### PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXIII.-On Tetrabromide of Carbon. No. II.

By THOMAS BOLAS and CHARLES E. GROVES.

IN a former paper\* we described several methods for the preparation of the hitherto unknown tetrabromide of carbon, and in the present communication we desire to lay before the Society the results of our more recent experiments. In addition to those methods of obtaining the carbon tetrabromide, which we have already published, the following are of interest, either from a theoretical point of view, or as affording advantageous means for the preparation of that substance.

### Action of Bromine on Carbon Disulphide.

Our former statement that<sup>+</sup> bromine had no action on carbon disulphide requires some modification, as we find that when it is heated to 180° or 200° for several hundred hours with bromine free from both chlorine and iodine, and the contents of the tubes are neutralised and distilled in the usual way, a liquid is obtained, which consists almost entirely of unaltered carbon disulphide; but when this is allowed to evaporate spontaneously, a small quantity of a crystalline substance is left, which has the appearance and properties of carbon tetrabromide. The length of time required for this reaction, and the very small relative amount of substance obtained, would, however, render this quite inapplicable as a process for the preparation of the tetrabromide.

## Action of Bromine on Carbon Disulphide in presence of Certain Bromides.

Having noticed in our former paper the remarkable influence which the presence of antimony terbromide had when added to the mixture of bronnine and carbon disulphide, we thought it would be interesting to study the effect produced when other bromides were substituted for that of antimony, and for this purpose selected the bromides of the following elements :---bismuth, arsenic, gold, platinum, cadmium, zinc, nickel, iron, tin, phosphorus, and sulphur. These bromides may, for our purpose, be divided into two groups, the first of which, comprising the metals bismuth, arsenic, gold, platinum, cadmium, zinc, and nickel,

*	Chem.	Soc. J.	xxiii,	161.	+ 1	bid.
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give results so far satisfactory that they might be substituted for the antimony bromide in the preparation of tetrabromide of carbon; but notwithstanding this we consider bromide of iodine in presence of excess of bromine to be the most convenient agent for converting carbon disulphide into carbon tetrabromide.

When heated with bisulphide of carbon and excess of bromine for a considerable time, bismuth converts a large proportion of the disulphide into tetrabromide, apparently yielding a result as good as that obtained with antimony; arsenic bromide under similar circumstances also transformed the greater portion of the carbon disulphide. These three elements, antimony, arsenic, and bismuth, as might have been expected from the great similarity in their chemical relations, yielded results which differed but little from one another.

Carbon disulphide was enclosed in a sealed tube along with one atomic proportion of metallic bismuth, and somewhat more than nine of bromine, and then heated for about sixty hours to a temperature of 180° to 190° C. The contents of the tube, when opened, had an odour of the carbon sulphobromide which is described in another part of this paper. After the addition of an excess of sodium hydrate, the product was submitted to distillation in the usual way, when carbon tetrabromide, together with a small quantity of unaltered carbon disulphide, was obtained. The experiment with arsenic bromide was conducted in a precisely similar manner, substituting metallic arsenic for the bismuth, the conversion of the disulphide into tetrabromide being even more complete than in the previous case. Gold when heated with the proper proportions of carbon disulphide and bromine in the manner above described, determined the formation of a considerable quantity of carbon tetrabromide. Platinum under similar circumstances also yielded a very satisfactory result. In the case of cadmium and zinc, it was necessary to add their bromides to the mixture of bisulphide of carbon and bromine, as we find that the metals themselves are scarcely acted upon by dry bromine, even at a temperature of 180°. Nickel was used in the metallic state. The last three experiments, namely, those with cadmium, zinc, and nickel, yielded results which are somewhat inferior as regards the quantity of tetrabromide The last four elements in the above list, viz., iron, tin, phosformed. phorus, and sulphur, when heated with carbon disulphide and bromine. gave unsatisfactory results, although in each case when the product was neutralised and distilled, after the water was separated and the excess of unaltered disulphide allowed to evaporate spontaneously, a white crystalline substance remained behind, which was identified as carbon tetrabromide, although the quantity obtained was insufficient for analysis.

#### ON TETRABROMIDE OF CARBON.

## Decomposition of Bromopicrin under the Influence of Heat.

Stenhouse has observed that when bromopicrin is heated to a temperature a little above 100°\* it decomposes with explosive violence, and we also found<sup>+</sup> that when a test-tube containing a few drops of the substance was strongly heated, a slight explosion ensued. When, however, a considerable quantity was cautiously and gradually heated, it became of a dark brown colour, from liberation of bromine, and decomposed quietly. From this it might be inferred that the explosion observed by Stenhouse and ourselves arose from the exposure of the vapour to a high temperature. This is well known to be the case with ethylic nitrate, and various other compounds which contain the higher oxides of nitrogen. The probability of this is increased from the fact that, during an experiment in which some ounces of bromopicrin were being distilled under the ordinary atmospheric pressure, the greater portion of it passed over without accident; but when the level of the liquid in the retort had become very low, so that the sides were strongly heated, a violent explosion took place, which shattered the apparatus.

With the object of more accurately ascertaining the nature of the decomposition which bromopicrin undergoes when submitted to the influence of heat, we determined to study its effect on a considerable quantity of the substance. After some preliminary trials to ascertain the best method of attaining this end, an apparatus was arranged in the following manner :-- One arm of a Y-tube condenser was connected with a small bolt-head by means of a digestion-tube bent twice at right angles, the longer limb of which had a length of about 60 centimetres. The other arm of the condenser communicated with the atmosphere through a two-necked Woulfe's bottle containing a layer of concentrated sulphuric acid, to intercept moisture; the tubes passed down to within a short distance of the acid, but did not dip into it. The condenser was kept cool by surrounding it with water contained in an inverted bell-jar, the tubulure passing through the neck and being connected there with the receiver. All the joints were fitted by means of caoutchouc corks.

It was found convenient to employ in each operation from 200 to 300 grams of bromopicrin, which were introduced into the bolt-head, and cautiously heated, when the liquid gradually became of a dark brown colour, from liberation of bromine, and after a time a brisk reaction set in. As soon as this took place, the light was removed, and the decomposition allowed to proceed without the aid of external heat: a considerable quantity of a dark red volatile liquid collected in the

\* Ann. Chem. Pharm., xci, 309.

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receiver, whilst nitrogen oxides and carbonic anhydride escaped by the exit-tube. After the first violence of the reaction was over, a gentle heat was applied, and the digestion continued for 30 or 40 hours, taking care that the bromopicrin did not distil over. In order to ascertain the progress of the decomposition, the contents of the bolt-head were tested from time to time by mixing a sample with water, and when this became solid, the digestion was discontinued. The dark-red liquid in the bolt-head, which, when allowed to stand some time, generally deposited very large tabular crystals of tetrabromide of carbon, was now mixed with water, and sufficient sodium hydrate added to neutralise the bromine. On heating the solution, the carbon tetrabromide fused into a cake under the liquid, but unless the digestion had been continued for a somewhat longer time than that above mentioned, it generally contained traces of bromopicrin; this, however, could be easily removed by heating it with an aqueous solution of potassium cyanide, which is without action on the tetrabromide of carbon, but entirely destroys the bromopicrin.\*

The tetrabromide of carbon thus obtained was found to contain a minute quantity of an oily substance, which was removed by powerful pressure between folds of bibulous paper before crystallisation. Analyses of the pure substance were then made with the following results :---

VII. 616 grm. substance gave 1.393 grm. silver bromide.
VIII. 4625 grm. substance gave 1.0435 grm. silver bromide.
IX. 185 grm. substance gave '419 grm. silver bromide.

		Theory.	VII.	VIII.	IX.	Mean.
с	12	3.61				
Br4	320	96·39	96.23	96·01	96·36	96·20
	332	100.00				

VII and VIII were made in the usual way by burning with pure lime. IX was made by introducing a weighed quantity of the substance into a tube, together with a sufficient quantity of a solution of sodium ethylate in alcohol, sealing the tube, and heating it to 100° C. for five or six hours. At the expiration of that time, it was carefully opened, and the contents diluted with a considerable quantity of water. The analysis was then proceeded with in the usual way.

The dark-red liquid which had collected in the receiver during the decomposition of the bromopicrin above described, was next examined

• When bromopicrin is heated with an aqueous solution of potassium cyanide, it is entirely decomposed, cyanogen bromide being at first formed; but on further application of heat, this is destroyed, whilst a compound of a dark brown colour remains in solution.

by submitting it to fractional distillation. The flask in which the liquid was heated, was connected with a digestion-tube about two metres in length, having a tubulure fused in near the top, at right angles to the main tube, the bulb of the thermometer, which was inserted in the top of the main tube, being just below the junction with the tubulure. The latter was connected with a condenser arranged in a manner similar to that employed in the decomposition of bromopicrin. In order to expel, as far as possible, any gaseous products that might have been dissolved in the liquid under examination, it was at first heated to such an extent, that the vapour which condensed in the main tube and ran back into the distilling flask, reached to within a few centimetres of the thermometer-bulb. As soon as most of the dissolved gas had been thus expelled, the heat was increased, so that the vapour might pass over into the condenser. The column of mercury in the thermometer then rose rapidly, until it reached 56°, at which temperature the bulk of the liquid distilled over. It is almost unnecessary to state that the apparatus was sheltered as much as possible from draughts during the operation. The portion which came over between 56°-56'5° C. was submitted to analysis.

I. 247 grm. substance gave '600 grm. silver bromide.

II. 414 grm. substance gave '900 grm. silver bromide.

I corresponds to 93.18 per cent. bromine, and II to 92.51 per cent. bromine, mean 92.84 per cent. This liquid had the dark brown colour and general appearance of bromine, but differed from it in having a somewhat lower boiling point, namely, 56.5°, whereas bromine boils at 59.5.°\* It is moreover readily soluble in water, yielding a pale-yellow solution, which was found to contain hydrobromic acid, nitric acid, and free bromine. When a small quantity of water is added to the liquid, it evolves much gas. With concentrated sulphuric acid it forms a colourless crystalline compound. It is very pungent, and attacks the eyes strongly, like chloropicrin. It destroys caoutchouc far more rapidly than bromine, causing it to swell up and become brittle. The analysis of this liquid does not enable us to decide whether it is simply a solution of a nitrogen oxide in bromine, or a definite compound containing nitrogen, oxygen, and bromine. Considering, however, its remarkably constant boiling point and general properties, we are The compound NOBr<sub>4</sub> requires inclined to believe the latter. 91.42 per cent. bromine, and the substance under consideration contains 92.84 per cent.

\* As the boiling point of bromine given in the Handbooks varies so much (45° to 63°), we thought it would be expedient to make a tolerably accurate determination, and found that when a considerable quantity of dry bromine was distilled under a pressure of 751 mm., it passed over between 59.5° and 59.75°, the stem of the thermometer being in the vapour.

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From the results of these experiments on the decomposition of bromopicrin, it might appear probable that the tetrabromide of carbon obtained by processes (c) and  $(d)^*$  (antimony terbromide, or iodine bromide, with excess of bromine on bromopicrin) resulted, not from any particular action exerted by the antimony bromide or bromide of iodine, but simply from the splitting up of the bromopicrin under the influence of heat. This, however, is not the case, as in experiments (c) and (d) the flask containing the materials was heated in a waterbath, and we have ascertained that bromopicrin alone does not decompose at 100° C. The action of heat on bromopicrin just described affords a ready and expeditious method of preparing small quantities of carbon tetrabromide, the yield being about 30 per cent.

### Action of Bromine on Iodoform.

The action of bromine on iodoform at the ordinary temperature has been studied by Serullas, † and subsequently by Bouchardat, ‡ who found that a portion of the iodine in the iodoform was replaced by bromine, forming bromiodoform, CBr<sub>2</sub>IH. From a consideration of the results of their experiments, it seemed likely that an excess of bromine, acting upon iodoform at a high temperature, would convert it In order to test the correctness of this into tetrabromide of carbon. supposition, one part of iodoform was introduced into a tube, and six times its weight of bromine added to it, when the mixture became warm, and much iodine was liberated. The tube was then sealed and heated to about 180° for 70 hours, and on opening it at the expiration of that time, a considerable quantity of hydrobromic acid escaped. The contents were then neutralised with sodium hydrate, and distilled in the The semi-solid crystalline mass, after being separated from usual way. the water, and having the greater portion of the oily matter removed by pressure, was examined, and found to be carbon tetrabromide, contaminated with a minute quantity of the above mentioned oil, which was, however, easily removed by crystallisation from spirit. In this experiment bromiodoform was undoubtedly first produced, the liberated iodine combining with the excess of bromine, and the bromide of iodine thus formed acting upon the bromiodoform, transformed it into tetrabromide of carbon.

### Action of Bromide of Iodine and Bromine on Chloroform.

As the last atom of hydrogen in bromoform had been so easily replaced by the action of bromide of iodine and excess of bromine,

- \* Chem. Soc. J. xxiii, 162.
- + Ann. Ch. Phys. [2], xxxiv, 225, and xxxix, 97.
- ‡ J. Pharm., xxiii, 10.

forming tetrabromide of carbon,\* we thought that if chloroform were submitted to the same treatment, the last atom of hydrogen in it might likewise be replaced by bromine, forming bromochloroform (trichlorbromomethane) CBrCl<sub>3</sub>. Dry chloroform was, therefore, heated to 150° with one part of iodine and three of bromine for three hours, when the tubes were opened to allow of the escape of the gas produced during the reaction; the tubes were then again closed and the heating continued until they ceased to emit gas when opened. The contents were then neutralised and distilled in the usual way, when a colourless liquid, having an ethereal odour, was obtained, which was submitted to fractional distillation. It began to boil at 95°, the temperature gradually rising, until at 200° the greater portion had passed From the temperature at which this mixture began to boil, it over. was evident that all the chloroform had been converted into other products. The lowest fraction (100° to 130° C.) was liquid at ordinary temperatures; the intermediate ones deposited large colourless crystals when cooled, and the highest (180° to 200° C.) at once solidified to a crystalline mass, somewhat resembling tetrabromide of carbon, which when crystallised from spirit, melted at 69°; another recrystallisation raised it to 70°. An analysis of this portion yielded the following results :---

 $^{199}$  grm. substance gave  $^{466}$  grm. mixed silver bromide and chloride, containing  $^{286}$  grm. metallic silver; this is equivalent to  $^{1545}$  grm. bromine and  $^{0255}$  grm. chlorine. This corresponds to  $^{77.62}$  per cent. bromine and  $^{12.81}$  of chlorine. The compound CBr<sub>3</sub>Cl requires  $^{83.48}$  bromine and  $^{12.35}$  chlorine.

Another rectification of the higher fraction yielded a substance which, after crystallisation from spirit, melted at 76° C., and on analysis gave 92.91 per cent. bromine and 3 per cent. chlorine. Tetrabromide of carbon containing 96.39 per cent. bromine, it would seem that the substance is simply the tetrabromide contaminated with a small quantity of CBr<sub>3</sub>Cl. From the analyses it would appear that tetrabromide of carbon, CBr<sub>4</sub>, and tribromochloromethane, CBr<sub>3</sub>Cl, are amongst the products obtained, and this unexpected result induces us to believe that the hydrogen in the chloroform is removed as hydrochloric acid; but the reaction requires further investigation.

In preparing tetrabromide of carbon from disulphide of carbon, it is necessary to employ a considerable excess of soda in order to decompose a sulphur-compound (sulphobromide of carbon), which otherwise comes over with the vapour of water, thus contaminating the tetrabromide of carbon. We have observed that there is always a small quantity of an oily substance present, together with the tetrabromide prepared by this process; it is advisable to remove this substance by

<sup>\*</sup> Chem. Soc. J., xxiii, 163.

pressure before it is finally purified by distillation, or crystallisation from spirit.

# Boiling point and Specific Gravity of Carbon Tetrabromide.

We thought it would be of interest to ascertain the boiling point of tetrabromide of carbon both at the ordinary and at diminished pressures; and two parallel series of experiments were therefore made with the tetrabromide prepared from bisulphide of carbon and from bromopicrin. The following table gives the results. Column I represents the pressure in millimetres; column II the boiling-point of the tetrabromide derived from carbon disulphide; column III the boiling point of that from bromopicrin:—

I.	II.	111.
mm.	CBr <sub>4</sub> from CS <sub>2</sub> .	CBr <sub>4</sub> from CNO <sub>2</sub> Br <sub>3</sub> .
50	101.75	101.75
100	120.50	121.00
228	143.00	143.50
280	150.00	150.50
380	160.25	161.00
<b>4</b> 30	<u> </u>	165.50
<b>4</b> 82		169.50
558		175.00

Tetrabromide of carbon under the ordinary pressure (760 mm.) boils at 189.5°, but at the same time it undergoes a slight decomposition, bromine being liberated. It can, however, be distilled without change *in vacuo*, but, when the pressure is increased to about 350 mm., a very slight decomposition commences. For this reason the experiments on the distillation of the tetrabromide from carbon disulphide, under diminished pressure, were not carried on above 380 mm., as the results corresponded so nearly with those in column III.

Several determinations were made of the specific gravity of tetrabromide of carbon obtained both from carbon disulphide and from bromopicrin; but owing to the fused substance crystallising as it cooled and forming cavities, the results were not so concordant as we could have wished. The highest result, however, and that which is probably the most correct, gave 3.42 as the specific gravity of carbon tetrabromide at a temperature of  $14^{\circ}$  C. When heated to  $200^{\circ}$ in a sealed tube, it undergoes partial decomposition, a small quantity of bromine being liberated. The same phenomenon takes place when the tetrabromide is exposed to bright sunshine, the substance at the same time showing a strong tendency to crystallise on the side of the tube nearest the light, in well-formed and very brilliant crystals.

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# Sulphobromide of Carbon.

During the preparation of tetrabromide of carbon by the action of bromine and bromide of iodine on bisulphide of carbon, we did not observe that substance immediately on neutralising, and it seemed probable that some intermediate product was formed which was afterwards decomposed by excess of sodium hydrate, yielding the tetrabro-In order to satisfy ourselves that this was really the case, some mide. bisulphide was heated with bromine and iodine in the way already described, and the product was poured into water. The iodine and excess of bromine were then removed by the cautious addition of dilute soda-solution, taking care that the liquid never became alkaline, which was easily accomplished, as bromine is somewhat soluble in a solution of sodium bromide. The slightly-coloured heavy oil was then separated from the aqueous liquid, dried by calcium chloride, and submitted to fractional distillation. In the first place a small quantity of unaltered carbon disulphide distilled over, and the liquid assumed a much darker colour, from incipient decomposition; the temperature then rose rapidly, and the bulk of the liquid came over between 150° and 165°. There was, however, considerable decomposition. A determination of the sulphur in the portion boiling at 165° was made, and found to be 7.81 per cent. The formula CBr<sub>2</sub>S requires 15.69 per cent. From this it would appear that the liquid obtained was very far from being pure carbon sulphobromide, but is that compound contaminated with carbon tetrabromide. Its odour somewhat resembles that of carbon sulphochloride, and, when heated with excess of soda-solution, it yields at once pure tetrabromide of carbon. Careful rectification in vacuo would probably yield more satisfactory results.

When bisulphide of carbon was heated with bromide of iodine and water, together with a large excess of bromine to  $100^{\circ}$ , it was completely decomposed, and, on opening the tube, a large quantity of gas was evolved, but no tetrabromide could be detected after the contents had been neutralised. The gas, which was principally hydrobromic acid, had an odour resembling that of phosgene, although not so well marked as that pointed out in our former paper, when carbon tetrabromide is heated with sulphuric acid. It is highly probable that this is due to carbonyl dibromide (bromophosgene) COBr<sub>2</sub>, which could doubtless be obtained by heating carbon tetrabromide and sulphuric anhydride in a manner precisely similar to that in which Schützenberger\* obtained carbonyl dichloride (phosgene) from carbon tetrachloride.

\* Compt. rend., lxix, 352.

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#### Carbon Tetrabromide and Silver Oxalate.

In order to study the action of carbon tetrabromide on silver oxalate, a preliminary experiment was made by heating a small quantity of silver oxalate with excess of the tetrabromide. A reaction took place, accompanied by evolution of gas and production of a substance having a peculiar pungent odour. It was therefore thought advisable to repeat the experiment on a larger scale with weighed quantities of material. Four grams of silver oxalate and two grams of carbon tetrabromide were placed in a stout glass tube previously closed at one end; the other end was then drawn out and bent over, so that any gas evolved might be collected over mercury. The tube was heated in a waterbath; but when the temperature had nearly reached  $100^{\circ}$  a violent explosion took place, shattering the cast-iron vessel employed as a water-bath and distorting the tripod on which it was placed. Owing to this unexpected result, we have not as yet repeated the experiment.

### Action of Ammonias on Carbon Tetrabromide.

Hofmann\* has shown that the action of aniline upon the tetrachlorinated derivative of marsh-gas, CCl<sub>4</sub>, yields triphenylated carbotriamine, or triphenylguanidine,  $N_{3} \begin{cases} C''''\\ (C_{6}H_{5})_{3} \end{cases}$ , and although he did not succeed  $H_{2}$ in preparing the carbotriamine itself from carbon tetrachloride when ammonia was substituted for aniline, he subsequently found that it

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could be obtained from chloropicrin.

Aniline acts with far greater readiness on the tetrabromide than on the tetrachloride of carbon. When one part of carbon tetrabromide was added to two parts of aniline and gently warmed, it dissolved, and on increasing the temperature to the boiling point, the mixture acquired an intense red colour. In a few seconds a powerful reaction set it, which completed itself without any further application of heat, and on cooling, the mixture solidified to a mass of crystalline plates.

$$6 \begin{array}{c} \mathbf{C}_{6}\mathbf{H}_{5} \\ \mathbf{H}_{2} \end{array} \right\} \mathbf{N} + \mathbf{C}\mathbf{Br}_{4} = (\mathbf{C}_{6}\mathbf{H}_{5})_{3} \\ \mathbf{H}_{3} \end{array} \right\} \mathbf{N}_{3} \cdot \mathbf{Br} + 3 \begin{bmatrix} \mathbf{C}_{6}\mathbf{H}_{5} \\ \mathbf{H}_{3} \end{bmatrix} \mathbf{N} \cdot \mathbf{Br} \cdot \end{bmatrix}$$

When boiled with water, it almost entirely dissolved, and the solu-

\* Proc. Roy. Soc., ix, 284. + Ann. Chem. Pharm., cxxxix, 107.

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tion treated with excess of caustic alkali set free the mixed bases. On being distilled with water, the aniline passed over with the aqueous vapour, whilst the triphenylguanidine remained in the retort. The base was converted into the hydrochlorate, purified by crystallisation, and a platinum salt prepared from it, which, when submitted to analysis, gave the following result :---

<sup>244</sup> grm. platinum salt gave <sup>048</sup> grm. platinum. This corresponds to 19.67 per cent. platinum, the theoretical for  $2\begin{bmatrix} C''''\\ (C_6H_5)_3\\ H_3 \end{bmatrix}$ Br, PtCl<sub>4</sub>, being 20.04 per cent.

## Action of Ammonia on Carbon Tetrabromide.

As the action of carbon tetrabromide on aniline is much sharper than that of the tetrachloride, taking place as it does so much more readily, and at the same time yielding a product which is almost entirely free from the black tarry substance which accompanies the triphenylguandine obtained from the tetrachloride, we thought it probable that more favourable results would be obtained by the action of ammonia on tetrabromide of carbon than those obtained by Hofmann with the tetrachloride.\* We therefore heated to 100° in a sealed tube for twelve hours, two parts of tetrabromide of carbon with one of ammonia dissolved in about sixteen of alcohol. At the expiration of that time, the solution had acquired a deep yellow colour, and on distilling it, the addition of water to the first portions of the distillate caused the separation of an oily substance heavier than water. This oil had the odour and taste of bromoform, and distilled between 144° and 146°. According to Borodine, † bromoform boils at about 145°. When submitted to analysis it gave the following results:-

I. 398 grm. substance gave 887 grm. silver bromide.

	Theory.	1.
C = 12	4.74	
$Br_{3} = 240$	94.86	94.84
H = 1	$\cdot 40$	
253	100.00	

It would appear therefore that bromoform is one of the principal products in this experiment, the quantity obtained being about onehalf that of the tetrabromide of carbon originally employed. The solution from which the bromoform had been removed by distillation contained a considerable quantity of ammonium bromide, and was treated successively with silver sulphate, barium hydrate, and hydro-

\* Ann. Chem. Pharm., cxxxix, 110.

+ Kekulé, Lehrb. ii, 145.

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chloric acid, to convert the bromides into chlorides. After separating the ammonium chloride, platinum tetrachloride was added to the solution, when a small quantity of guanidine platino-chloride was obtained.

### Action of Alcohol on Carbon Tetrabromide.

It naturally suggested itself that the bromoform obtained in the reaction just described, was formed by the mutual action of the alcohol and tetrabromide, independently of the ammonia; and with the object of ascertaining the correctness of this hypothesis, a solution of carbon tetrabromide in alcohol was heated to  $100^{\circ}$  for twelve hours. On opening the tube, a strong odour of aldehyde was apparent, and when the contents were distilled and water added to the first portions which came over, bromoform was precipitated. The amount of bromoform obtained in this operation was about three-fourths of the carbon tetrabromide originally employed, but on rectification it was found to contain a small percentage of unaltered tetrabromide. The formation of aldehyde and hydrobromic acid which we had previously noticed\* shows that the decomposition takes place in the following manner:—

$$CBr_4 + C_2H_6O = CHBr_3 + HBr + C_2H_4O.$$

The quantity of bromoform obtained corresponds to this equation, theory requiring  $76 \cdot 2$  per cent., while experiment gave  $75 \cdot 0$  per cent. The principal action of alcoholic ammonia on carbon tetrabromide is undoubtedly similar to that of pure alcohol, which accounts for the small quantity of guanidine we obtained.

### Action of Antimony on Carbon Tetrabromide.

When these two substances were heated together, the tetrabromide lost a portion of its bromine, and on continuing the heat a carbonaceous substance was produced. The results did not encourage further investigation.

## Recovery of Bromine from Residues.

As a large quantity of bromine was obtained in this research in the form of residues, it was a matter of some importance to us to find a more convenient process of recovering the bromine than distillation with sulphuric acid and peroxide of manganese. After several trials we found the following to be the best method. The solution of the alkaline bromide is introduced into a retort with the requisite quantity of acid potassium chromate in crystals, and an excess of sulphuric acid previously diluted with half its weight of water is gradually added

\* Journ. Chem. Soc., xxiii, 164.

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through a thistle-funnel. After the first powerful reaction is over, heat may be applied to the retort. By employing the acid chromate, almost the whole of the bromine is readily recovered, and there is no danger of breaking the retort. We may also allude to the great advantage we have derived when working with bromine, from the use of the charcoal respirator invented by Dr. Stenhouse, as with it and a suitable mask for the eyes, the operator may work with ease in an atmosphere highly charged with bromine-vapour.