ART. XXXI.— *On some derivatives of Trichlormethyl-sulphon-chlorid*, $(CCl_3)SO_2Cl$; by O. LOEW, Assistant in the Chemical Department of the College of the City of New York.

THIS chlorid, discovered by Berzelius and Marcet in 1812, was the subject of extended investigations by Kolbe. Since that time no investigations on this compound have been made, although it possesses many interesting properties. I find that the simplest way to prepare it, is the following: 300 grms. bichromate of potassium in pieces of the size of a pea, 500 grm. common hydrochloric acid, 200 grm. nitric acid of the common strength, and 30 grm. bisulphid of carbon are mixed in a flask, filling it to one-fourth of its capacity and loosely stoppered. It is kept cool in the beginning and shaken from time to time. In about eight days the process is finished. In direct sunlight only four days are required. By addition of water the chlorid and nitrate of potassium are dissolved, and there remains the insoluble trichlormethyl-sulphon-chlorid. It is filtered off, washed, and pressed between sheets of filter-paper.

When this chlorid is dissolved in absolute alcohol and treated with sulphuretted hydrogen, sulphur is deposited, and hydrochloric acid and another compound of an acid character remain in solution. By neutralization with dry carbonate of sodium, the sodium salt of this new acid remains dissolved in the alcohol, and crystallizes by evaporation in shining scales.

0·469 grm. yielded 0·146 grm. sulphate of sodium = 11·33 per cent Na.
0·236 grm. yielded 0·490 grm. AgCl = 51·37 per cent Cl.
0·511 grm. yielded 0·605 grm. sulphate of barium = 16·24 per cent S.

The sodium salt of the trichlormethyl-sulphurous acid requires: 11·14 per cent Na; 51·95 per cent Cl; 15·56 per cent S; 15·56 per cent O; 5·81 per cent C.

To obtain the free trichlormethyl-sulphurous acid, the sodium salt is decomposed by dilute hydrochloric acid and agitated with ether. The ether yields by evaporation this new acid in radiating needles. Both the acid and its salts are not of great stability; at a moderate temperature, especially when water is present, decomposition takes place and a very offensive odor is evolved.

The formation of this acid takes place according to the following equation:

$$\underbrace{(CCl_3)\,SO_2Cl}_{\text{Trichlormethyl-sulphon-chlorid.}}{}^{*} + H_2S = \underbrace{(CCl_3)\,SO\,OH}_{\text{Trichlormethyl-sulphurous acid.}} + HCl + S.$$

The decomposition of this acid and its salts by bromine and nitric acid is very striking; the acid disappears and new insoluble compounds are formed.

The action of bromine is expressed by the following equation:

$$\underbrace{(CCl_3)\,SO\,OH}_{\text{Trichlormethyl-sulphurous acid.}} + Br_2 = \underbrace{(CCl_3)\,SO_2\,Br}_{\text{Trichlormethyl-sulphon-bromid.}} + HBr.$$

and the action of nitric acid:

$$\underbrace{(CCl_3)SO\,OH}_{\text{Trichlormethyl-sulphurous acid.}} + \underbrace{NO_3H}_{\text{Nitric acid.}} = \underbrace{(CCl_3)SO_2(NO_2)}_{\text{Trichlormethyl-sulphon-nitrid.}} + H_2O$$

The trichlormethyl-sulphon-bromid is a white crystalline body of a faint acrid smell, insoluble in water but soluble in alcohol and ether. On the application of heat a part is sublimed without change while another part is decomposed. Ammonia dissolves it with evolution of nitrogen.

0·358 grm. yielded 0·313 sulphate of barium corresponding to 12·01 per cent S.

0·492 grm. yielded 1·158 grm. AgCl+AgBr and this mixture yielded by reduction 0·808 Ag, which proportions correspond to 30·77 per cent Br, and 40·22 per cent Cl.

The theory demands 12·19 per cent S, 40·57 per cent Cl, 30·43 per cent Br.

When trichlormethyl-sulphurous acid is brought into contact with concentrated nitric acid, a violent reaction takes place and a blue oil is deposited which loses nitrous acid by contact with the air and is converted into a white crystalline body, the odor of which inflames the eyes and is very suffocating when inhaled. This is the trichlormethyl-sulphon-nitrid especially interesting in this, that a nitrid of an organic sulph-acid has been hitherto unknown. It is insoluble in water, soluble in ether and alcohol. Water added to the alcoholic solution precipitates it unchanged. It does not melt in boiling water but is volatilized with the steam. Ammonia dissolves it slowly with decomposition, alcoholic solution of caustic potassa decomposes it quickly. When it is treated with zinc and hydrochloric acid it disappears and is converted into sulphydrate of methyl and ammonia:

* C=12 S=32 O=16.

$$\underbrace{(CCl_3)SO_2(NO_2)}_{\text{Trichlormethyl-sulphon-nitrid.}} + 18H = \underbrace{CH_3SH}_{\text{Sulphydrate of methyl.}} + H_4NCl + 2HCl + 4H_2O$$

0·5285 grm. yielded 0·532 sulphate of barium and 0·973 AgCl, corresponding to 13·83 per cent S and 46·12 per cent Cl.
Theory demands 14·00 per cent S and 46·61 per cent Cl.

On treating trichlormethyl-sulphon-chlorid with ammonia, trichlormethyl-sulphurous acid is formed in an unexpected manner, nitrogen is evolved and the chlorid is slowly dissolved. On evaporation broad tabular crystals are obtained. In the mother-liquor there remains chlorid of ammonium, some sulphate of ammonium and a certain quantity of this new compound. The crystals must be recrystallized with great care because at a moderate temperature an acid reaction sets in and a partial decomposition begins. These crystals show with bromine as well as with nitric acid the formation of the above mentioned bromid and nitrid. The action of the nitric acid is extremely violent.

By mixing with diluted hydrochloric acid and agitating with ether the above mentioned trichlormethyl-sulphurous acid is obtained.

0·431 grm. yielded 0·911 grm. AgCl = 52·24 per cent Cl.
0·668 grm. yielded 0·725 ammonio-chlorid of platinum = 6·80 per cent N.
0·753 grm. yielded 0·894 grm. sulphate of barium = 16·23 per cent S.
Theory demands 53·11 per cent Cl, 6·98 per cent N, 15·96 per cent S.

The crystals are therefore the ammonium salt of the trichlormethyl-sulphurous acid and their formation can be expressed by the following equation :

$$\underbrace{3((CCl_3)SO_2Cl)}_{\text{Trichlormethyl-sulphon-chlorid.}} + 8H_3N = \underbrace{3((CCl_3)SO_2H_4N)}_{\text{Trichlormethyl-sulphite of ammonium.}} + 2N + 3H_4NCl$$

On treating trichlormethyl-sulphon-chlorid with cyanid of potassium, evolution of cyanogen and hydrocyanic acid takes place and the potassium salt of trichlormethyl-sulphurous acid is formed :

$$(CCl_3)SO_2Cl + 2KCy = (CCl_3)SO\,OK + KCl + 2Cy$$

But when the solution is hot and very concentrated, there is also another derivative of this acid formed, one atom of Cl being replaced by one atom of OH.

$$(CCl_3)SO\,OK + H_2O = (CCl_2OH)\,SO\,OK + HCl,$$

which latter decomposes another part of the cyanid of potassium.

A glance at the following formulas will show the relation between these new bodies and several others already known :

Trichlormethyl-sulphon-chlorid ($C Cl_3$)SO_2Cl (Kolbe).
Trichlormethyl-sulphon-bromid ($C Cl_3$)SO_2Br.
Trichlormethyl-sulphon-nitrid (CCl_3)$SO_2(NO_2)$.

Trichlormethyl-sulphur*ic* acid (CCl_3)SO_2OH (Kolbe.)
Trichlormethyl-sulphur*ous* acid ($C Cl_3$)$SO OH$.
Methylsulphur*ic* acid (CH_3)SO_2OH (Kolbe.)
Methylsulphur*ous* acid (CH_3)$SO OH$ (Hobson.)

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