

XV.—*On some Compounds of Ether with Anhydrous Metallic Chlorides.*

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(1.) *Ether and Oxychloride of Vanadium.*

IF equal parts of ether and vanadium oxychloride are carefully mixed, the liquid becomes slightly warm, and the canary-coloured

oxychloride changes to a dark brown tint. On heating for 2—3 hours in a closed glass tube to a temperature of  $60^{\circ}$ — $70^{\circ}$ , the liquid separates into two layers, the lower of which is a brown oily liquid, while the upper consists of excess of ether holding in solution a portion of the new compound. In order to purify the substance, the mixture is distilled under a pressure of 160—200 mm. on a water-bath. First ether distils over, and then a brown oil, which, on exposure to a low temperature solidifies, and even condenses in the neck of the retort, in the form of long needle-shaped crystals, which however, melt with the warmth of the hand. The distillation is stopped as soon as the residue in the retort begins to solidify. Water decomposes this body slowly into ether, vanadium pentoxide, and hydrochloric acid. The analysis, therefore, offers no particular difficulties. The chlorine is first determined in a nitric acid solution, and the filtrate, after removing the silver, is evaporated down, and yields on ignition the fused vanadium pentoxide.

Analyses 2 and 3 are of one preparation; 4, 5, and 6 are of another. They show that the substance is a compound of one molecule of vanadium oxychloride with one of ether.

1. Weight of substance taken = 0.604 gram.  
     "    AgCl obtained   = 1.0345 "    = 42.37 per cent. Cl.  
     "    V<sub>2</sub>O<sub>5</sub>         "    = 0.215 "    = 20.00 "    V.
2. Weight of substance taken = 0.2805 gram.  
     "    AgCl obtained   = 0.477 "    } = 42.52 per cent. Cl.  
     "    Ag                = 0.004 "    }  
     "    V<sub>2</sub>O<sub>5</sub>         "    = 0.1055 "    = 21.13 "    V.
3. Weight of substance taken = 0.315 gram.  
     "    AgCl obtained   = 0.5445 "    } = 43.11 per cent. Cl.  
     "    Ag                = 0.0035 "    }  
     "    V<sub>2</sub>O<sub>5</sub>         "    = 0.1165 "    = 20.78 "    V.
4. Weight of substance taken = 0.468 gram.  
     "    AgCl obtained   = 0.790 "    } = 42.20 per cent. Cl.  
     "    Ag                = 0.0065 "    }  
     "    V<sub>2</sub>O<sub>5</sub>         "    = 0.1635 "    = 19.63 "    V.
5. Weight of substance taken = 0.396 gram.  
     "    CO<sub>2</sub> formed     = 0.276 "    = 19.00 per cent. C.  
     "    H<sub>2</sub>O         "    = 0.163 "    = 4.57 "    H.
6. Weight of substance taken = 0.4755 gram.  
     "    CO<sub>2</sub> formed     = 0.3495 "    = 20.04 per cent. C.  
     "    H<sub>2</sub>O         "    = 0.1945 "    = 4.54 "    H.

Results.	Calculated.	Mean.	1.	2.	3.	4.	5.	6.
V..	20·70	20·36	20·00	21·13	20·78	19·63	—	—
Cl <sub>3</sub> .	42·97	42·55	42·37	42·52	43·11	42·20	—	—
C <sub>4</sub> ..	19·37	19·52	—	—	—	—	19·00	20·04
H <sub>10</sub> .	4·03	4·55	—	—	—	—	4·57	4·54
O <sub>2</sub> ..	12·93	—	—	—	—	—	—	—
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100·00								

Freshly prepared, this substance forms splendid long or stelliform crystals, which by transmitted light appear of a reddish brown colour, and possess a green metallic lustre; they melt under 20°. The substance is a very unstable one, and soon undergoes spontaneous decomposition, even when sealed up in glass tubes, yielding a brown liquid. The brown residue left in the retort contains, together with some oxychloride of vanadium, the oxides of the metal.

### (2.) *Ether and Titanium Tetrachloride.*

By the action of alcohol on titanium tetrachloride, Demarçay (*Compt. rend.*, lxxx, 51—53) obtained a crystallised compound  $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{Cl.HCl}$ , which when treated with sodium ethylate is converted into ethyl titanate,  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ . In his remarks on this compound, Demarçay states that Friedel had already obtained a titanium ethyl-chlorhydrin,  $\text{TiCl}_3(\text{OC}_2\text{H}_5)$ , by the action of alcohol or ether on titanium tetrachloride. This compound is not, however, the immediate product of the action of ether on titanium chloride, but is formed from one, or probably two, molecular compounds of these two bodies, the chlorhydrin being obtained from them by the action of heat.

Ether acts violently on chloride of titanium, and, therefore, when these two bodies are brought together, care must be taken that they are both well cooled. The yellow colour of the chloride soon changes to a brown, and, on cooling, yellow crystals separate out, which can only with difficulty be separated from the dark thick mother-liquor. In order to isolate this body, the mixture of equal parts of ether and titanium chloride is distilled; the excess of ether distils off, and as soon as the temperature reaches 100°, an amber-coloured liquid distils over, which solidifies on cooling. When the temperature, which slowly rises, has reached 130°, the distillation is stopped, as that which now comes over deposits little or none of the crystalline substance. The compound decomposes violently when brought in contact with water, ether, hydrochloric acid, and titanium dioxide being formed, which latter remains in solution.

For analysis the aqueous solution was treated with a slight excess of ammonia, and the oxide filtered off; in the filtrate, after acidifica-

The analyses Nos. 1, 7, 8 are made from one portion of the substance which distilled between 100°—125°, whilst No. 2 distilled from 118°—120°; that used for Nos. 3 and 4 between 117°—120°, and that for Nos. 5 and 6 between 114°—118°.

- \* In these cases the weights 0.004 gram and 0.005 of  $\text{TiO}_2$  were got by evaporating the filtrates and igniting the residue.

Results.	Calculated.	Mean.	1.	2.	3.	4.	5.	6.	7.	8.
Ti.	18.79	18.41	18.77	18.45	—	—	18.16	18.27	—	—
Cl <sub>4</sub> .	53.39	53.28	54.14	53.41	53.08	52.41	—	—	—	—
C <sub>4</sub> .	18.04	17.84	—	—	—	—	—	—	17.87	17.81
H <sub>10</sub> .	3.75	4.03	—	—	—	—	—	—	4.00	4.06
O.	6.03	—	—	—	—	—	—	—	—	—

This body, which corresponds to the tin compounds  $\text{SnCl}_4 + \text{C}_4\text{H}_{10}\text{O}$  discovered by Kuhlman, forms a yellow crystalline mass which melts between  $42^\circ$ — $45^\circ$ , and boils between  $118^\circ$ — $120^\circ$ . On cooling the liquid, small tabular crystals separate out first; these increase in size until at last the whole mass solidifies.

This compound also undergoes a spontaneous alteration when kept in hermetically sealed tubes, first becoming of a greenish colour, and then gradually liquefying.

If more ether be added to the mixture of ether and titanium chloride used for the preparation of this compound, the whole dissolves, forming a thick brown liquid, from which, when the excess of ether is driven off in a current of dry air, no crystals can be obtained. This residue gave analytical results which correspond with the formula  $2\text{TiCl}_4 + 3\text{C}_4\text{H}_{10}\text{O}$ .

### (3.) *Titanium Trichlorhydrin.*

When the residue obtained in the preparation of the two preceding compounds is strongly heated, first titanium tetrachloride, and afterwards Friedel's trichlorhydrin, distil over. In order to obtain the latter in considerable quantity, the mixture of ether and titanium chloride may be quickly heated in an oil-bath. Ether and a little of the compound  $\text{TiCl}_4(\text{C}_4\text{H}_{10}\text{O})$  first distil over, and then the titanium chloride and the chlorhydrin. At the same time a combustible gas, burning with a green-mantled flame is evolved, which condenses on passing through a freezing mixture, and, therefore, consists of chloride of ethyl. The chlorhydrin separates on cooling from the portion boiling between  $160^\circ$ — $172^\circ$  in crystalline nodular masses. The pure substance melts between  $76^\circ$ — $78^\circ$ , and boils between  $186^\circ$ — $188^\circ$ . The following analyses show that the formula is  $\text{TiCl}_3(\text{OC}_2\text{H}_5)$ .

- Weight of substance taken = 0.5285 gram.
 

“	$\text{TiO}_2$ obtained	= 0.2175	“	= 25.08	per cent.	Ti.
“	AgCl	“	= 1.1205	“	} = 53.27	“ Cl.
“	Ag	“	= 0.014	“		

2. Weight of substance taken = 0.904 gram.  
 „  $\text{TiO}_2$  obtained = 0.3745 „ = 25.19 per cent. Ti.  
 „  $\text{AgCl}$  „ = 1.937 „ } = 53.80 „ Cl.  
 „ Ag „ = 0.0195 „ }

Combustion :—

3. Weight of substance taken = 0.371 gram.  
 „  $\text{CO}_2$  formed = 0.163 „ = 11.90 per cent. C.  
 „  $\text{H}_2\text{O}$  „ = 0.0865 „ = 2.59 „ H.  
 4. Weight of substance taken = 0.3495 gram.  
 „  $\text{CO}_2$  formed = 0.151 „ = 11.76 per cent. C.  
 „  $\text{H}_2\text{O}$  „ = 0.081 „ = 2.57 „ H.  
 5. Weight of substance taken = 0.458 gram.  
 „  $\text{CO}_2$  formed = 0.200 „ = 11.90 per cent. C.  
 „  $\text{H}_2\text{O}$  „ = 0.1125 „ = 2.73 „ H.

Results.	Calculated.	Mean.	1.	2.	3.	4.	5.
Ti ..	24.81	25.13	25.08	25.19	—	—	—
$\text{Cl}_3$ ..	52.85	53.53	53.27	53.80	—	—	—
$\text{C}_2$ ..	11.91	11.83	—	—	11.90	11.76	11.90
$\text{H}_5$ ..	2.48	2.63	—	—	2.59	2.57	2.73
O ..	7.95	—	—	—	—	—	—
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