisfactory.

A much better method of separating the two substances was found to consist in distilling the crude $C_6H_6Cl_6$ in a current of steam, in which the α -compound alone is volatile; this process, although somewhat slow, is a quantitative one, as in this way the α -compound can be entirely separated, for the most part collecting in the Liebig's

* The only substances I definitely recognised amongst the decomposition products of the α -derivative by Meunier's process were diphenyl and ammonium cyanide. From the odour, I suspected the presence of naphthalene, but have not been able to identify it.

condenser, leaving the β -compound behind. The latter can then be obtained in a state of purity by a single crystallisation from alcohol, without any subsequent sublimation being necessary.

The steam-distilled α -derivative was further purified by recrystallisation either from moderately strong alcohol or from about 80 per cent. acetic acid; it forms very characteristic crystals shaped like fern-leaves, and melts quite constantly at 157° (corr.) without leaving any unmelted residue.

Two determinations of the molecular weight of the α -substance were made by Raoult's method, the first in benzene solution and the second in acetic acid, as it was thought possible that some decomposition might take place in benzene solution. The results were as follows:—

	I. In benzene.	II. In acetic acid.	
Wt. of substance ..	1.3142 grams.	3.2744 grams.	
Wt. of solvent	100 ,,	100 ,,	
Depression of freezing point of solvent	0.26	0.595	Theory for $C_6H_6Cl_6$.
Molecular weight. .	248	270	291

There does not seem to be any record of α -benzene hexachloride having been previously obtained free from the β -derivative. It is a colourless substance, insoluble in water, but readily soluble in all the ordinary organic solvents. It is very stable, and resists the action of most reagents, except that of alcoholic potash or soda, or of alcoholic potassium cyanide at the boiling temperature. Fuming nitric acid is without action, the substance merely dissolving when heated, and crystallising out again on cooling. It is not altered by long-continued boiling with chromic acid; with potassium permanganate, only a very slight action takes place even on heating. The substance resisted all attempts to further chlorinate it. Aqueous ammonia is without action on it, as is a boiling alcoholic solution of silver nitrate. On distilling it over zinc-dust, a colourless, crystalline compound was obtained smelling strongly of diphenyl. On heating the substance above its melting point, it evolves hydrogen chloride, and forms a liquid product, probably $C_6H_3Cl_3$ [1 : 2 : 4].

The β -benzene hexachloride left as a residue, after the α -modification has been distilled off, when recrystallised from alcohol, exactly resembles the substance prepared by Meunier's method. It forms small and very brilliant crystals which are almost colourless, and on careful sublimation, without previous fusion, it forms a snow-white powder consisting of microscopic crystals.

It is even more stable than the α -compound, not only being unacted

on by all the reagents incapable of decomposing the α -modification, but even boiling alcoholic potassium cyanide does not affect it, and it is only completely decomposed by boiling for three hours with alcoholic potash.

It is very much less soluble than the α -modification in all solvents tried, although strangely the two substances do not appear to be separable by fractional crystallisation. Its solubility in acetic acid and in benzene was determined.

100 grams of acetic acid at 15.6° dissolve 0.289 gram (mean of two experiments).

100 grams of benzene at 22° dissolve 1.204 grams (mean of two experiments).

A molecular weight determination was made in benzene solution by Raoult's method (acetic acid cannot be used owing to the insolubility of the substance).

0.0752 gram of substance dissolved in 15.1182 grams of benzene caused a depression of 0.085° in the freezing point.

Found.	Theory.
287	291

The substance dissolves readily in hot benzene and acetic acid, but is much less soluble in boiling alcohol.

An attempt was made to determine its vapour density by Victor Meyer's method, but from the dissociation of the substance no definite results as to its molecular weight were obtained, but the figures are interesting as a study of dissociation.

	I.	II.	III.
Temperature of bath*.	295° .	330° .	370° .
Wt. of substance..	0.0963 gram	0.0686 gram	0.0491 gram.
Volume of gas collected	22.75 c.c.	17.84 c.c.	17.04 c.c.
Height of barometer	739.4 mm.	739.4 mm.	739.4 mm.
Temperature of gas	13°	12.5°	13°
Vapour density ...	3.43	3.24	2.44

$$\text{Theory for } \frac{\text{C}_6\text{H}_6\text{Cl}_6}{4} = \text{C}_6\text{H}_3\text{Cl}_3 + 3\text{HCl} = 2.52.$$

Meunier (by Hofmann's method) obtained the vapour densities 9.365 and 9.207 (theory for $\text{C}_6\text{H}_6\text{Cl}_6$, 10.08). Thus, at about 180° ,

* The temperatures were taken by means of one of Müller's mercury thermometers containing nitrogen gas under pressure.

dissociation has already begun, and steadily increases with the rise of temperature, till at 370° , the dissociation into 4 mols. is complete.

From the above results, and from the fact that the β -modification is capable of being sublimed, it was attempted to synthesise the substance from $C_6H_3Cl_3$ [1 : 2 : 4] and hydrogen chloride, but, although several methods have been tried, at present without success.

Both modifications of benzene hexachloride yield the same trichlorobenzene [1 : 2 : 4], when treated with hot alcoholic potash, although the β -modification possesses much greater stability. The two substances were decomposed side by side in two flasks; in the case of the α -compound the reaction was complete after a few minutes' boiling; the β -compound was digested for three hours. The products of the reactions were diluted, acidified, and extracted with ether; on distilling off the ether, two oils of similar odour were left. They were placed in a desiccator and allowed to stand for some days, but neither oil showed signs of crystallisation. To further prove the identity of the two, they were both converted into nitro-derivatives by boiling with fuming nitric acid. The nitro-derivatives were precipitated with water, washed, and recrystallised from aqueous alcohol. Both solutions deposited crystals of almost colourless, interlaced needles, which were evidently the same substance. The melting points were taken: that of the $C_6H_2Cl_3(NO_2)$, obtained from α -benzene hexachloride melted at $57.5-58^{\circ}$; the nitro-derivative obtained from the β -hexachloride melted at $58-58.5^{\circ}$; the melting point of $C_6H_2Cl_3(NO_2)$ is given by Beilstein as 58° . Both hexachlorides therefore yield the same trichlorobenzene on treatment with alcoholic potash.

There seems to be very little doubt that both the α - and β -hexachlorides of benzene have the composition $C_6H_6Cl_6$. All the evidence we at present possess goes to show that the two compounds are isomeric, namely, first, the analyses of Meunier and Schüpphaus; second, the vapour density determinations made by Meunier; third, the molecular weight determinations by Raoult's method*; fourth, the fact that both compounds yield the same trichlorobenzene when acted on by alcoholic potash.

The reason for the existence of two isomeric hexachlorides of benzene is not very clearly shown by any of the benzene formulæ at present proposed, unless we assume that an intramolecular change has taken place, and that some of the carbon atoms in the molecule of one of the addition products are connected with 2 atoms of chlorine and others with 2 atoms of hydrogen.

* I have recently found that the molecular weights of α - and β -benzene hexachlorides have also been determined by Paternò and Nasini (*Gazzetta*, **19**, 195-209), and that their figures give $C_6H_6Cl_6$ as the formula for both compounds.

That some intramolecular change had taken place in the formation of one of the hexachlorides did not appear improbable when the substances were made by either of the older methods, either by passing chlorine into boiling benzene or into benzene exposed to direct sunlight, but the chance of any such change was lessened by the formation of the same trichlorobenzene when the substances were acted on by alcoholic potash; now that the hexachlorides can be prepared, if necessary, in a freezing mixture and in darkness, the chance of any such change is greatly decreased.

From some work that I am at present engaged upon, but which is not yet quite ready for publication, it seems that monochlorobenzene yields hexachlor-addition products similar to those of benzene, $[C_6H_5Cl_7]$, which on treatment with alcoholic potash yield tetrachlorobenzene $[1 : 3 : 4 : 5]$. This shows that in the hexachlorides of chlorobenzene at least four of the carbon atoms are directly connected to chlorine, and thus greatly increases the probability that in both the α - and β -benzene hexachlorides each carbon atom is directly connected with an atom of chlorine.

I have made many attempts to convert these substances from one modification to the other, but hitherto without success.

It seems rather early to hazard a speculation as to the constitution of these two substances, but as all the benzene formulæ fail to explain why two symmetrical isomers of the composition $C_6H_6Cl_6$ should exist, I think a certain amount of speculation is justifiable.

It seems to me not impossible that the α -compound may have the constitution—

and that the β -compound may be represented by the formula

that is to say, that the chlorine has become triadic, and has formed a second ring consisting of 6 chlorine atoms. This hypothesis would go far towards explaining the superior stability of the β -substance.

I have found that bromine acts additively under similar conditions to chlorine, and further, that addition compounds of other derivatives of benzene, toluene, xylene, naphthalene, &c., and their derivatives may be obtained by slight modifications in the method of working.

These reactions are being investigated, and I hope to contribute the results in a future paper to the Chemical Society.

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