

XXI.—On Tetrabromide of Carbon.

By THOMAS BOLAS and CHARLES E. GROVES.

SOME of the combinations of bromine and carbon have been already investigated, but the tetrabromide has remained unknown up to the present time. The dibromide C_2Br_4 was obtained many years ago by Löwig* in studying the action of bromine on alcohol and ether. Völckel,† however, did not succeed in preparing it by this method. In 1862, Lennox‡ took up this subject and investigated the tetrabrominated ethylene C_2Br_4 , which he obtained by the alternate action of bromine and potassic hydrate on ethylene. The tribromide C_2Br_6 is mentioned by Reboul§ as obtained from ethylene dibromide by substitution.

We will now proceed to describe the methods of preparation, and some of the principal reactions of the tetrabromide, which, as already announced, we have succeeded in obtaining.

Tetrabromide of Carbon from Carbonic Disulphide.

We can fully confirm the observation made by Kolbe that bromine does not act on carbonic disulphide, when heated with it for a considerable time, at a high temperature (150° — 180° C.), and the bromide does not appear to be formed even when the mixed vapours are passed through a red-hot tube.

The bromination of the bisulphide may, however, be effected by two different methods: by submitting it to the action of bromine in the presence either of bromide of iodine, or of antimony tribromide. It may be as well to mention that the bromine employed in all these experiments was free from chlorine.

Preparation.—(a.) 2 parts of bisulphide of carbon, 14 parts dry bromine, and 3 parts iodine were heated together in a sealed tube to a temperature of 150° C. for about 48 hours; the

* Löwig, Ann. Chem. Pharm., iii, 292.

† Völckel, Ann. Chem. Pharm., xli, 119.

‡ Lennox, Ann. Chem. Pharm., cxxii, 126.

§ Reboul, Ann. Chem. Pharm., cxxiv, 271.

contents of the tube were then washed into a flask, excess of caustic soda solution added, and the mixture distilled until no more tetrabromide of carbon came over with the water. After it had been collected, it was freed, as far as possible, from adhering moisture, dissolved in a small quantity of hot spirit, filtered, and allowed to cool, when it crystallised out in large lustrous plates. It was necessary to avoid boiling the alcoholic solution, as otherwise considerable loss occurred.

As the presence of a small portion of unaltered carbonic disulphide will cause the distillate to remain liquid after being separated from the water, it should, under these circumstances, be exposed to the air in order to allow it to evaporate, when the tetrabromide is left behind in the solid state.

(b.) Antimony terbromide may be substituted for bromide of iodine in the above process, employing 4 parts terbromide, 7 parts bromine, and 1 of carbonic disulphide. When the reaction was complete, the contents of the tube were treated in the same manner as when bromide of iodine was employed. The above reactions take place, although slowly, at 100° C.

Tetrabromide of Carbon from Bromopicrin.

We find that the action of brominating agents on bromopicrin, as in the case of carbonic disulphide, produces tetrabromide of carbon; but since bromopicrin itself decomposes under the influence of heat with liberation of bromine and evolution of nitrous fumes, it is advisable to conduct the operation in a flask furnished with a digestion tube, in preference to heating the materials in a sealed tube.

(c.) When terbromide of antimony was employed as the reagent, the following proportions were taken:—12 parts terbromide of antimony, 10 parts bromopicrin, and 8 of bromine; the reaction was generally complete in about 36 hours; but this could be readily ascertained by neutralizing a small portion of the contents of the flask, when the presence of any unaltered bromopicrin rendered itself sensible by its characteristic odour. When it was thus ascertained that the reaction was finished, the contents of the flask were neutralized and treated in a manner similar to that already described in the preparation of the tetrabromide from carbonic disulphide. The quantity obtained by this process is, however, small in proportion to the

quantity of substance employed. This is what might be expected, considering the readiness with which bromopicrin decomposes under the influence of heat. The quantity of the bromide of carbon was usually less than 40 per cent. of the bromopicrin employed.

(d.) Bromide of iodine may be substituted for the antimony terbromide in the above process, but its action is much less rapid.

Tetrabromide of Carbon from Bromoform.

As in the case of carbonic disulphide and bromopicrin, tetrabromide of carbon is formed by the action of the brominating agents above-mentioned on bromoform, viz., bromide of iodine and terbromide of antimony.

(e.) In effecting the substitution of bromine for the remaining equivalent of hydrogen in bromoform by means of bromide of iodine, the following proportions were taken :—2 parts of bromoform, 3 parts of bromine, and 1 of iodine were heated together in a sealed tube to 150°—160° C. for about 24 hours; this was occasionally opened in order to allow the escape of the hydrobromic acid formed during the reaction. When no more gas escaped on opening the tube, the contents were neutralized and distilled.

(f.) When antimony terbromide was employed the operation was conducted, as in the case of the bromide of iodine experiment, using 2 parts of bromoform, 2 parts bromine, and 3 of the antimony terbromide.

Analyses of Tetrabromide of Carbon.

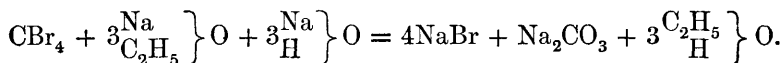
- I. .338 grms. substance gave .763 grms. silver bromide.
- II. .8620 grms. substance gave .1148 grms. carbonic anhydride.
- III. .568 grms. substance gave 1.286 grms. silver bromide.
- IV. .5465 grms. substance gave 1.240 grms. silver bromide.
- V. .6487 grms. substance gave .0860 grms. carbonic anhydride.
- VI. .519 grms. substance gave 1.173 grms. silver bromide.

		Theory.	I.	II.	III.	IV.	V.	VI.	Mean.
C ..	12	3.61	—	3.63	—	—	3.62	—	3.62
Br ₄ ..	320	96.39	96.06	—	96.36	96.54	—	96.16	96.28
		<u>332</u>							
		100.00							

II. and III. were obtained from carbonic disulphide, I., IV., and V. from bromopicrin, and VI. from bromoform.

Carbon tetrabromide is a white substance crystallising in lustrous plates, and melting at $91^{\circ}\text{C}.$; that from bromopicrin, however, had a somewhat higher melting point (about $93^{\circ}\text{C}.$), probably arising from the presence of a minute quantity of the bromide C_2Br_6 , produced by the decomposition of the bromopicrin. It has an ethereal odour somewhat resembling that of tetrachloride of carbon, and a sweetish taste.

It is almost insoluble in water, to which, however, it communicates its odour and taste. It is exceedingly soluble in ether, bisulphide of carbon, tetrachloride of carbon, chloroform, bromoform, benzol, and American oil. It is also very soluble in hot alcohol from which it is deposited in the crystalline state on cooling. When the alcoholic solution is heated it is decomposed, aldehyde being formed, and hydrobromic acid found in the solution. We endeavoured to avail ourselves of this reaction to estimate the bromine in the tetrabromide, but failed, as the decomposition appears to be incomplete, even after digestion for some time at $100^{\circ}\text{C}.$ in a closed tube. The alcoholic solution burns with a pale green flame. Although it is acted on but slowly by cold alcohol, both alcoholic potash and soda rapidly decompose it:



It is unaffected at the ordinary temperature by aqueous solutions of potash and soda, and only very slowly decomposed at $100^{\circ}\text{C}.$, but at $150^{\circ}\text{C}.$, and upwards, the action goes on with much greater rapidity.



It is unacted on by cold sulphuric acid, but on applying heat a slight decomposition occurs, with production of an odour resembling that of phosgene. With care it can be sublimed unchanged, but when the vapour is passed through a red hot tube, a great portion is split up into its constituent elements, the carbon being deposited in the tube, and the bromine distilling over; a small quantity of a crystalline substance, however, was

obtained, whose reactions and high melting point agreed with those ascribed to the tribromide C_2Br_6 by Reboul.

Action of reducing agents on Tetrabromide of Carbon.

A saturated solution of the tetrabromide in cold alcohol was mixed with an equal volume of water, which caused the precipitation of a considerable quantity of the substance in a finely divided state; on the addition of sodium amalgam, the solid portion gradually disappeared, being replaced by an oily body. This was separated, dried, and submitted to analysis, with the following results:—

·1016 grms. substance gave ·2208 grms. silver bromide; this corresponds to 92·48 per cent. bromine; bromoform requires 94·86 per cent. bromine, and dibromide of methylene, 91·95 per cent.

		Theory.	Analysis.			Theory.
C.....	12	4·74	—	C.....	12	6·90
Br ₃ ...	240	94·86	92·48	Br ₂	160	91·95
H	1	·60	—	H ₂	2	1·15
		<hr/>			<hr/>	
	253	100·00			174	100·00

From the analyses it is evident that the reducing action of the sodium amalgam first converts the tetrabromide into bromoform, and that a portion of this then undergoes a further change into methylene dibromide. In order to confirm this, a portion of the oily substance was reconverted into tetrabromide of carbon, by the action of bromide of iodine.

We have not yet investigated the action of the ammonias upon the new substance, nor the silver-salts (oxalate, cyanide, &c.), both of which promise interesting results.