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JAMES SOWDEN JENNINGS,

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SOME NEW TITANIUM COMPOUNDS.

METALLIC COMPOUNDS OF α-BENZOINOXIME.

I wish to express my gratitude to Dr.William Wardlaw for valuable advice and assistance, and for helpful criticism throughout these investigations.

C O N T E N T S .

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P A R T I.

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SECTION A.

SOME ESTERS OF ORTHOTITANIC ACID.

SECTION B.

TWO ETHERATES OF TITANIUM TETRACHLORIDE.

P A R T II.

METALLIC COMPOUNDS OF α-BENZOINOXIME.

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PART I.

SECTION. A.

SOME ESTERS OF ORTHOTITANIC ACID.

SECTION B.

TWO ETHERATES OF TITANIUM TETRACHLORIDE.

SECTION A.

SOME ESTERS OF ORTHOTITANIC ACID.

Group IV may be considered as a transition group linking the more positive metals of Groups I - III with the more negative elements of Groups V - VIII ; as a result, metals and non-metals are more evenly balanced in this group than in any of the others, and in keeping with the generalisations of the periodic system, both subgroups show an increase in metallic character with rise of atomic weight.

As would be expected from the general considerations, the quadrivalent halides show little tendency to ionise in aqueous solution, the presence of ions in solutions of these halides can only be demonstrated in a few cases. Instead, they are readily hydrolysed (except carbon tetrachloride which is unaffected), and the extent of hydrolysis is variable. As a rule clear solutions are at first obtained and the hydrolysis is gradual, intermediate products being frequently formed.

According to N.V.Sidgwick[1], when ionisation is impossible, the water has a tendency to attach itself to the molecule, subsequently reacting with the halogen. This happens in the case of silicon tetrachloride. Although the silicon atom in silicon tetrachloride has completed its octet, it can expand this to 12 - covalency 6 - and so can take up two water molecules by co-ordination. The hydrolysis of titanium tetrachloride and other

non-ionised chlorides is similarly explained.

A general survey of the known properties of titanium tetrachloride indicates that in many respects it bears a striking resemblance to the tetrachloride of silicon.

The present work was undertaken to ascertain how far titanium tetrachloride could be brought into line with silicon tetrachloride as regards its reaction towards some alcohols.

The first silicon ester was prepared by M.Ebelmen[2] by the reaction between silicon tetrachloride and absolute alcohol, the preparation being repeated, later by C.Friedel and J.M.Crafts[3], who named their product ethyl silicate. These investigators extended the work studying the chloro ethyl silicates and discovered that ethyl silicate would react with a further molecule of silicon tetrachloride to yield a dichloro silicate (dichloro diethoxy silicon , $Si(OEt)_2Cl_2$.) Furthermore, by allowing another alcohol to react with the dichloro diethoxy silicon they obtained a mixed alkoxy silicon, e.g., $Si(OEt)_2(OC_5H_{11})_2$.

Again, C.Friedel and A.Ladenburg[4] found that tetraethoxy silicon would react with acetyl chloride to form chloro triethoxy silicon in accordance with the equation :-

$$Si(OEt)_4 + CH_3.CO.Cl = Si(OEt)_3Cl + CH_3.CO.OEt.$$

The esters of orthosilicic acid are well known, tetraethoxy silicon, $Si(OEt)_4$, having many interesting technical applications. The corresponding titanium compounds are , however, much less familiar and in the literature many conflicting statements are recorded.

An early investigator, E.Demarcay[5], described $Ti(OEt)_4$ as a white crystalline compound but his analytical data were unsatisfactory. He attributed the discrepancies in his results to the presence of variable quantities of titanic acid in his product.

More recent workers, F.Bischoff and H.Adkins[6] concluded, that although the methyl derivative, $Ti(OMe)_4$, was a solid, yet the ethyl analogue was a colourless liquid as were also the propyl and butyl derivatives. They expressed the opinion that Demarcay's compound was actually an oxytitanate and that he had never isolated the ester, $Ti(OEt)_4$.

During the present investigation the ester, $Ti(OEt)_4$ was prepared and found to be a liquid, thereby confirming the statement of F.Bischoff and H.Adkins. Furthermore, the preparation of tetramethoxy titanium has been re-investigated and isolated as a white solid.

The method of preparation of the esters $R(OEt)_4$ where R equals Si or Ti emphasises a most striking difference between the reactions of the tetrachlorides

of these two elements. Though tetraethoxy silicon is readily obtained from the tetrachloride and alcohol :

$$SiCl_4 + 4EtOH = Si(OEt)_4 + 4HCl ,$$

yet tetraethoxy titanium can only be obtained from the reaction between titanium tetrachloride and sodium ethoxide :

$$TiCl_4 + 4NaOEt = Ti(OEt)_4 + 4NaCl.$$

If ethyl alcohol is used instead of sodium ethoxide a white crystalline compound is isolated to which E.Demarcay assigned the formula (I) $TiCl(OEt)_3.HCl$. Prolonged action of boiling alcohol fails to alter the composition of this substance and no hydrogen chloride is eliminated when the compound is confined over solid potassium hydroxide. This is very remarkable, for one would not have expected a molecule of hydrogen chloride to be bound so firmly to the complex.

Reference to Demarcay's paper shows that the structure assigned to this compound is based solely on the results of analysis. Therefore, the possibility is not excluded that the compound is really (II) $TiCl_2(OEt)_2.EtOH$; in fact the experimental data of Demarcay support this formula (II) for it explains why boiling alcohol does not eliminate hydrogen chloride.

To test the possibility that the compound had the formula (II) , the compound $TiCl(OEt)_3$ was prepared from the reaction between tetraethoxy titanium and acetyl chloride in equimolecular proportions in accordance with the equation :-

$Ti(OEt)_4 + CH_3.CO.Cl = TiCl(OEt)_3 + CH_3.CO.OEt.$

This compound did not combine with hydrogen chloride on being dissolved in alcoholic hydrogen chloride but yielded instead crystals of a new substance $TiCl(OEt)_3.EtOH$. Crystals of the same composition were obtained by dissolving $TiCl(OEt)_3$ in a small quantity of ethyl alcohol. It seems most unlikely, therefore , that Demarcay's compound possesses the formula he assigned to it.

The compound $TiCl_2(OEt)_2$ was now prepared by refluxing titanium tetrachloride and ethyl alcohol for several hours and then distilling the products under reduced pressure. One product , obtained as an oil which yielded a white solid , was the required substance $TiCl_2(OEt)_2$. When this was dissolved in the minimum amount of warm alcohol and then cooled, a mass of needle shaped , colourless crystals separated. These crystals proved to be $TiCl_2(OEt)_2.EtOH$, identical in crystalline form and composition with Demarcay's compound. These results appear to prove that formula (II) is correct and that the compound is not of the type supposed by Demarcay .

Experiments have been extended to the reactions between titanium tetrachloride and other alcohols , viz.,

methyl, isopropyl and isobutyl alcohols. In every instance a compound has been obtained of the formula $TiCl_2(OR)_2.ROH$, where R equals CH_3 ; C_2H_5 ; $C3H_7$; C_4H_9 . Furthermore, by heating these substances under reduced pressure derivatives without alcohol of crystallisation, viz., $TiCl_2(OR)_2$ were obtained except in the case of $TiCl_2(OMe)_2.MeOH$.

The dichloro dialkoxy titaniums which have been isolated during this investigation are white solids very soluble in alcohol and to a smaller extent in ether , acetone and other organic solvents and are rapidly hydrolysed in air. They dissolve in water instantly yielding clear solutions.

By treating two of these dichloro dialkoxy titaniums, $Ti(OC_4H_9)_2Cl_2$ and $Ti(OEt)_2Cl_2$ with ethyl and methyl alcohol respectively the compounds $Ti(OC_4H_9)_2Cl_2.EtOH$ and $Ti(OC_4H_9)_2Cl_2.MeOH$ were produced on the one hand ,and $Ti(OEt)_2Cl_2.EtOH$ and $Ti(OEt)_2Cl_2.MeOH$ on the other.

It seems reasonable to suppose that the compounds of the general type $TiCl_2(OR)_2$ have a great tendency to combine with alcohol and crystallise from this solvent in alcoholated form.

From the reaction between $Ti(OEt)_4$ and acetyl chloride in the appropriate proportion a new compound

$Ti(OEt)_3Cl$ has been prepared as a pale yellow, viscous liquid :

$$Ti(OEt)_4 + CH_3.CO.Cl = Ti(OEt)_3Cl + CH_3.CO.OEt .$$

From alcohol it crystallises as colourless needles with the composition $TiCl(OEt)_3.EtOH$.

The following series of compounds are now known :- $Ti(OEt)_4$; $Ti(OEt)_3Cl$; $Ti(OEt)_2Cl_2$.

The preparation of the trichloro ethoxy titanium deemed to have been obtained by C.Friedel[7] , and mentioned by E.Demarcay[8] , was attempted but proved unsuccessful. The methods were those outlined by P.P.Bedson[9], Viz., the reaction between ethyl alcohol (1 mol.) and titanium tetrachloride (1 mol.), and secondly by the action of ether on titanium tetrachloride. The last named reaction was also studied by H.R.Ellis[10], whose findings , an oil and three different crystalline products, neither agree with those of P.P.Bedson, who claims the obtaining of a compound $2TiCl_4.3(C_2H_5)_2O$, nor with C.Friedel postulating the trichloro ethoxy titanium, nor with the results of the present work.

The first attempt, viz., the reaction between titanium tetrachloride and alcohol in unimolecular proportions, resulted in the formation of a yellow viscous mass which distilled at 100°- 110° under reduced pressure (18mm.). On cooling, it solidified yielding a bright

yellow coloured solid which was extremely unstable, evolving copious quantities of hydrogen chloride on exposure to air.

The investigation of the reaction between ether and titanium tetrachloride led to the production of two etherates of that compound ; these are discussed in the second part of this work.

Too marked a parallelism cannot be drawn between the action of alcohol on silicon tetrachloride and that on titanium tetrachloride. While the former gives rise to tetraethoxy silicon, the entire chlorine content having been replaced by ethoxy groups, the latter only gives rise to the dichloro diethoxy titanium ; more drastic means are necessary to effect complete substitution, sodium ethoxide must be used.

Secondly, the tetraalkoxy derivatives of the two elements are similar as regards their ability to react with acetyl chloride and give rise to analogous compounds, viz., $Si(OEt)_3Cl$; $Ti(OEt)_3Cl$ and $Si(OEt)_2Cl_2$; $Ti(OEt)_2Cl_2$. But the titanium esters, here mentioned, are capable of crystallising in alcoholated form, not only with the alcohol from which they were derived , but also with a different alcohol of crystallisation, whereas alcoholated silicon esters have not been reported.

Again , while silicon tetrachloride can form mixed alkyl silicates, e.g. by the reaction between dichloro diethoxy silicon and amyl alcohol, titanium tetrachloride once it has suffered the substitution of two ethoxy groups for two chlorine atoms seems immune from further attack by alcohol.

The two series of esters undergo hydrolysis, probably following the same mechanism, owing to the fact that water can form compounds with them by co-ordination with subsequent decomposition of these substances in the manner indicated by N.V.Sidgwick.[1]

E X P E R I M E N T A L .

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Throughout this investigation 'all-glass' apparatus was employed , and the use of rubber and corks eliminated.

TETRAMETHOXY TITANIUM.

This compound was prepared according to the method of F. Bischoff and H.Adkins[6]. Sodium (12.5 g.) was dissolved in methyl alcohol (150 g.) and the solution placed in an ice-cooled flask fitted with a tap-funnel having a side arm . Precautions were taken against the ingress of moisture. Titanium tetrachloride (25 g.) was added dropwise from the funnel with constant shaking of the mixture, the addition being spread over a period of two hours. The mixture was then refluxed at 80°- 100° for one hour. At the end of this period the excess alcohol was distilled off and the residue further distilled under reduced pressure. At about 300°/ 18 mm., a sublimate was formed. This white substance had the composition $Ti(OMe)_4$.

Found : Ti, 28.02 , 27.97.

Calculated for $TiO_4C_4H_{12}$, Ti, 27.90 % .

TETRAETHOXY TITANIUM.

This substance was prepared by the same method (loc. cit.). To a solution of sodium (12.5 g.) in ethyl alcohol (185 g.) titanium tetrachloride (25 g.) was added, and the mixture well cooled . It was then

refluxed at 80° - 100° for three hours when excess alcohol was removed. The white, solid residue in the flask was then distilled under reduced pressure. At 140° - 150° a colourless liquid was collected (b.pt. 142°/ 18 mm.), which proved to have the composition $Ti(OEt)_4$.

Found : Ti, 20.90 , 21.01 .

Calcuated for, $TiO_4C_8H_{20}$, Ti, 21.05 %.

DICHLORO DIMETHOXY TITANIUM.

To dry methyl alcohol (40 c.c.) contained in a flask, fitted with a tap-funnel having a side arm, titanium tetrachloride (25 g.) was slowly added, the mixture being frequently shaken, and kept well cooled by immersion in an ice-bath. The reaction was extremely vigourous. The pale yellow liquid produced was then distilled under reduced pressure at 70° - 80° when excess alcohol was removed. The residue in the flask solidified on standing to give a white solid which was dried in a desiccator over phosphoric oxide. It proved to have the composition $Ti(OMe)_2Cl_2.MeOH$.

Found : Ti, 22.82 , 22.94 ; Cl, 33.01 , 32.96.

$TiO_3C_3H_{10}Cl_2$ requires , Ti , 22.53 ; Cl, 33.34 %.

MONO CHLORO TRIETHOXY TITANIUM.

The apparatus consisted of a flask fitted with a Claisen neck adapter supporting a tap-funnel and condenser. Precautions against the ingress of moisture were taken by fitting a phosphoric oxide tube to the mouth of the condenser. To tetraethoxy titanium (13 g.) contained in the flask, acetyl chloride (4.5 g.) was added from the funnel. The reaction proceeded with some vigour being accompanied by the evolution of ethyl acetate. The mixture was then refluxed at 70° - 80° for three hours and then fractionally distilled. At 190° - 200° a pale yellow liquid was obtained, (b.pt. 176° / 18 mm.) ; on cooling this became viscous. It had the composition $Ti(OEt)_3Cl$.

Found : Ti, 21.89 , 21.96 ; Cl, 16.28 , 16.26.

$TiO_3C_6H_{15}Cl$ requires, Ti, 21.97 ; Cl, 16.25 %.

To this product (5g.) was added warm ethyl alcohol (5 c.c.) and from the solution a mass of colourless needles separated. These were washed with alcohol and dried in a desiccator over phosphoric oxide. They had the composition $Ti(OEt)_3Cl.EtOH$.

Found : Ti, 18.06 , 18.11 ; Cl, 13.37 , 13.47.

$TiO_4C_8H_{21}Cl$ requires, Ti, 18.14 ; Cl, 13.42 %.

A further quantity (5 g.) was similarly treated with alcoholic hydrogen chloride (5 c.c.). From the solution colourless needles separated on standing, and proved to have the same composition .

Found : Ti, 18.01 , 17.97 ; Cl, 13.72 , 13.61.
$TiO_4C_8H_{21}Cl$ requires, Ti, 18.14 ; Cl, 13.42 %.

DICHLORO DIETHOXY TITANIUM.

(i) Mono chloro triethoxy titanium, $Ti(OEt)_3Cl$, (10 g.) and acetyl chloride (3.7 g.) were refluxed together at 70° - 80° for two hours. At the end of this period the mixture was fractionally distilled under reduced pressure. At 150° - 160° a pale yellow liquid was obtained (b.pt. 142° / 20 mm.), which on cooling gave a pale yellow solid which had the composition $Ti(OEt)_2Cl_2$.

Found : Ti, 22.81 , 22.72 : Cl, 33.84 , 33.68.
$TiO_2C_4H_{10}Cl_2$ requires, Ti, 22.97 ; Cl, 33.98 %.

(ii) To ethyl alcohol (25 g.),contained in a flask fitted with a Claisen neck adapter supporting a tap-funnel and condenser, titanium tetrachloride (25 g.) was added gradually. During the addition the mixture

was well shaken and effectively cooled by immersion in an ice bath. When all had been added the resulting pale yellow liquid was refluxed at 80°- 100° for 24 hours. Upon cooling it yielded a whitish, viscous mass which was then fractionally distilled. At 180°- 200° a pale yellow liquid was collected (b.pt. 142°/ 20 mm.) , which on cooling gave a white solid and had the composition $Ti(OEt)_2Cl_2$.

Found : Ti, 22.88, 22.91; Cl, 33.81, 33.75 .
$TiO_2C_4H_{10}Cl_2$ requires, Ti, 22.97 ; Cl, 33.98 %.

To this product (4 g.) warm methyl alcohol (3 c.c.) was added, and on cooling a mass of needle shaped, colourless crystals separated. After washing with alcohol and drying in a desiccator over phosphoric oxide their composition corresponded to $Ti(OEt)_2Cl_2.MeOH$.

Found ; Ti, 19.87 , 19.78 ; Cl, 29.39 , 29.30 .
$TiO_3C_5H_{14}Cl_2$ requires, Ti, 19.92 ; Cl, 29.46 %.

Another solution was made by dissolving dichloro diethoxy titanium (4g.) in warm ethyl alcohol . From this solution a mass of needle shaped colourless crystals separated. These were washed with alcohol and dried

in a desiccator over phosphoric oxide. They proved to have the composition $Ti(OEt)_2Cl_2.EtOH$.

Found : Ti, 18.76, 18.71 ; Cl, 27.74, 27.71.
Calculated for $TiO_3C_6H_{16}Cl_2$, Ti, 18.82 ; Cl, 27.85 %.

This product was also prepared by the following method of E.Demarcay[8].

To ethyl alcohol (25 g.) contained in an ice-cooled flask, fitted with a tap-funnel, titanium tetrachloride (25 g.) was added dropwise with constant shaking of the mixture. This was then distilled at 80°- 100° under reduced pressure. The solid product remaining in the flask was then dissolved in the minimum amount of warm ethyl alcohol. On cooling, needle shaped colourless crystals separated. These were removed, washed with alcohol and dried over phosphoric oxide. They had the composition $Ti(OEt)_2Cl_2.EtOH$.

Found : Ti, 18.78, 18.76 ; Cl, 27.57, 27.62.
Calculated for $TiO_3C_6H_{16}Cl_2$, Ti, 18.82 ; Cl, 27.85 %

DICHLORO DIISOPROPOXY TITANIUM.

To isopropyl alcohol (33 g.) contained in a flask, fitted with a Claisen neck adapter supporting a

tap-funnel and condenser, titaniumtetrachloride (25g.) was added, the mixture being subsequently refluxed at 80° - 100° for nine hours. At the end of this time it was fractionally distilled, and at 160° - 170° a pale yellow liquid was collected (b.pt. 160°/ 18 mm.). Upon cooling this yielded a white solid which proved to have the composition $Ti(OC_3H_7)_2Cl_2$.

Found : Ti, 20.14 , 20.11 ; Cl, 29.87 ; 29.90

$TiO_2C_6H_{14}Cl_2$ requires, Ti, 20.25 ; Cl, 29.96 %

When this product (3g.) was dissolved in isopropyl alcohol (5 c.c.) colourles , needle shaped crystals separated which after washing with ether and drying over phosphoric oxide had the composition $Ti(OC_3H_7)_2Cl_2.C_3H_7OH$.

Found : Ti, 15.97 , 15.91 ; Cl, 23.85, 23.31.

$TiO_3C_9H_{22}Cl_2$ requires, Ti, 16.15 ; Cl, 23.91 %.

The same compound was also prepared by adding titanium tetrachloride (25g.) to isopropyl alcohol (33g.) and refluxing the mixture at 80° - 100° for nine hours. Upon cooling, a white solid separated which was washed with ether and dried over phosphoric oxide. It had the composition $Ti(OC_3H_7)_2Cl_2.C_3H_7OH$.

Found : Ti, 16.01, 15.95 ; Cl, 23.82 , 23.76 .

$TiO_3C_9H_{22}Cl_2$ requires, Ti, 16.15 ; Cl, 23.91 %

DICHLORO DIISOBUTOXY TITANIUM.

Isobutyl alcohol (50 g.) was placed in a flask fitted with a Claisen neck adapter supporting a tap-funnel and condenser, precautions being taken against the ingress of moisture. Titanium tetrachloride (25g.) was then added dropwise from the funnel. When all had been added the mixture was refluxed for 24 hours at 80° - 100°. It was then fractionally distilled, and at 190° - 200° a pale yellow liquid was obtained (b.pt. 184° / 18 mm.). Upon cooling, it gave a white solid having the composition $Ti(OC_4H_9)_2Cl_2$.

Found : Ti, 17.92 , 17.90 ; Cl, 26.67 , 26.70.
$TiO_2C_8H_{18}Cl_2$ requires, Ti, 18.11 ; Cl, 26.80%.

This product (5 g.) was dissolved in warm methyl alcohol (4 c.c.) and from the solution a mass of colourless needles separated which after washing with ether and drying over phosphoric oxide had the composition $Ti(OC_4H_9)_2Cl_2.MeOH$.

Found : Ti, 16.05 , 16.05 ; Cl, 23.71 , 23.82.
$TiO_3C_9H_{22}Cl_2$ requires, Ti , 16.15 ; 23.91 %

From a solution of dichloro diisobutoxy titanium, $Ti(OC_4H_9)_2Cl_2$, (5g.) in warm ethyl alcohol (5 c.c.)

a quantity of needle shaped, colourless crystals separated on cooling. They had the composition $Ti(OC_4H_9)_2Cl_2.EtOH$.

Found : Ti, 15.40 , 15.34 ; Cl, 22.71 , 22.78.
$TiO_3C_{10}H_{24}Cl_2$ requires, Ti, 15.43 ; Cl, 22.83 %.

When dichloro diisobutoxy titanium (5 g.) was dissolved in warm isobutyl alcohol (5 c.c.) a mass of colourless needles were obtained on cooling, and had the composition $Ti(OC_4H_9)_2Cl_2.C_4H_9OH$.
Found : Ti, 13.98 , 14.07 ; Cl, 20.88 , 20.90.
$TiO_3C_{12}H_{28}Cl_2$ requires, Ti, 14.16 ; Cl, 20.94 %.

The same compound was also prepared in the following manner. To isobutyl alcohol (50 g.), contained in a flask fitted with a tap-funnel, titanium tetrachloride (25 g.) was slowly added. The mixture was then distilled under reduced pressure at 100° - 110°. The solid residue in the flask was then dissolved in warm isobutyl alcohol and on cooling a white mass separated, which after washing with ether and drying over phosphoric oxide had the composition $Ti(OC_4H_9)_2Cl_2.C_4H_9OH$.
Found : Ti, 13.72 , 13.68 ; Cl, 20.81 , 20.88.
$TiO_3C_{12}H_{28}Cl_2$ requires, Ti, 14.16 ; Cl, 20.94 %

B I B L I O G R A P H Y .

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S E C T I O N B.

T W O E T H E R A T E S O F

T I T A N I U M T E T R A C H L O R I D E .

Many metallic halides such as sodium chloride, potassium bromide, silver iodide and calcium chloride show no reaction towards ether. On the other hand there are certain metallic chlorides and bromides which combine with ether and under special circumstances react with it.

Observations recorded by some investigators, A.Coldridge[1], B.Lewy[2], show that stannic chloride reacts violently with ether forming a compound which, on heating, sublimes unchanged. Analytical data indicate that it has the formula $SnCl_4.(C_2H_5)_2O$. To this compound H.R.Ellis[3] assigned an oxonium structure.

M.Nickles[14] claimed that stannic bromide and ether react to yield deliquescent crystals containing one molecule of each component, and further, report the synthesis of an etherate of aluminium trichloride, $AlCl_3(C_2H_5)_2O$. In contrast to the etherates of tin halides which distil unchanged, an iron compound, $FeCl_3.(C_2H_5)_2O$, prepared by A.Foster , C.Cooper, and G.Yarrow[5], began to decompose slowly at 100° and at red heat evolved ethyl chloride, and yielded a residue of iron oxychloride.

The reaction between silicon tetrachloride and ether was studied by F.S.Kipping and A.G.Murray[6] who found that reaction proceeded to a slight extent even

at ordinary temperatures. They asserted that in all probability the reaction took place in accordance with the equation :-

$$SiCl_4 + (C_2H_5)_2O = SiCl_3(OC_2H_5) + C_2H_5Cl .$$

Reference to their paper shows that not only is the reaction slight but also reversible.

C.Friedel[7] investigated the action of ether on titanium tetrachloride and reported that it yielded trichloro ethoxy titanium, $TiCl_3(OC_2H_5)$: he named it the trichlorhydrin. Furthermore, he claimed to have obtained the same compound from the reaction between titanium tetrachloride and ethyl alcohol.

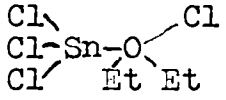
Later, P.P.Bedson[8] re-investigated the ether-titanium tetrachloride reaction and stated that the compound $TiCl_3(OC_2H_5)$ is not the immediate product of the reaction, but that it probably results from the effect of heat upon one or two molecular compounds of ether and titanium tetrachloride formed during the initial reaction. He reports that the first stage of the reaction gives rise to yellow crystals, the isolation of which he effected in the following manner. Equal quantities of ether and titanium tetrachloride were allowed to react and by fractional distillation an amber coloured liquid, (B.pt.100°), was obtained. This amber coloured liquid solidified on

cooling and corresponded to the compound of tin, $SnCl_4.(C_2H_5)2O$, discovered by F.Kuhlman[9] . By using excess of ether he obtained a thick brown liquid which did not crystallise. It proved to have the composition $2TiCl_4.3(C_2H_5)_2O$.

He then investigated the action of heat upon the residue obtained in the above preparations and claimed to have obtained a product $TiCl_3(OC_2H_5)$ together with some titanium tetrachloride. He detected some ethyl chloride.

H.R.Ellis[3] re-opened the investigation of the same reaction and claimed to have obtained several products. His method of preparation was similar to that of P.P.Bedson, but his products, obtained by fractional distillation, were more numerous. The first fraction (36°) contained ether, hydrogen chloride and a yellow liquid which subsequently crystallised. A second fraction (60°) yielded gem-like crystals. Again at 160° a yellow liquid was obtained which produced yellowish white crystals on cooling. Finally, at 170° - 196° he obtained a distillate which gave orange coloured crystals (m.pt. 70°) on cooling. No analyses, except that of the residue, are recorded and the various fractions are described as decomposing slowly in air evolving ethyl chloride and hydrogen chloride. He concludes that his products were double compounds of titanium tetrachloride and ether,

similar in structure to the crystalline body obtained when stannic chloride and ether react. He formulates this compound of tin as an oxonium derivative and assigns the formula



In the present work the reaction of ether and titanium tetrachloride has been re-investigated. As regards the experiments of C.Friedel, it has already been shown (Part I. p.7.) that the compound $TiCl_3(OC_2H_5)$ could not be obtained either from the reaction between titanium tetrachloride (1 mol.) and alcohol (1 mol.) ,or from that between titanium tetrachloride and ether. As far as the last reaction is concerned, continued distillation of the residue beyond 160° merely resulted in the production of free titanium tetrachloride, some ether and subsequent decomposition.

Moreover, it is rather surprising that C.Friedel did not report the production of a pale yellow compound in the initial stages, which has been observed by other investigators, and has been produced and isolated during the present investigation.

Up to a point, the observations made here agree with those of P.P.Bedson. It has been found that from the reaction of ether upon titanium tetrachloride a

yellow crystalline compound, $TiCl_4.2(C_2H_5)_2O$, sublimes without the slightest difficulty in the form of yellow needles. On further heating, the crystals melt and then distil giving a yellow coloured oil which has the composition $TiCl_4.(C_2H_5)_2O$. P.P.Bedson does not record the preparation of this substance but claims to have obtained an oil of the composition $2TiCl_4.3(C_2H_5)_2O$. This appears to be a mixture of $TiCl_4.(C_2H_5)_2O$ and $TiCl_4.2(C_2H_5)_2O$.

Unfortunately, H.R.Ellis in his investigation did not give any analytical results for his products. It has not been possible to confirm the existence of the many products he mentions.

It seems most unlikely that the etherates of titanium tetrachloride are any other that co-ordination compounds. The analytical data ; the existence of only two compounds; the donor character of ether ; the compliance with the covalency rule ; the entire absence of ethyl chloride during their preparation, all point to the probability that the compounds are

$$\begin{matrix}(C_2H_5)_2O \searrow \\ (C_2H_5)_2O \nearrow \end{matrix} TiCl_4 \qquad \text{and} \qquad (C_2H_5)_2O \rightarrow TiCl_4$$

E X P E R I M E N T A L .

TITANIUM TETRACHLORIDE DIETHERATE.

Dry ether (40 c.c.) was placed in a flask fitted with a tap-funnel having a side arm to which was attached a U-tube standing in an ice-salt bath. Precautions were taken against the ingress of moisture by closing the apparatus with a calcium chloride tube. The flask was also immersed in an ice bath and allowed to attain the low temperature before starting the reaction. Titanium tetrachloride (25 g.) was added dropwise from the funnel. An immediate and vigourous reaction ensued with the separation of a bright yellow coloured solid. When all had been added, the apparatus was sealed and left overnight. The yellow compound was then transferred to an apparatus specially devised in order to sublime as much material as possible and to provide for a quick dismantling and removal of the product to a vessel which could be effectively sealed.

The apparatus consisted of a tube $1\frac{1}{2}$ inches wide and closed at one end. The stopper which fitted it was attached on its under side to another similar tube which fitted exactly inside the first tube, the inner one being drawn out to $\frac{1}{4}$ inch, passed through the stopper and then bent at right angles. The apparatus was closed by means of a calcium chloride tube. A duplicate of the first tube and a spare stopper were held in readiness for use later.

The apparatus was then heated to 70° and maintained at that temperature for three hours, during which period beautiful, yellow needles sublimed into the upper part of the inner tube. No ethyl chloride was detected . The stopper and inner tube were then removed and placed in the duplicate first tube. A few taps served to shake the sublimate into the lower tube which was then closed with the spare stopper. The crystals proved to have the composition $TiCl_4.2(C_2H_5)_2O$.

Found : Ti, 14.18 , 14.15 ; Cl, 41.91 , 41.86.

$TiO_2C_8H_{20}Cl_4$ requires , Ti, 14.23 ; Cl, 42.02 %

TITANIUM TETRACHLORIDE MONOETHERATE.

The above preparation was repeated and the total yield placed in a boiling tube with its side arm bent at right angles and connected to another similar tube standing in a water bath maintained at 40° - 50°. This second tube was attached to two U-tubes, the first of which stood in cold water and the second in an ice-salt bath, the apparatus being closed by means of a calcium chloride tube to prevent the ingress of moisture. The dietherate was then distilled and at 110° and oily liquid was obtained. 15 to 20 c.c. of ether collected in the first U-tube but

no ethyl chloride or hydrogen chloride was detected. When distillation ceased (after $1\frac{1}{2}$ hours) the temperature was raised to 120° - 130° yet nothing further distilled. At a higher temperature decomposition set in with the production of some ether and free titanium tetrachloride. The oily liquid did not solidify and proved to have the composition $TiCl_4.(C_2H_5)_2O$.

Found : Ti, 17.96 , 18.13 ; Cl, 53.68 , 53.67.

$TiOC_4H_{10}Cl_4$ requires, Ti, 18.18 ; Cl, 53.80 %.

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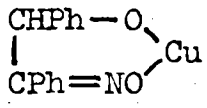
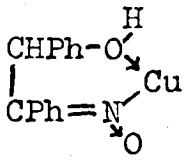
P A R T 2.

M E T A L L I C C O M P O U N D S O F α-B E N Z O I N O X I M E .

Benzoinoxime is one of a number of organic reagents recently employed in the detection and estimation of metals. The copper derivative, discovered by Feigl[1], is a deep green amorphous compound which is insoluble in water and organic solvents and when dried at 105°-115° contains 22.02% copper in accordance with the formula(I) assigned to it by Feigl. This structure, however, cannot be regarded as fully established.



(I)

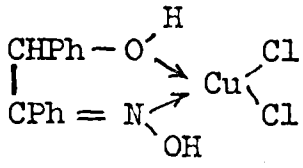


)II(

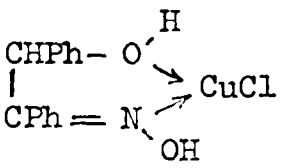
It is unusual to find the hydrogen atom of the secondary alcoholic group replaced by copper ; moreover , benzoinoxime is a reducing agent and one would expect it to reduce a proportion of the cupric salt to the cuprous state. From the analytical data, structure (II), which is that of a cuprous compound, is a possible alternative to (I). Decomposition of Feigl's compound with hydrochloric acid yielded cuprous chloride, but, as hydroxylamine hydrochloride was formed simultaneously, this is no indication of the valency state of the copper.

Convincing evidence in favour of (I) has, however, been obtained by treating Feigl's compound

with alcoholic hydrogen chloride ; the green crystalline salt (IIa) then separates with a molecule of alcohol of crystallisation.



(IIa)

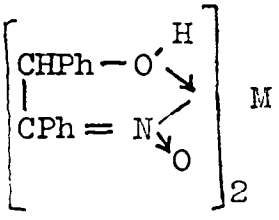


(IIb)

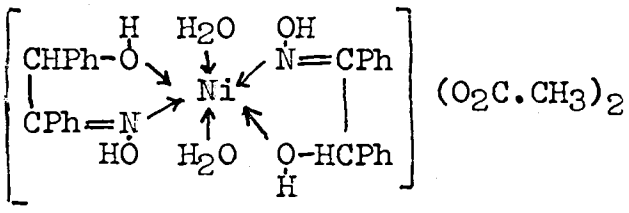
With hot water, two molecules of hydrogen chloride are eliminated from (IIa) and the original compound (I) is produced. A compound of formula (II) would give the derivative (IIb) on treatment with alcoholic hydrogen chloride. Whilst Feigl's compound must have structure (I) , there is, at present no decisive evidence whether the ring is five or six-membered.

Feigl states that nickel and cobalt salts do not give precipitates with benzoinoxime, but it is mentioned in " Organic Reagents for Metals"[2] that this is incorrect. Observations made in the present work confirm the latter opinion for it has been found that these metals give respectively a brown and a buff precipitate with the reagent. In addition, bivalent palladium and platinum give derivatives with benzoinoxime ; the former immediately the latter slowly. Considerable difficulty was experienced in preparing any of these compounds pure, owing to the coprecipitation of the benzoinoxime, which is difficultly soluble in aqueous alcohol.

However, pure products were obtained in all cases except that of cobalt, and these were covalent compounds of the type (III), where M equals Ni, Pd, Pt. In no case, by varying the experimental conditions, could a derivative similar to that of copper be obtained.



(III)



(IV)

In this work it has been possible to show in the case of nickel that the oxime can function as a chelate group attached by two co-ordinate links. It has been found that, when an alcoholic solution of benzoinoxime reacts with aqueous nickel sulphate in presence of large concentrations of ammonium acetate or excess of sodium acetate and acetic acid, the usual brown precipitate of nickel dibenzoinoxime is first produced, but on standing at 40° for an hour, the substance changes to a brilliant green complex salt. It is sparingly soluble in hot water, and with dilute sulphuric acid yields acetic acid. The water of crystallisation is not removed from it on drying for 12 hours in a desiccator over phosphoric oxide. It appears to have the structure (IV), and when it is warmed with ammonia, alcohol, or acetone, the brown nickel compound of type (III) is produced.

It will be seen that the α-benzoinoxime may function as a chelate group in three ways. In Feigl's formula (I), it may be attached to a copper atom by two principal valencies. With other bivalent metals it may be associated by either one principal valency and one co-ordinate link, as in (III); or by two co-ordinate links, as in (IV) and (IIa).

The nickel compound (III) is a buff-coloured substance, which dissolves very readily in benzene, chloroform, acetone, and carbon tetrachloride, brown solutions being produced. If the solution in the last solvent is kept in the cold for about ten minutes, minute crystals separate, the process continuing for 2 - 3 days. After 12 hours, however, little of the substance remains in solution, the product consisting of orange-coloured crystals. $\left[(C_{14}H_{12}O_2N)_2Ni\right],CCl_4$. On standing in air for a few days, or on heating at 90° for 4 - 5 hours, the solvent of crystallisation is lost, and the colour of the material changes to reddish-brown. This second variety of nickel dibenzoinoxime is almost completely insoluble in all organic solvents except chloroform ; evaporation of the chloroform solution gives the first variety. Thus the two forms of nickel dibenzoinoxime are interconvertible :

$$\text{First variety} \underset{CHCl_3}{\overset{CCl_4}{\rightleftharpoons}} \text{second variety.}$$

Alcohol and acetone convert the first of the nickel compounds into the second variety, but the process is always accompanied by decomposition. When either variety is treated with alcohol or acetone at 40°, benzoinoxime is liberated. Benzene and ether behave similarly to carbon tetrachloride, but are less suitable for producing the second modification, the former on account of the much slower rate of change, and the latter on account of its volatility. Phenol does not cause any change in either material below 75°, but there is a partial conversion of the second form into the first form above this temperature. The molecular weight of the first variety was therefore determined cryoscopically in phenol ;the results prove it to be monomeric. No means of determining the molecular weight of the second variety could be found, since in chloroform, the only solvent for it, it reverted to the first modification.

The first platinum compound of type (III) is formed when potassium chloroplatinite and the oxime are kept at 40° in aqueous alcohol for 2 - 3 hours. The substance is dark yellow, and resembles the nickel compound in its ready solubility in organic solvents. Moreover, it reverts to a second form in carbon tetrachloride after some days. Ethyl alcohol, however , accomplishes the conversion more speedily, but even here the process

is slow in comparison with the rate of change of the nickel isomerides. The second variety of the platinum benzoinoxime is pink-brown, amorphous, and soluble only in chloroform, behaving in the same manner as the second nickel compound.

The addition of benzoinoxime to potassium chloropalladite gives, immediately, a bulky primrose-yellow precipitate of palladium dibenzoinoxime (III). Although soluble in most of the usual organic solvents, it has not the great solubility of its nickel and platinum analogues, and it gives yellow solutions instead of the brown solutions always produced by the derivatives of these metals. In acetone, alcohol, benzene and carbon tetrachloride, it reverts to a second variety, which has a slightly deeper yellow colour and is almost insoluble in all the usual organic reagents.

The molecular weight of the first palladium compound was determined in phenol, as was also that of the first platinum complex in chloroform ; both proved to be unimolecular.

Thus, nickel, platinum, and palladium dibenzoinoximes each exist in two forms. Their melting points varied with the rate of heating , owing to slow decomposition occurring before the true melting points were reached. This was particularly noticeable with the first platinum

benzoinoxime, which became bright red at 132°, and after being kept at this temperature for some minutes, melted at 140°, whereas the melting point recorded in the usual way was 150° - 155°. Similar fluctuations were observed in the melting points of the nickel and palladium derivatives.

We have no satisfactory explanation why two nickel derivatives of α - benzoinoxime exist. Professor S.Sugden very kindly examined these substances for us, and found them to be paramagnetic. This is against the idea that they have a planar configuration. On the other hand, the palladium derivatives were diamagnetic, so that the possibility that they have a planar configuration is not excluded. The two modifications in the three cases may arise from purely optical isomerism. α-Benzoinoxime is a dl-mixture, and when a complex compound is made with two benzoinoxime residues, there is the possibility that it may be a meso- or a racemic dl-modification. Against this view, however, is the experimental evidence that the two modifications are never present in the original preparations, and it seems most unlikely that dissolution in carbon tetrachloride would change a meso-form into a dl-mixture, or vice versa. Both varieties of the metallic derivatives give α-benzoinoxime when treated with cold dilute hydrochloric acid (N/2). The

last possibility is that one form is a polymeride of the other ; as the metal atoms in each case have the expected covalency of four this does not appear probable.

E X P E R I M E N T A L .

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COPPER BENZOINOXIME.

An aqueous solution of cupric chloride(15g;200 c.c.) was mixed with an alcoholic solution of α-benzoinoxime (2g.; 100 c.c.),the mixture being rendered faintly ammoniacal by the careful addition of aqueous ammonia (3N). A dark green precipitate formed immediately. This was washed with hot 1% aqueous ammonia, alcohol, and hot water and dried at 110°- 115°.

Found : Cu, 21.95.

Calculated for $C_{14}H_{11}O_2NCu$, Cu , 22.02%

COPPER BENZOINOXIME DICHLORIDE.

Copper benzoinoxime (1g.) was dissolved in hot alcoholic hydrogen chloride (20c.c.). The filtered solution, on cooling, deposited bright emerald-green crystals of copper benzoinoxime dichloride containing one molecule of alcohol of crystallisation. These were removed, washed with alcohol (10 c.c.) , and air dried.

Found : Cu, 15.56 , 15.55 ; Cl, 17.31.

$(C_{14}H_{13}O_2N)CuCl_2.C_2H_5OH$ requires Cu, 15.57 ; Cl, 17.38 %

After some days the crystals lost their alcohol of crystallisation. They were readily soluble in

alcohol and acetone, but were decomposed by water, yielding the original green copper benzoinoxime and free hydrogen chloride.

NICKEL DIBENZOINOXIME.

FIRST FORM.

Nickel sulphate (2 g. ; $NiSO_4.7H_2O$) and ammonium chloride (5 g.) were dissolved in water (180 cc.). Aqueous ammonia (20 c.c.; 3 N) was then added, and the mixture heated to 65° - 70°. α-Benzoinoxime (1 g.) dissolved in alcohol (100 c.c.) was added. A buff-coloured precipitate formed immediately, and was filtered off after ten minutes. The product was extracted twice with 30% aqueous alcohol (300 c.c.) at 60° to remove unchanged benzoinoxime, and then washed with hot water till free from inorganic impurities. The material was dried in a desiccator over phosphoric oxide for three days or placed in an oven at 90° for 5 hours.

Found : Ni, 11.52 ; N, 5.37.

$(C_{14}H_{12}O_2N)_2Ni$ requires, Ni, 11.49 ; N , 5.48 %

In this preparation, concentrations of alcohol greater than 35 % must be avoided, since this may cause some decomposition or effect a partial transformation to the second variety, whilst with low concentrations of alcohol much benzoinoxime is always precipitated, particularly at low temperatures.

Analysis of the product is best effected by warming with N - hydrochloric acid, the precipitated oxime being filtered off, and the nickel estimated as the dimethylglyoxime compound. Complete decomposition of the substance with concentrated nitric acid causes the formation of benzaldelhyde which is most undesirable.

SECOND FORM.

The first variety (1 g.) was dissolved in carbon tetrachloride (40 c.c.) ,an intense brown colour being produced. The solution was filtered as rapidly as possible. After 10 minutes' standing , the formation of a precipitate began and continued for 2 or 3 days. At the end of the first day, the orange-coloured crystalline product was removed. Analysis showed that it contained one molecule of carbon tetrachloride of crystallisation.

Found : Ni, 8.82 , 8.88 ;

$Ni(C_{14}H_{12}O_2N)_2.CCl_4$ requires, Ni, 8.83 %

The carbon tetrachloride of crystallisation was removed by 5 hours' heating at 90, the colour of the substance becoming reddish-brown.

Found : Ni, 11.37, 11.38 ; N, 5.46 %

NICKEL DIBENZOINOXIME DIACETATE.

Nickel sulphate (12 g.; hydrated salt) and ammonium acetate (20 g.) were dissolved in water (200 cc.)

and heated to 40°. Benzoinoxime (4 g.), dissolved in alcohol (100 c.c.) and heated to 40°, was added to the aqueous solution and the mixture maintained at this temperature for 1 hour. The brown nickel dibenzoinoxime dissolved slowly, and ~~the~~ an emerald-green precipitate formed. This was filtered off, extracted with warm 50 % aqueous alcohol, washed with water, and dried in a desiccator.

Found : Ni, 8.74 ; N, 4.43.

$Ni(C_{14}H_{13}O_2N)_2\ (CH_3.CO_2)_2.2H_2O$ requires, Ni, 8.80 ; N, 4.20%

This substance was also prepared by the following method. Nickel sulphate (2 g. hydrated salt) and sodium acetate (10 g.) were dissolved in water (200 c.c.) at 40°, and a solution of benzoinoxime (2 g.) in alcohol (100 c.c.) also at 40°, was added. Brown nickel benzoinoxime was precipitated immediately. N - Acetic acid (25 c.c.) was then added slowly with stirring. The brown precipitate dissolved rapidly, and the green nickel dibenzoinoxime diacetate crystallised gradually during 1½ hours. The product was removed, washed twice with 50 % aqueous alcohol (100 c.c.) at 40°, and with hot water. It was then dried in a desiccator.

Found : Ni, 8.78 ; N, 4.20 %

PALLADIUM DIBENZOINOXIME

FIRST FORM.

To potassium chloropalladite (1.5 g.) dissolved in water (200 c.c.), an alcoholic solution of benzoinoxime (2.5 g., 100 c.c.) was added, and the mixture warmed at 60° for about 20 minutes. The very pale primrose-yellow precipitate, which formed immediately, was removed, extracted twice with 33 % aqueous alcohol, washed thoroughly with hot water, and finally dried in a desiccator over phosphoric oxide.

Found : Pd, 19.10 ; N, 4.85.

$Pd(C_{14}H_{12}O_2N)_2$ requires Pd. 19.10 ; N, 5.01 %

Excess of chloropalladite must be avoided in this preparation, or the product will be contaminated with another substance of higher palladium content.

SECOND FORM.

The above palladium dibenzoinoxime (1g.) was dissolved in chloroform (50 c.c.) and filtered as quickly as possible. After 10 minutes, a precipitate had formed, but the process of separation was allowed to continue for 24 hours, whereupon the pale primrose-yellow coloured solid was removed, and dried in a desiccator. Carbon tetrachloride, acetone, or alcohol may be used instead of chloroform with equally good results.

Found, in the product from $CHCl_3$, Pd , 19.10 ; N, 5.01%

Platinum Dibenzoinoxime

First Form.

Potassium chloroplatinite (1g.) was dissolved in water at 45°. Benzoinoxime (1 g.) dissolved in alcohol, was added to the solution, and the mixture maintained at 40° - 45° for three hours, while the platinum dibenzoinoxime formed slowly. This ochre-coloured material was filtered off, extracted twice with 30 % alcohol (100 c.c.) at 40°, and washed with warm water. It was then dried in a desiccator with phosphoric oxide.

Found : Pt, 30.12 ; N , 4.36.

$Pt(C_{14}H_{12}O_2N)_2$ requires, Pt, 30.15 ; N , 4.35 %

If, during this preparation, the temperature of the mixture is allowed to rise above 50°, intensely reddish brown impurities result, and above 70°, the product melts to a separate layer which solidifies on cooling to an intensely brown mass of high platinum content. Attempts to accelerate the reaction by the addition of sodium acetate were unsuccessful ; the presence of free miner al acid apparently has no effect on the reaction.

Second Form.

The foregoing product (1g.) was dissolved in carbon tetrachloride (50 c.c.) filtered, and the intensely brown solution set aside. A precipitate formed very slowly, and after three weeks, the pink brown deposit was removed, and dried in a desiccator. Alternatively, the

the first variety (1 g.) is dissolved in alcohol (100 c.c.) and the solution filtered ; after 2 days, the pink-brown precipitate is removed and dried.

Found, using carbon tetrachloride, Pt, 29.93 ;

using alcohol. Pt , 30.21 ; N, 4.32 %

MOLECULAR-WEIGHT DETERMINATIONS.

Below are recorded the results from the molecular-weight determinations with the first forms of the metallic derivatives of α- benzoinoxime.

Cryoscopic determinations in phenol (constant = 7.27° per 1000 g.)

	Concn. (g./1000g.)	At.	M Found.	M Calc.
$Ni(C_{14}H_{12}O_2N)_2$...	11.21	0.165°	494	511
	20.05	0.295°	494	511
$Pd(C_{14}H_{12}O_2N)_2$...	9.80	0.126°	565	559

Ebullioscopic determinations in chloroform (constant 2.6°/1000cc.)

	(g./1000c.c.)			
$Ni(C_{14}H_{12}O_2N)_2$...	17.91	0.091°	512	511
	20.71	0.105°	513	511
$Pt(C_{14}H_{12}O_2N)_2$...	23.29	0.095°	637	647
	31.58	0.128°	641	647

B I B L I O G R A P H Y .

F. Feigl , Ber., 1923 , 56 , 2083 . A . ii , 880

"Organic Reagents for Metals" 1934 , p. 19.