Summary

The properties and molecular weight determinations of a number of simple aromatic arsenic compounds have been recorded. Some of these compounds are stable in air, others absorb oxygen instantly; certain arseno compounds, indifferent toward oxygen, react instantly with the gas in the presence of traces of certain reagents. A number of aromatic arsenicals which contain an arsenic atom attached to arsenic or some other atom by a double bond are associated in the dissolved state.

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SUBSTITUTION OF ONE ATOM OF NITROGEN FOR THREE ATOMS OF CHLORINE IN ORGANIC COMPOUNDS. I. ACTION OF AMMONIUM CHLORIDE ON BENZO-TRICHLORIDE

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The present paper describes some work in continuation of an investigation begun more than a quarter of a century ago and of which the first contribution was published[1] in 1904. The investigation was interrupted and has only lately been resumed.

While the first paper reported the results obtained from the study of the action of ammonium chloride on metallic chlorides, the present communication is concerned with the action of sal ammoniac on benzo-trichloride, is concerned with the beginning of a study of the substitution of one atom of nitrogen for three atoms of chlorine in organic compounds.

I. It was expected that benzo-trichloride and ammonium chloride when heated in a closed tube would react as follows

$$C_6H_5CCl_3 + NH_3HCl = C_6H_5CN + 4HCl$$

In accordance with the above equation monomolecular quantities of benzo-trichloride and ammonium chloride are required. I soon learned, however, that only with an excess of at least 60% of benzo-trichloride a smooth reaction takes place whereby all the ammonium chloride is used up in the formation of benzonitrile. The experiments here described were all carried out using such an excess of benzo-trichloride.

In the end the following procedure was adopted. The glass tubes contained each 2.14 g. (4 mols) of ammonium chloride and 12.52 g. (6.4 mols) of benzo-trichloride. The heating took place between 210 and 220°. Heating periods of four to six hours are convenient. As with the quantities of the reacting bodies indicated, nearly 6 g. of hydrogen chloride was set

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[1] Fireman, THIS JOURNAL, **26**, 741 (1904).

free, a number of consecutive heatings of the same tube were required. The heating was discontinued when no more gas escaped. The final product is a thick liquid which becomes semi-solid on standing.

The product from 11 tubes, 77 g. in all, was subjected to distillation. Four fractions were separated weighing together 50.32 g. The first and fourth amounted to but a few cc. each. The first fraction went over below 182°, to which the temperature rose rapidly. The second fraction distilled over between 183 and 189°, mostly near the latter temperature. The third passed over at 189 to 197°. The fourth was collected up to 215°. The boiling point of benzonitrile is 190.6° and that of benzo-trichloride 214°. The nitrogen contents of the four fractions were, respectively, 7.2, 10.7, 12.19 and 10.6%. Thus benzonitrile predominated, as it contains, calculated, 13.59% of nitrogen. It was recognizable by its odor resembling that of bitter almond oil.

The residue in the flask, from which the benzonitrile and the benzo-trichloride were distilled off, was solid and brown-black in color. A wider bent tube was now inserted and the distillation continued. A readily solidifying liquid went over at a temperature between 235 and 260°. It solidified in the short side tube and in a small beaker which served as a receiver. About 4 g. was collected of a readily melting substance. It was for the most part easily soluble in alcohol, leaving a small residue which was very sparingly soluble in this medium. The bulk of this fraction, upon a few recrystallizations, showed a melting point of 121° and was recognized as benzoic acid. Its formation was obviously due to the presence of moisture, which acted on benzo-trichloride during the heating in the closed tubes. The sparingly soluble fraction showed a melting point of 242.5° and so proved to be kyaphenine $(C_6H_5CN)_3$ as corroborated by a nitrogen determination.

A further fraction was separated from the residue by distillation under diminished pressure. For that purpose an Auschütz distilling flask with a fused-on receiving tube was used. The distillation was carried out at 15-mm. down to 7-mm. pressure at temperatures of 265 to 335°. About 6 g. of a white, slightly yellowish product was obtained. This distillate was separated into two substances by boiling with alcohol. Copious quantities of the latter dissolved out a white substance, leaving the other, much larger in amount, exceedingly little soluble in that menstruum.

After repeated treatments with boiling alcohol a white powder was obtained which melted at 233° and proved to be kyaphenine $(C_6H_5CN)_3$.

The less difficultly alcohol-soluble white substance, upon recrystallization, shows a melting point of 269–270°. A combustion gave: C, 91.96; H, 6.67—indicating a hydrocarbon. A search in the "International Critical Tables" suggested tetraphenylmethane, with a melting point of 285° (corr.), as most nearly corresponding to the results obtained: calcd.

for $(C_6H_5)_4C$: C, 93.75; H, 6.25. Gomberg,[2] who was the first to prepare tetraphenylmethane, gave at first 272° as its melting point, later 280° and last 281.5–282°, which corrected is 285°. He crystallized this hydrocarbon from benzene, which when hot dissolves it freely. My white substance upon crystallization from benzene presented a network with occasional separate slender long crystals or sheaf-like formations of fine needles and now melted at 271°. I take it to be tetraphenylmethane containing a small admixture of kyaphenine. Its formation may have taken place according to the reaction

$$3C_6H_5CN + C_6H_5CCl_3 = (C_6H_5)_4C + 3CNCl$$

This supposition I intend to submit to an experimental test.

As a last residue, after all distillations, there remained a black lustrous substance which had solidified from a molten state.

II. The Reaction Autocatalytic.—Early in this investigation it was observed that on successive heatings and openings of the same tube, increasing quantities of hydrogen chloride were set free in equal periods of time. The following experiments, a few of many, will show this strikingly.

Though the heating was carried out in an ordinary bomb furnace of the Lothar Meyer type (with flaps at the ends), great care was used to make the successive heatings in each set of experiments as nearly alike as possible. The fluctuations of the temperatures in the middle of the furnace during the four-hour heatings rarely exceeded ±1°.

On opening the tubes only a portion of the hydrogen chloride formed

TABLE I

HYDROGEN CHLORIDE LIBERATED

	Expt. at 215°		Expt. at 220°		Expt. at 210°
Period	Tube 1, g.	Tube 2, g.	Tube 1, g.	Tube 2, g.	Tube 1, g.
I	0.328	0.330	0.441	0.385	0.266
II	.457	.457	.562	.603	.371
III	.758	.600	.827 (.107)[a] (.515)[b]	.895 (.108)[a] (.565)[b]	.440
IV	.905	.832	1.915	1.972	.590
V	1.490	1.085	1.553	1.343	.740
VI	1.605	1.825			1.353
VII	0.565	0.888			1.380
VIII					0.783
Total HCl, g.	6.108	6.017	5.890	5.871	5.923

Calcd., 5.840 g.

[a] One of the four tubes heated at the same time exploded before 220° was reached (at 217°) causing discontinuance of the heating. [b] In resuming the heating, another tube exploded seventy-one minutes after 220° was reached.

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[2] Gomberg, *Ber.*, **30**, 2045 (1897); THIS JOURNAL, **20**, 776 (1898); Gomberg and Berger, *Ber.*, **36**, 1909 (1903); Gomberg and Cone, *ibid.*, **39**, 1463 (1906).

rushes out. A number of days must be allowed the escape of gas for its entire removal. During that time considerable moisture is liable to enter the tubes. A calcium chloride tube was slipped over the tip to prevent this. All tubes were heated during four-hour periods, opened after each period and resealed again.

The growing speed in successive periods at once becomes evident. Obviously the increasing velocity of the reaction corresponds to the increasing accumulation of benzonitrile.

I am inclined to believe that the cause of benzonitrile serving as a cata lytic agent is the ability of this nitrile to absorb hydrogen chloride. Benzonitrile seems to form a feeble compound with the latter under pressure greater than the atmospheric. This compound gradually decomposes on opening the tubes.

Summary

1. When benzo-trichloride and ammonium chloride are heated in a closed tube at about 200° and above, substitution of one atom of nitrogen for three atoms of chlorine takes place, with the formation of benzonitrile and hydrogen chloride.

2. All the nitrogen of ammonium chloride can be utilized for such a substitution only in the presence of an excess of at least 60% of benzotrichloride.

3. A small part of the benzonitrile polymerizes to tribenzonitrile, or kyaphenine.

4. A small amount of tetraphenylmethane is also found as a product of the reaction.

5. The reaction is autocatalytic.

It may be noted that the substitution of nitrogen for chlorine in benzotrichloride is by no means a unique case. Already Liebig[3] through the action of gaseous ammonia and ammonium chloride on phosphorus pentachloride obtained "chlorophosphuret of nitrogen" which, as Gladstone and Holmes[4] later showed, had the composition $(PNCl_2)_3$. Also long ago Heintz[5] was able, by heating a solution of ammonia in absolute alcohol with chloroform at a temperature of 180–190°, to obtain at times ammonium cyanide, at times paracyanogen $(CN)_x$. Shortly later Cloëz[6] found the following reaction to take place

$$CHBr_3 + 5NH_3 = NH_3HCN + 3NH_3HBr$$

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[3] Liebig, *Ann.*, **11**, 146 (1834).

[4] Gladstone and Holmes, *J. Chem. Soc.*, [2] **2**, 225 (1864).

[5] Heintz, *Ann.*, **100**, 369 (1856).

[6] Cloëz, *Compt. rend.*, **46**, 348 (1858).