635. *The Halides of Niobium (Columbium) and Tantalum.* Part V.*
Diethyl Ether Complexes of the Pentachlorides and Pentabromides; the
Solubility of Tantalum Pentaiodide in Ether.

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Crystalline 1 : 1 complexes between diethyl ether and $NbCl_5$, $TaCl_5$, $NbBr_5$, and $TaBr_5$ have been prepared, and their compositions established by analysis and vapour-pressure measurements. TaI_5 does not form an ether complex. The solubilities of the pentachlorides and pentabromides in ether are greater than the ideal: that of TaI_5 is less.

The complexes decompose at about 100° into ethyl halide and metal oxytrihalide. The oxytrihalides disproportionate at higher temperatures into pentoxide and pentahalide.

Niobium and tantalum pentafluorides [1] and pentachlorides [2] are Friedel–Crafts-type catalytic metal halides. We now find that tantalum pentachloride and both pentabromides are also. These halides are therefore electron acceptors or Lewis acids, and should form addition compounds with ethers, although no such compounds appear to have been described. These ether complexes are relevant to the general chemistry of these metals and in particular to their co-ordination with oxygen, which dominates it in aqueous systems.

We have examined the interaction between the pentachlorides and pentabromides and diethyl ether and in each case isolated a stable crystalline 1 : 1 complex with a dissociation pressure, at 16°, of less than 1 cm. Hg.

We were unable to find any evidence of complex formation between ether and tantalum pentaiodide, nor does this halide appear to possess any significant Friedel–Crafts-type catalytic activity; whereas the solubility of the pentachlorides and the pentabromides is greater than ideal, that of tantalum pentaiodide is less.

Pyrolysis of the ether complexes splits the ether at temperatures near 100° with the formation of ethyl halide and metal oxytrihalide, the latter disproportionating at higher temperatures into the pentahalide and pentoxide.

We approached the problem both by the study of the temperature variation of the solubility of the halides in ether and by the measurement of the vapour pressure of ether–halide systems.

EXPERIMENTAL

Preparation of Halides.—Niobium pentachloride was prepared from the pure metal sheet and dry chlorine at 300—350°, as described by Alexander and Fairbrother.[3] Tantalum pentachloride was prepared by passing dry hydrogen chloride over the metal sheet at 350—400°. The

* Part IV, *J.*, 1954, 1031.

[1] Fairbrother and Frith, *J.*, 1951, 3051.

[2] Grosse and Ipatieff, *J. Org. Chem.*, 1937, **1**, 559; Dermer and Billmeier, *J. Amer. Chem. Soc.*, 1942, **64**, 464.

[3] Alexander and Fairbrother, *J.*, 1949, S223.

bromides were very conveniently prepared, in excellent yield and free from hydrolysis products, by the following technique. About 5 g. of sheet metal were placed in a silica boat in the tube shown in Fig. 1, and an excess of dry bromine run into the end limb through C, which was then sealed off. The bromine was degassed and then solidified in liquid air, and the rest of the tube heated and evacuated through D, which was then sealed off. The section A–B was heated to 400—450°, and the bromine allowed to warm to room temperature. Reaction proceeded smoothly, the bromide condensing in the sealed end E.

Tantalum pentaiodide was prepared as described by Alexander and Fairbrother [4] from iodine vapour and a cylinder of the metal, heated in an induction furnace. The halides were all purified by five or six fractional sublimations *in vacuo* and finally sublimed into fragile hook-ended ampoules.

Ether.—Anæsthetic ether was distilled from one-fifth of its volume of sulphuric acid, kept over phosphoric oxide for at least a week, decanted, fractionated under dry nitrogen, and finally stored over bright sodium wire.

Solubility Measurements.—These were carried out in an all-glass sealed apparatus by using the technique described by Fairbrother, Scott, and Prophet.[5] For solubilities below room temperature the apparatus was agitated in a methylated spirits–water thermostat, continually cooled by a refrigerator unit, and heated by a conventional heater. An upper limit was set to the range of temperature by the b. p. of the ether and the necessity to ensure that it did not split. In every case, at the end of a completed run a small amount of ether was condensed from the remaining solution, and its infrared absorption spectrum examined. This confirmed the absence of any decomposition.

The ether was pre-treated similarly [5] with the halide under examination. The ampoules containing the saturated ether solution were cracked about the middle without separation and broken under water. After standing for 4—5 hr. the solution was heated to about 90°, cooled, and filtered, and the halide determined volumetrically. The filtered oxide was also ignited and weighed as a check on the halide determination. The latter, however, being capable of a greater precision, was used in calculation of the solubilities. In the Table are given the solubilities (s) as g. of halide dissolved by 100 g. of ether, and in Fig. 2 the log mole-fraction of solute (x_1) as a function of $1/T$.

NbCl$_5$		TaCl$_5$		NbBr$_5$		TaBr$_5$		TaI$_5$	
t	s	t	s	t	s	t	s	t	s
2·6°	10·93	−5·8°	13·24	2·2°	2·99	3·0°	6·41	3·0°	2·29
10·1	12·99	1·8	14·78	5·6	3·20	8·5	7·52	5·8	2·43
15·7	14·99	7·0	15·78	10·0	3·53	18·9	8·80	9·0	2·56
20·0	18·32	16·3	18·39	14·6	3·65	21·4	10·09	15·7	2·94
22·6	23·37	18·5	21·08	17·1	3·73			20·0	3·27
24·9	24·92	20·5	26·61	20·9	4·34				

The accurate computation of the ideal solubilities of these compounds by the formula given by Hildebrand and Scott [6] *viz.*,

$$\log_{10} x_1 = \frac{-\Delta H^\circ{}_{T(m)}}{4 \cdot 575 T(m)} \left(\frac{T(m)}{T} - 1 \right) + \frac{\Delta C^\circ{}_p}{4 \cdot 575} \left(\frac{T(m)}{T} - 1 \right) - \frac{\Delta C^\circ{}_p}{1 \cdot 987} \log_{10} \frac{T(m)}{T}$$

where x_1 is the mole-fraction of solute and $T(m)$ the melting point, is precluded by the absence of any data regarding the change in molar heat capacity on fusion, $\Delta C^\circ{}_p$. Nevertheless, since this quantity is usually very small in comparison with the molar heat of fusion at the melting point, $\Delta H^\circ{}_{T(m)}$, a sufficiently approximate value of the ideal solubility can be gained by the use of the first term only. Neglect of the terms in $\Delta C^\circ{}_p$ would not invalidate the present argument. The " ideal " solubilities given in Fig. 2 are calculated on this basis. The values for the melting points and heats of fusion are taken from the work of Alexander and Fairbrother.[3,4]

From Fig. 2 it can be seen that the molar solubilities of niobium and tantalum pentachlorides are almost indistinguishable over the range of temperatures examined. This holds also for the ideal solubilities, in which case the slightly lower heat of fusion of NbCl$_5$ is compensated by its lower melting point.

[4] Alexander and Fairbrother, *J.*, 1949, 2472.
[5] Fairbrother, Scott, and Prophet, *J.*, 1956, 1164.
[6] Hildebrand and Scott, " The Solubility of Non-Electrolytes," New York, 3rd edtn., 1950.

At the higher temperatures the actual solubilities of the pentachlorides and pentabromides are roughly parallel to their ideal solubilities, lying in each case much higher, as would be expected from complex formation. The smaller gradient of the $\log x_1$–$1/T$ curves at lower temperatures is probably due to additional solvation of the complex. This is supported by the evidence of a greater apparent molecular weight at these temperatures as deduced from vapour-pressure measurements. In the case of the bromides, the differences between their actual solubilities and between their ideal solubilities are very close, which again indicates a very similar energy of interaction with ether.

Tantalum pentaiodide, on the other hand, was exceptional (insufficient for the less stable niobium pentaiodide was available for similar experiments); vapour-pressure measurements
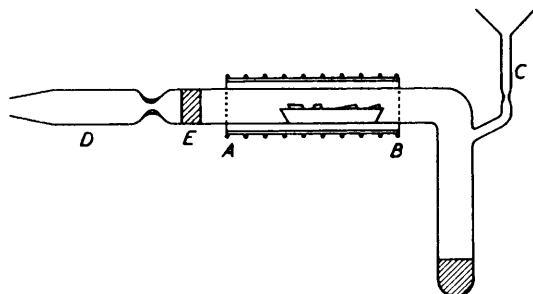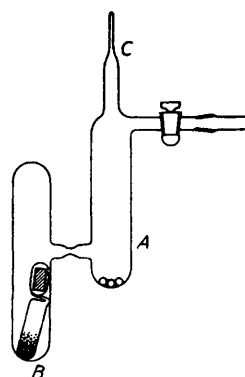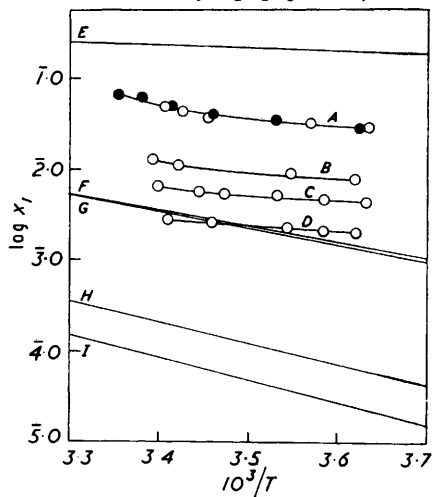
FIG. 1.

FIG. 3.

FIG. 2. *Plots of* $\log x_1$ *against* $1/T$.

A, $NbCl_5$ (black circles), $TaCl_5$ (open circles); B, $TaBr_5$; C, $NbBr_5$; D, TaI_5. Curves E, F, G, H, and I are the ideal solubility curves for TaI_5, $NbCl_5$, $TaCl_5$, $TaBr_5$, and $NbBr_5$ respectively.

gave no evidence of complex formation and the ether could be distilled away, leaving the pentaiodide apparently unchanged. The molar solubility of this halide is much less than of the other four and its solubility lies well below the ideal. As regards the actual position of the ideal solubility curve, this is calculated with the use of the rather low heat of fusion (1·6 kcal./mole) derived as a difference between the relatively much larger heats of sublimation (19·7 kcal./mole) and of volatilisation (18·1 kcal./mole). Any errors in the magnitude of the heat of fusion, however, would be unlikely to affect qualitatively the present conclusion. We were also unable to observe any Friedel–Crafts-type catalytic activity of tantalum pentaiodide. This lack of acceptor properties in tantalum pentaiodide is probably due to the greater screening of the metal acceptor atom by the large iodine atoms. The pentafluorides are excellent Friedel–Crafts catalysts.[1]

Vapour-pressure Measurements.—These were carried out in a conventional type of apparatus in which a measured amount of dry ether contained in a 25 c.c. graduated pipette was condensed by cooling on a weighed quantity of halide contained in a 100 c.c. conical reaction flask. The halide was introduced under nitrogen in a sealed ampoule, cracked about its middle and broken, by shaking, under the ether. The reaction flask contained also a quantity of dry glass wool to assist in the attainment of equilibrium. It was attached to the rest of the apparatus by a flexible glass spiral and continuously shaken mechanically under the surface of the thermostat

water. Ingress of moisture through the joint (B24) of the removable reaction vessel was prevented by a thick layer of Apiezon-Q compound covered in turn by a layer of collodion. In each system, measurements were made at the temperature of melting ice and at about 16° ($\pm 0.02°$). The thermostat could be lowered from the reaction vessel, and the entire measuring system was enclosed in a large air thermostat kept at 19—20° $\pm$ 0.5°, the manometers being read from a distance by a cathetometer. The measuring system also included an additional bulb into which pure ether was condensed which, with its associated manometer, permitted readings to be made of the depression of vapour pressure.

Portions of the ether were removed from the reaction system from time to time by cooling the pipette, which was then returned to 20° for measurement, due allowance being made for the ether present in the " dead space " of the apparatus.

Even with the aid of the glass wool and with continuous agitation, equilibrium was sometimes established very slowly, especially when solid phase was present.

At the conclusion of a run the reaction vessel was filled with dry nitrogen, and samples of the complex were removed, in a dry box, for analysis. A number of specimens for analysis and for X-ray examination were also prepared independently as described below.

All the pressure–composition diagrams were of the usual type, showing a rather ill-defined break which corresponded approximately to the solubility measurements, a very sharp " knee " where the pressure dropped abruptly, at a composition of 1 mol. of halide to 1 mol. of ether, to the low dissociation pressure of the ether complex. The complexes were so stable and the dissociation pressures so low that in most cases it was very difficult to pump off any more ether and condense it in liquid nitrogen. These were as follows:

Complex	Temp.	Press. (mm.)	Temp.	Press. (mm.)	Complex	Temp.	Press. (mm.)	Temp.	Press. (mm.)
$NbCl_5,Et_2O$	0°	0·39	16·69°	0·73	$NbBr_5,Et_2O$	0°	2·06	15·89°	3·21
$TaCl_5,Et_2O$	0	0·92	15·92	1·96	$TaBr_5,Et_2O$	0	6·32	15·90	9·63

Each tantalum complex has a higher dissociation pressure than the niobium, and each bromide than the chloride.

Calculations were made, from the lowering of the vapour pressure in dilute solution, by use of Raoult's law and the assumption that the complex was MX_5,Et_2O, *i.e.*, virtually increasing the concentration by this amount of ether complexed. No great accuracy is claimed for the results, which showed a considerable scatter, but the mean values were sufficiently close to show that at 16° MX_5,Et_2O was essentially the species present in solution but that at 0° the solutions were effectively more concentrated, a result of the further solvation of the complexes.

System Niobium Pentachloride–Diethyl Ether.—Niobium pentachloride dissolved readily to give a yellow solution, which deposited green-yellow crystals of the *ether complex*, m. p. 83° (decomp.) [Found: Nb, 27·3, 27·1, 27·2; Cl, 51·2, 51·1, 51·2%; M, in solution at 0°, 1096; at 16·7°, 354. $NbCl_5,(C_2H_5)_2O$ requires Nb, 27·0; Cl, 51·5%; M, 355].

System Tantalum Pentachloride–Diethyl Ether.—Tantalum pentachloride dissolved readily to give a colourless solution which deposited colourless crystals of the *ether complex*, m. p. 80° (decomp.) [Found: Ta, 41·4, 42·5, 42·1; Cl, 40·1, 40·8, 40·8%; M, in solution at 0°, 680; at 15·9°, 422. $TaCl_5,(C_2H_5)_2O$ requires Ta, 41·9; Cl, 41·0%; M, 444].

System Niobium Pentabromide–Diethyl Ether.—Niobium pentabromide dissolved to give a red solution which deposited brown crystals of the *ether complex*, m. p. 71° (decomp.) [Found: Nb, 17·3, 17·5, 17·7, 16·3, 16·8, 16·6; Br, 70·0, 69·4, 69·0, 62·1, 61·9, 63·6%; M, in solution at 0°, 854; at 15·9°, 594. $NbBr_5,(C_2H_5)_2O$ requires Nb, 16·4; Br, 70·5%; M, 567].
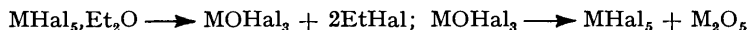
System Tantalum Pentabromide–Diethyl Ether.—Tantalum pentabromide dissolved to give an orange-coloured solution which deposited orange crystals of the *ether complex*, m. p. 77° (decomp.) [Found: Ta, 27·5, 27·8, 27·9, 28·1, 27·9, 27·9; Br, 59·6, 61·2, 59·8, 60·2, 58·6, 59·0%; M, in solution, at 0°, 854; at 15·9°, 675. $TaBr_5,(C_2H_5)_2O$ requires Ta, 27·6; Br, 61·0%; M, 655].

X-*Ray Examination.*—Samples of the ether complexes for this purpose and for analysis were prepared in the apparatus shown in Fig. 3 in which C is a thin-walled Pyrex glass capillary. The halide B and dry ether were successively sublimed into A. After the reaction and removal by pumping of excess of ether, the crystals of the complex were ground by shaking with glass balls on a vibro-shaker. The apparatus was then inverted, and the etherate shaken into the capillary. The apparatus was then filled with dry nitrogen, and the capillary broken off and quickly sealed with soft wax.

Diffraction photographs were taken with Cu-K_α radiation by use of a nickel filter and a 19 cm. camera. The X-ray photographs were very complex and many-lined. Photographs of the pure halides were also taken for comparison.

The two chlorides and the two bromides all showed similar X-ray patterns: with a given halogen the spacings were almost indistinguishable. On the other hand, although the ether complexes of the two pentachlorides are isomorphous, those of the two pentabromides appear to differ from one another and from those of the pentachlorides.

Pyrolysis of the Ether Complexes.—This was investigated primarily as a possible route to the preparation of the oxyhalides, though this proved not to be the best method of preparing them. The ether complexes were heated in a vacuum for varying periods at several temperatures up to about 500°. The volatile products were condensed at −195°, and both they and the involatile residues analysed. The results indicated that the essential stages in the decomposition were

$$\text{MHal}_5,\text{Et}_2\text{O} \longrightarrow \text{MOHal}_3 + 2\text{EtHal}; \quad \text{MOHal}_3 \longrightarrow \text{MHal}_5 + \text{M}_2\text{O}_5$$

The composition of the solid products varied according to the temperature and time of heating, but in general, heating at about 100° led to a solid product, which was analysed as the oxytrihalide. Heating at higher temperatures gave products which varied according to the halide under examination. Ether complexes of niobium pentachloride and pentabromide at 90° and 112°, respectively, gave oxytrihalides. These, on further heating *in vacuo* at 200° and 250°, sublimed very slowly without decomposition, giving very fine crystals (diffuse X-ray pattern), but disproportionated at still higher temperatures. The tantalum halide complexes, however, showed a marked disproportionation of the oxytrihalides below 300°. After the tantalum pentachloride complex had been heated at 490° for 16 hr. and the pentabromide complex at 450° for 6 hr., almost all the halogen was eliminated, with a sublimate which was found to be the pentahalide, and a residue which X-ray diffraction showed to be the pentoxide. In all cases ethyl halide was eliminated as a volatile product.