In working on ores carrying large amounts of silica it is advisable to dissolve the sample in hydrochloric acid and evaporate down to dryness, then moisten with hydrochloric acid and heat until the mass softens, and then add a few cubic centimeters of strong nitric acid ; evaporate again until chlorine is driven out and then add hot water and filter off the silica and evaporate filtrate and determine manganese as usual.

I wish to acknowledge my thanks to Mr. W. Walley Davis, chief chemist, for his suggestions in regard to arranging the analytical data for publication.

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ON TRIVALENT CARBON.

(THIRD PAPER).[1]

BY M. GOMBERG.

Received July 5, 1901.

IT has been shown in the papers published by me on this subject that by the action of metals upon triphenylchlormethane the halogen can be removed quantitatively and that there results an extremely unsaturated hydrocarbon. From the behavior of this substance towards halogens and towards oxygen, the conclusion was drawn that it is an unsaturated radicle, triphenylmethyl. It was shown that the same body results whether carbon disulphide, benzene, ether, or acetic ether is employed as a solvent. It was stated that in the case of the first two mentioned solvents the unsaturated hydrocarbon remains in solution, while with ether or acetic ester as a solvent the hydrocarbon separates in the form of large transparent crystals. This crystalline body possessed all the properties of the unsaturated hydrocarbon, and was also identical with the substance which was obtained when triphenylchlormethane in benzene was acted upon by zinc and the resulting hydrocarbon was precipitated from its concentrated solution by means of ether or acetic ester. Facts have since been discovered which necessitate a modification of this view, and I desire to publish the results even in their present incomplete state.

THE ACTION OF ZINC IN ETHER AS A SOLVENT.

When triphenylchlormethane is dissolved in absolute ether and a strip of zinc is introduced, the solution at once turns yellow and

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[1] First paper : This Journal, **22**, 757 ; Second paper : *Am. Chem. J.*, **25**, 320.

a dark viscous mass begins to separate. After a while crystals begin to form which adhere to the zinc and to the sides of the vessel. If the reaction be carried on in a sealed tube it will be noticed that in a few days the black mass begins to diminish in quantity, and in about three weeks it will disappear completely. The solution still remains yellow but the crystals are colorless. It is impossible to get the ether and the reagents so absolutely free from moisture but that at least a few bubbles of hydrogen will be formed during the reaction.[1] The viscous mass which is formed at the beginning of the reaction is not zinc chloride, but a double salt of it with triphenylchlormethane.[2] Zinc chloride, I find, is soluble in ether, while the double salt is not. The thick yellow mass which was described under the experiments with benzene is also a double salt of a similar or of identical composition, and not a compound of zinc chloride with benzene, as has been previously supposed. Such a double salt when treated with water would give up all its chlorine to the latter, and this accounts for the somewhat misleading results which were obtained in the estimation of chlorine in the insoluble residue from benzene.[3] On allowing the ethereal solution to stand for some weeks the double salt is completely broken up by the metallic zinc, but in benzene this does not occur. There is no separation of the double salt when acetic ether is employed as a solvent for the simple reason that the salt is very soluble in this solvent.

The same double salt is formed with the greatest readiness when a solution of zinc chloride in ether or in acetic ether is added to a solution of triphenylchlormethane in benzene or in absolute ether. All attempts to bring it to crystallization have failed, but a number of other double salts of triphenylhalogenmethanes, and especially of tritolylchlormethane, were obtained in sufficient purity to establish the remarkable tendency of these halogen bodies towards the formation of double compounds with metallic salts. Substances of the following composition were obtained, and they will be fully described in a later paper:

$$2(C_6H_5)_3CCl.3HgCl_2,\ (C_6H_5)_3CBr.3HgBr_2,\ (C_6H_4CH_3)_3CCl.ZnCl_2$$
$$(C_6H_4CH_3)_3CCl.HgCl_2,\ (C_6H_4CH_3)_3CCl.FeCl_3.$$

All these compounds are beautifully crystalline, and are charac-

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[1] *Am. Chem. J.*, **25**, 320.

[2] This Journal, **22**, 761.

[3] *Ibid.*, **22**, 761.

terized by intense coloration, from yellow to red. There is no doubt that the yellow color which is imparted to the solution when zinc or any metal acts upon triphenylchlormethane is due in a large measure, but not entirely, to the formation of these double salts. The transparent yellow crystals which are formed when a solution of triphenylchlormethane in ether or in acetic ether is treated with zinc are not triphenylmethyl itself, but a compound of that with each of the two solvents respectively.

COMPOUND OF THE UNSATURATED HYDROCARBON WITH ETHER.

Samples of the above-mentioned yellow crystalline compound were analyzed from time to time, but the results usually fell from 2 to 3 per cent. short of 100 for the sum of carbon and hydrogen. This was at first ascribed to the absorption of oxygen by the unsaturated hydrocarbon during the washing and transference of the material. I then came back to the use of benzene as a solvent. An apparatus was constructed by means of which the benzene solution of the hydrocarbon could be concentrated in a vacuum at 30° C.; ether could then be added, and the crystals that were so formed could be filtered, washed, and thoroughly dried in an atmosphere of carbon dioxide,—all these operations being conducted in the same single piece of apparatus, without any rubber connections whatever. The crystalline product obtained in this way is almost insoluble in ether. It was washed with ether from fifteen to twenty times to insure the complete removal of the accompanying products such as triphenylmethane, triphenylcarbinol, etc. The crystals are at first perfectly colorless, but soon turn pale-yellow, the color increasing with standing. Twenty grams of triphenylchlormethane give about 7 grams of the insoluble crystalline compound. Molecular weight determinations of this substance were first made and the results were fairly satisfactory as calculated for triphenylmethyl.[1] An elementary analysis, however, gave the following results:

0.2884 gram substance gave 0.9488 gram carbon dioxide and 0.1900 gram water.

	Calculated for $(C_6H_5)_3C$.	Found.
Carbon	93.76	89.72
Hydrogen	6.24	7.37

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[1] The determinations were made by the method of the lowering of the freezing-point, in an atmosphere of nitrogen, as carbon dioxide was found to be soluble in benzene to a sufficient degree to impair the results.

A fresh sample was then prepared in a similar way and was dried over sulphuric acid in a vacuum desiccator (previously filled with carbon dioxide) over night. It gave the following results :

0.2375 gram substance gave 0.7832 gram carbon dioxide and 0.1560 gram water.

	Per cent.
Carbon	89.94
Hydrogen	7.35

A new sample was then prepared, dried, and analyzed in the same day, but the results were almost the same.

0.2447 gram substance gave 0.8060 gram carbon dioxide and 0.1585 gram water.

	Per cent.
Carbon	89.83
Hydrogen	7.25

The next sample was prepared by the addition of a mixture of acetic ether and acetic acid instead of absolute ether, in order to hold better in solution any zinc salts which might possibly have accompanied the previously mentioned samples. This sample was washed first with acetic ether and then with absolute ether. It looked whiter and more distinctly crystalline than any before obtained, but the analysis gave figures for carbon and hydrogen, the sum of which was only 95.67 per cent. The close concordance of the first three samples, and the fact that when acetic ether, which carries almost twice as much oxygen as ethyl ether, is used for precipitating the hydrocarbon, a product proportionately richer in oxygen is obtained, suggested the idea that the substances analyzed must be compounds of the hydrocarbon with the solvents.

	Calculated for $2(C_6H_5)_3C + (C_2H_5)_2O$.	Found. I.	II.	III.
Carbon	89.93	89.72	89.94	89.83
Hydrogen	7.21	7.37	7.35	7.25

That we have here such a compound is proved by the following experiment : 0.9430 gram of the ether compound was placed in a platinum boat and gently heated at 70° C. in a tube, in a stream of carbon dioxide. The loss in weight was 0.1090 gram.

	Calculated for $2(C_6H_5)_3C + (C_2H_5)_2O$.	Found.
Loss	13.22	11.56

The escaping ether was easily identified by its odor, and a few droplets were also condensed in a small U-tube which was sealed on to the further end of the tube. The amorphous yellow residue shows all the properties of the unsaturated hydrocarbon. It absorbs iodine with great eagerness ; a solution of it, when exposed to air, gives the triphenylmethyl peroxide. An analysis of the residue gave the following results :

0.1620 gram substance gave 0.5520 gram carbon dioxide and 0.1020 gram water.

	Calculated for $(C_6H_5)_3C$.	Found.
Carbon	93.76	92.93
Hydrogen	6.24	7.05

It remains yet to be settled whether this residue represents pure triphenylmethyl or a mixture of it with some of its decomposition products.

COMPOUND OF THE UNSATURATED HYDROCARBON WITH ACETIC ETHER.

A reaction entirely analogous to the one described above takes place when acetic ether is substituted for absolute ether. A compound of the unsaturated hydrocarbon with acetic ether is at once formed when triphenylchlormethane, dissolved in the ester, is treated with zinc. It is also produced when the metal is allowed to act upon the halogen compound dissolved in benzene, and to the concentrated solution acetic ether is added. The sample which furnished the results given below was prepared by the second method ; it was washed fifteen times with acetic ester, and was thoroughly dried in an atmosphere of carbon dioxide.

0.3160 gram substance gave 1.0180 gram carbon dioxide and 0.2080 gram water.

	Calculated for $2(C_6H_5)_3C + CH_3CO_2C_2H_5$.	Found.
Carbon	87.74	87.86
Hydrogen	6.69	7.37

The compound of the hydrocarbon with the ester is perfectly colorless when first prepared, but soon turns pale-yellow. It is more stable than the corresponding ether compound, and can be kept much longer without discoloration. It can be obtained in large crystals or in the form of a granular crystalline powder. On heating, it loses the ester.

1.1170 gram substance lost at 100° C. 0.1575 gram.

	Calculated for $2(C_6H_5)_3C + CH_3CO_2C_2H_5$.	Found.
Loss	15.50	14.10

The escaping acetic ester was condensed and identified as such.

The residue, after driving off the ester, looked like that obtained from the ether compound. It was amorphous, yellow, soluble in benzene and in carbon disulphide; it absorbed iodine and gave the peroxide. An analysis gave the following results:

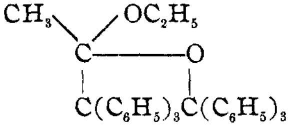
0.2135 gram substance gave 0.7250 gram carbon dioxide and 0.1322 gram water.

	Calculated for $(C_6H_5)_3C$.	Found.
Carbon	93.76	92.61
Hydrogen	6.24	6.93

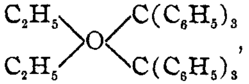
It will be noticed that in both instances the per cent. of carbon is somewhat low for triphenylmethyl. This may be accounted for by a slight oxidation, but I have no explanation at present as to the cause of the rather high per cent. of hydrogen.

WHAT IS THE NATURE OF THESE COMPOUNDS?

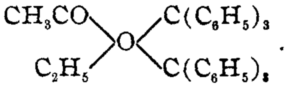
It is impossible to tell at this time whether in these two instances the ether and the acetic ester are those of crystallization or of constitution. Such a distinction is at best but an arbitrary one. One would expect that ether of crystallization would be easily driven off *in vacuo* over sulphuric acid,—which is not the case in this instance. From the extreme unsaturation of the hydrocarbon it may be assumed that it might add itself to acetic ester, giving a body something like this:



But it could hardly be expected that mere heating at 80°–100° C. would break up a chain of three carbon atoms in such a way as to regenerate the ester. Then, again, the combination with ethyl ether precludes any such addition theory in that instance. If it is not ether of crystallization, then the following constitution of that body suggests itself:



and the acetic ester compound may be supposed to have the corresponding constitution



In support of such a constitution might be cited the remarkable avidity of the hydrocarbon for oxygen, and the possibility of oxygen to act as tetravalent. Such a possibility was foreshadowed by van 't Hoff as long ago as 1877.[1] There has since been accumulating a considerable amount of evidence of physical nature pointing to such a possibility. In connection with this may be mentioned the recent work of Kanonnikow. From a study of alcohols and ethers at their critical condition, Kanonnikow[2] comes to the conclusion that in these compounds, under these conditions, the oxygen behaves as if it were tetravalent. The extreme unsaturation of triphenylmethyl presents an excellent opportunity to test the theory of the tetravalence of oxygen. The above formulas for the two compounds must be looked upon, at present, as a mere suggestion. It is my intention to extend this study to other oxygen compounds, as well as to nitrogen derivatives, and I beg to reserve this field for further work.

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June 29, 1901.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 56.]

THE ATOMIC WEIGHT OF ANTIMONY.

BY G. CLAUSEN FRIEND AND EDGAR F. SMITH.

Received June 8, 1901.

KNOWING that antimony oxide could be completely expelled from its combinations in a current of hydrochloric acid gas it appeared probable that a new ratio might be established for antimony, by exposing potassium antimonyl tartrate to the action of this gas. It will be recalled that by this procedure the atomic weights of molybdenum and arsenic had been previously determined in this laboratory. In these particular instances sodium molybdate and sodium pyroarsenate were exposed in porcelain boats, at a moderate heat, to the action of the gas, and from the weight of the residual sodium chloride the respective atomic weights were calculated. The method of work adopted with these metals was pursued with potassium antimonyl tartrate, but it was soon discovered that as carbon dioxide and water escaped the salt swelled up and was projected from the boat, so that a double crucible was substituted for the latter. On trial this de-

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[1] "Ansichten über die organische Chemie."

[2] *J. Russ. phys. chem. Soc.*, **33**, 197.