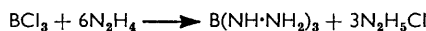


809. *Hydrazine Complexes of Titanium(IV).*

By D. NICHOLLS and R. SWINDELLS.

The reactions of titanium(IV) halides with hydrazine, phenylhydrazine, and 1,1-dimethylhydrazine are described. Whilst reduction occurs with hydrazine in non-aqueous media, with substituted hydrazines solvolysis occurs, with no apparent reduction. Reactions have been studied conductimetrically in nitromethane, and products of overall composition $TiCl_4 \cdot 2PhNH \cdot NH_2$ and $TiX_4 \cdot 4Me_2N \cdot NH_2$ ($X = Cl, Br, \text{ or } I$) have been isolated from benzene solution. In dilute solution in dimethylhydrazine, titanium(IV) chloride ionises forming anionic complexes probably having the formula $[Me_2NH \cdot NH_2]_2[TiCl_x(NH \cdot NMe_2)_{6-x}]$.

HYDRAZINES are of considerable interest as ligands in view of the variety of bonding possibilities they exhibit. One possibility is that the two nitrogen atoms, whilst being incapable of bonding to the same metal through steric and symmetry considerations, may co-ordinate to two different metal atoms, thus forming polymeric chains with hydrazine bridges. Such a structure has recently been found¹ in $[Zn(N_2H_4)_2]Cl_2$; co-ordination around the zinc atom is octahedral and the Zn-N distance (2.15 Å) is indicative of a covalent bond. Studies of hydrazine derivatives of the transition metals have been limited mainly to products formed in aqueous solutions. Thus there is no report of solvolysis of any transition-metal halide; uranium(IV) chloride forms hydrazinates $UCl_4 \cdot 6N_2H_4$ and $UCl_4 \cdot 7N_2H_4$.² Bains and Bradley³ have obtained moderately stable hydrazinates of titanium(IV) alkoxides, *i.e.*, $Ti(OEt)_4 \cdot \frac{1}{2}N_2H_4$ and $Ti(OPr)_4 \cdot N_2H_4$; their structures are unknown. Recently the reactions of hydrazines with some covalent non-metal halides have been reported. Patterson and Onyszchuk⁴ have shown that boron trichloride reacts with hydrazine in tetrahydrofuran according to:



and Gibson, Schug, and Crook⁵ have obtained monomeric tetrakis-(1,1-dimethylhydrazino)-silane by hydrazinolysis of silicon tetrachloride. We now report the reactions of hydrazine, phenylhydrazine, and 1,1-dimethylhydrazine with the titanium(IV) halides.

RESULTS AND DISCUSSION

Reactions of the titanium(IV) halides with hydrazine are strongly exothermic and cannot be moderated by cooling since hydrazine freezes at 2°. The heat produced in the reaction causes decomposition of the endothermic hydrazine, and heterogeneous reaction products are obtained. Unfortunately hydrazine is not appreciably soluble in solvents which are unreactive towards titanium halides so that the best way of moderating the reaction is to dilute the hydrazine in the gas phase. The red adduct of titanium(IV) chloride and hydrazine formed by passing hydrazine vapour (diluted with nitrogen) through an iso-octane solution of the halide is unstable *in vacuo*; its decomposition product contains titanium(III). Titanium(IV) iodide is apparently reduced by hydrazine in liquid ammonia but the explosive nature of the reaction product did not permit further investigation. Under non-aqueous conditions titanium(IV) is reduced by hydrazine, but in aqueous acidic solutions titanium(III) reduces the hydrazinium ion to ammonium ion.

Solvolysis without reduction occurs in the reactions of titanium(IV) halides with phenylhydrazine and 1,1-dimethylhydrazine. The red diamagnetic, $TiCl_4 \cdot 2PhNH \cdot NH_2$ can be isolated from reactions of titanium(IV) chloride with phenylhydrazine in a number of organic

¹ Ferrari, Braibanti, and Bigliardi, *Acta Cryst.*, 1963, **16**, 498.

² Kalnins and Gibson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 55.

³ Bains and Bradley, *Canad. J. Chem.*, 1962, **40**, 1350.

⁴ Patterson and Onyszchuk, *Canad. J. Chem.*, 1963, **41**, 1872.

⁵ Gibson, Schug, and Crook, *Inorg. Chem.*, 1963, **2**, 876.

[1964]

solvents. It remains unchanged when heated in refluxing benzene but decomposes violently when heated above 70° in the dry state. This fact, coupled with the infrared (i.r.) spectrum, which clearly shows the presence ⁶ of $\text{PhNH}\cdot\text{NH}_3^+\text{Cl}^-$, leads us to formulate this product as a mixture:



No separation of the constituents has been achieved, however; the insolubility of $\text{TiCl}_3(\text{NH}\cdot\text{NHPh})$ in organic solvents is a strong indication that it is polymeric.

The conductimetric titration curve obtained when phenylhydrazine is added to a solution of titanium(IV) iodide in nitromethane is shown in Fig. 1. The curves are

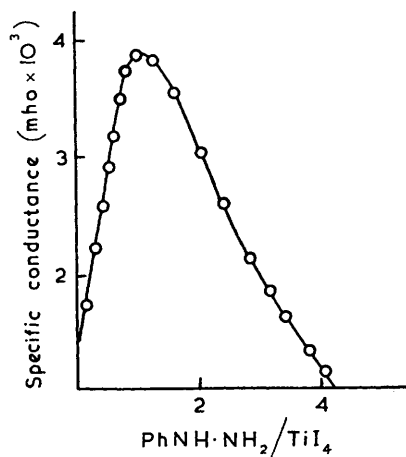
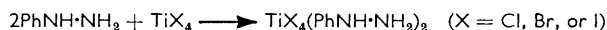


FIG. 1. Conductimetric titration of phenylhydrazine against titanium(IV) iodide in nitromethane.

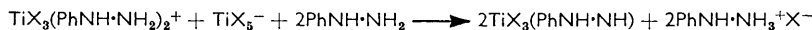
almost identical for the three halides, the conductance peaks occurring between 0.9 and 1.0 mole-ratio. The general shape of the curves is similar to those obtained by Chandler *et al.*⁷ in the titration of titanium(IV) fluoride with di-*n*-propylamine; the conductance peak in that reaction, however, occurs around 0.4 mole-ratio of base to halide. As the first few drops of the phenylhydrazine solutions are added a precipitate appears, but this rapidly dissolves upon stirring in the excess of titanium(IV) halide solution. After one mole-ratio of the base has been added, a permanent red precipitate is present and the conductance of the solution rapidly diminishes. It seems likely therefore that the initial reaction is the formation of an adduct by co-ordination through the lone pair on the nitrogen of the amino-group:



In the presence of excess of the titanium(IV) halide, conducting species are formed, *e.g.*,



giving a maximum of conductance at the 1 : 1 equivalence point. Thereafter the addition of phenylhydrazine removes the conducting species and precipitates the "dihydrazinate" (phenylhydrazine hydrochloride not being soluble enough to contribute significantly to the conductance):



The addition of more phenylhydrazine results in a continuous drop in conductance. These suggested reaction schemes have been simplified by omitting solvent participation; it is well known that nitromethane forms weak complexes with the titanium(IV) halides.⁸

⁶ Evans and Kynaston, *J.*, 1963, 3151.

⁷ Chandler, Wuller, and Drago, *Inorg. Chem.*, 1962, 1, 65.

⁸ Emeléus and Rao, *J.*, 1958, 4245.

The conductimetric titrations with 1,1-dimethylhydrazine and the three halides TiCl_4 , TiBr_4 , and TiI_4 are similar to those with phenylhydrazine for up to two mole-ratios of base added (Fig. 2). In addition there is a conductance minimum at four mole-ratios of base added. The end-product here is the "tetrahydrazinate," $\text{TiX}_4 \cdot 4\text{Me}_2\text{N} \cdot \text{NH}_2$; the increase in conductance thereafter is probably due to the conductance of the free hydrazine. When the titration is carried out in reverse fashion (Fig. 3), *i.e.*, the titanium(IV) halide solutions are added to an excess of the dimethylhydrazine, the titration curves show a minimum at 0.25 mole-ratio $\text{TiX}_4 : \text{Me}_2\text{N} \cdot \text{NH}_2$. Precipitation occurs as the conductance drops, but when the $\text{TiX}_4 : \text{Me}_2\text{N} \cdot \text{NH}_2$ ratio exceeds 0.25 the precipitate begins to dissolve until

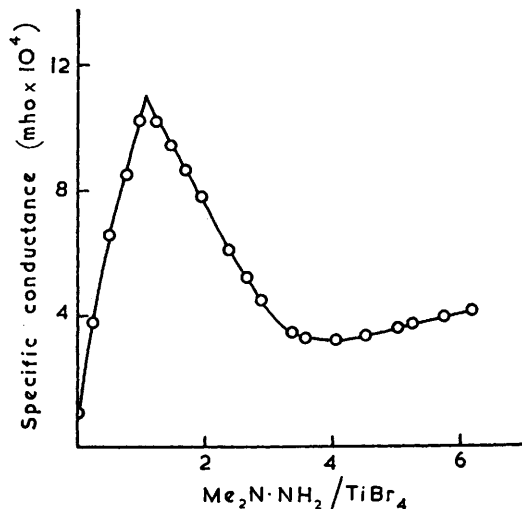


FIG. 2. Conductimetric titration of 1,1-dimethylhydrazine against titanium(IV) bromide in nitromethane.

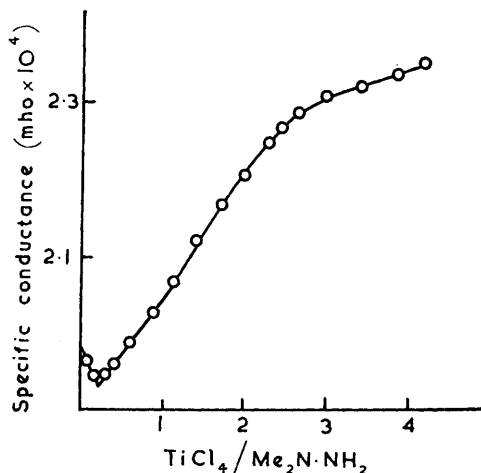
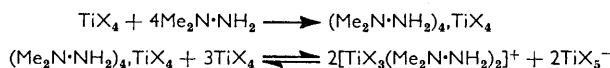


FIG. 3. Conductimetric titration of titanium(IV) chloride against 1,1-dimethylhydrazine in nitromethane.

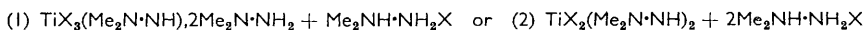
eventually a clear yellow solution is obtained. The formation of one "compound" only, *i.e.*, $\text{TiX}_4 \cdot 4\text{Me}_2\text{N} \cdot \text{NH}_2$, is again demonstrated, just as is the solubility and ionisation of the product in the presence of an excess of titanium(IV) halide:



The nature of these ions is not known, and other anions containing co-ordinated ligand cannot be ruled out for this stoichiometry, *e.g.*,



The reaction of 1,1-dimethylhydrazine with titanium(IV) chloride, bromide, and iodide in benzene yields precipitates of composition $\text{TiX}_4 \cdot 4\text{Me}_2\text{N} \cdot \text{NH}_2$. Whilst eight-co-ordinated titanium does exist in ditertiary arsine complexes,⁹ this structure can be ruled out here if we assume that the hydrazine is monodentate. The i.r. spectra of the products show the presence of the dimethylhydrazinium cation, $\text{Me}_2^+\text{NH} \cdot \text{NH}_2$,⁵ and in addition show some extra absorptions which are presumably associated with $\text{Ti}(\text{NH} \cdot \text{NMe}_2)_2\text{X}_2$. Thus the precipitates may be formulated as



Now, if the two molecules of dimethylhydrazine are loosely co-ordinated to $\text{TiX}_3(\text{Me}_2\text{N} \cdot \text{NH})$ as in (1) we might expect these to be liberated upon heating *in vacuo*. In fact, up to 56°,

⁹ Clark, Lewis, and Nyholm, *J.*, 1962, 2460.

the material of composition $\text{TiCl}_4 \cdot 4\text{Me}_2\text{N} \cdot \text{NH}_2$ is surprisingly stable. Dimethylhydrazine is slowly evolved upon heating to 100° , and the composition of the residue then approximates to $\text{TiCl}_4 \cdot 3\text{Me}_2\text{N} \cdot \text{NH}_2$. Charring occurs at 130° and complete decomposition sets in, evolution of ammonia indicating fission of the N-N bond. We therefore believe that two of the Ti-X bonds are broken in $\text{TiX}_4 \cdot 4\text{Me}_2\text{N} \cdot \text{NH}_2$. The greater extent of solvolysis with 1,1-dimethylhydrazine as compared with phenylhydrazine is in agreement with the much greater base strength expected for the former by virtue of the inductive effect of the methyl groups and the base-weakening effect of the phenyl group. An alternative possibility arises if $\text{TiX}_4 \cdot 4\text{Me}_2\text{N} \cdot \text{NH}_2$ is formulated as in (1), and either (a) one of the two ligand molecules is held more strongly than the other in $\text{TiX}_3(\text{Me}_2\text{N} \cdot \text{NH}) \cdot 2\text{Me}_2\text{N} \cdot \text{NH}_2$, or (b), on heating, reduction occurs, giving $\text{TiX}_3(\text{Me}_2\text{N} \cdot \text{NH})_2 + \text{Me}_2\text{NH} \cdot \text{NH}_2\text{Cl}$.

Titanium(IV) chloride and iodide are very soluble in 1,1-dimethylhydrazine, yielding viscous yellow solutions which exhibit a large lowering of the vapour pressure at 15° . Tensimetric studies are therefore not practicable but removal of the excess of the hydrazine over a considerable period at 15° does yield the composition $\text{TiCl}_4 \cdot 4\text{Me}_2\text{N} \cdot \text{NH}_2$. On treatment of the solution of the chloride in dimethylhydrazine with an anion exchange resin, it was found that titanium is present as an anion and that the cation associated with this anion is the dimethylhydrazinium ion. In dimethylhydrazine solution, therefore, complex formation occurs similar to that with the titanium(IV) halides in other protonic solvents, *e.g.*, water and ammonia.¹⁰



The complex breaks down in the solid state, just as does $\text{H}_2[\text{TiCl}_4(\text{OH})_2]$ and $(\text{NH}_4)_2[\text{TiI}_3(\text{NH}_2)_3]$. The visible absorption spectrum of the titanium(IV) chloride solution in dimethylhydrazine shows merely a broad charge-transfer spectrum over the region 300—400 $\text{m}\mu$ with no trace of a *d-d* transition which might arise from reduction of titanium(IV) by the ligand. The three dimethylhydrazine complexes were readily hydrolysed by moist air; they gave colourless or yellow solutions in dilute sulphuric acid. Oxidation-state titrations, *e.g.*, with ceric sulphate could not be performed in the presence of the hydrazine.

EXPERIMENTAL

All reactions and reaction products were studied under rigorously anhydrous conditions either in an atmosphere of dry nitrogen or *in vacuo*.

Materials.—Titanium(IV) halides were prepared and purified as described previously.¹⁰ Hydrazine (95%; Whiffen and Sons Ltd.) and 1,1-dimethylhydrazine were dried by refluxing them over crushed barium oxide and distilled from fresh drying agent. (*Warning:* In no circumstances should the barium oxide be crushed even in a clean iron pestle and mortar; an explosion occurred when hydrazine was refluxed over barium oxide crushed in this way, which we attribute to a trace of rust in the desiccant.) Phenylhydrazine was distilled under reduced pressure from barium oxide, the middle fraction (b. p. $119\text{--}120^\circ/12\text{ mm.}$) being collected. Nitromethane (F. W. West and Co. Ltd., spectroscopically-pure grade) was fractionated from phosphorus pentoxide; other organic solvents were dried by standard methods.¹¹

Analyses.—Titanium was determined gravimetrically as TiO_2 . Chloride, bromide, and iodide ions were determined gravimetrically as the silver salts after the hydrazines had been destroyed with acidified sodium nitrite.

Conductimetric Titrations.—The cell consisted of a three-necked flask equipped with a burette with a greaseless stopcock, platinum electrodes, and a stopcock connection to the high-vacuum lines. Two cells were used, with volumes of 50 and 200 ml.; the titration of phenylhydrazine with the iodide (Fig. 1) was performed in the smaller cell and thus the specific conductance was larger than that shown in Figs. 2 and 3, since approximately the same weight of tetrahalide was taken in each case. The solvent was distilled *in vacuo* into the

¹⁰ Fowles and Nicholls, *J.*, 1959, 990.

¹¹ Weissberger, "Technique of Organic Chemistry," Vol. VII, Interscience Publ., Inc., New York, 1955.

cell on to a weighed quantity (0.5—1.0 g. of TiX_4) of one reactant. Dry oxygen-free nitrogen was then admitted and the mixture stirred magnetically. The resistance of the solution was measured, and portions of the other reactant (as a strong solution in the same solvent) added from the burette, readings being taken until the conductivity was constant with time after each addition. Resistances were measured with a Phillips type PR 9500 bridge. Despite an extensive search, no suitable solvent other than nitromethane was found for these titrations (most polar solvents solvolyse the titanium halide; halogen-containing solvents and carbonyl compounds react with the hydrazines; acetonitrile is polymerised by this system).

Infrared Spectra.—These were recorded on a Grubb-Parsons double-beam instrument fitted with sodium chloride optics. Solids were studied as mulls, made under dry-box conditions with Nujol and hexachlorobutadiene.

Reactions of Titanium(IV) Halides with Anhydrous Hydrazine.—Direct reaction between the halides and liquid hydrazine is exceedingly exothermic. On account of the violent nature of the reaction the products are heterogeneous; hydrolysis of the residue in dilute sulphuric acid gives blue-violet solutions characteristic of trivalent titanium. Two experiments were performed in an attempt to obtain a homogeneous product.

(i) When hydrazine vapour, well-diluted with dry oxygen-free nitrogen, was passed through titanium(IV) bromide in iso-octane, a red precipitate, similar in appearance to the red diammoniate $TiBr_4 \cdot 2NH_3$,¹⁰ was formed. On filtration and evacuation of the precipitate decomposition occurred, giving a brown solid, which reacted violently with dilute sulphuric acid, giving a violet solution.

(ii) Hydrazine was condensed on to a yellow solution of titanium(IV) iodide in liquid ammonia. No precipitation occurred but the colour of the solution soon became violet and a permanent gas was evolved as the hydrazine was oxidised. Ammonia was removed from the solution and hydrazine was condensed on to the solid in an attempt to extract it. Filtration left a violet-black solid. This was evacuated at 50° to remove hydrazine and after 1 hr. a severe detonation occurred. In view of the hazardous nature of reactions with anhydrous hydrazine, reactions with mono- and di-substituted hydrazines were chosen for more detailed study.

Reaction of Titanium(IV) Chloride with Phenylhydrazine.—Preparation of $TiCl_4 \cdot 2PhNH \cdot NH_2$ was carried out successfully in iso-octane, methylene dichloride, and benzene. In a typical experiment, titanium(IV) chloride (3.305 g.) was dissolved in benzene (200 ml.) and a solution of phenylhydrazine (3.93 g.) in benzene (50 ml.) added dropwise with stirring under an atmosphere of dry nitrogen. The red precipitate was filtered off, washed with benzene, and dried *in vacuo* (Found: Ti, 12.0; Cl, 35.3. $TiCl_4 \cdot 2PhNH \cdot NH_2$ requires Ti, 11.8; Cl, 35.3%). The product was diamagnetic (by Gouy method) and gave a colourless solution in dilute sulphuric acid. It was insoluble in organic solvents except those with which it reacted. The i.r. spectrum showed all the absorptions expected for phenylhydrazine hydrochloride and in addition had two strong absorptions at 1190 and 1230 cm^{-1} . Also in the NH deformation region there are two sharp peaks at 1570 and 1600 cm^{-1} , whilst there is only a single absorption in $PhNH \cdot NH_3Cl$ at 1580 cm^{-1} . On thermal decomposition the "compound" decomposed violently above 70°. On refluxing in benzene, however, neither reduction of the titanium nor decomposition of the complex occurred.

Reaction of Titanium(IV) Halides with 1,1-Dimethylhydrazine.—Preparations were carried out in benzene solutions, as described for $TiCl_4 \cdot 2PhNH \cdot NH_2$, hydrazine being in excess. The following products were isolated: a salmon-pink powder (Found: Ti, 11.2; Cl, 33.1. $TiCl_4 \cdot 4Me_2N \cdot NH_2$ requires Ti, 11.1; Cl, 33.0%); a yellow powder (Found: Ti, 8.1; Br, 51.2. $TiBr_4 \cdot 4Me_2N \cdot NH_2$ requires Ti, 7.9; Br, 52.6%); a pale brown powder (Found: Ti, 6.2; I, 65.5. $TiI_4 \cdot 4Me_2N \cdot NH_2$ requires Ti, 6.0; I, 63.8%). All the products gave colourless or pale yellow solutions in dilute sulphuric acid; they were insoluble in non-polar solvents. Their i.r. spectra showed the presence of the dimethylhydrazinium salts; in all of the spectra there was a sharp absorption at 1023 cm^{-1} whereas only a very weak one occurred in that of $[Me_2NH \cdot NH_2]^+$. In $TiBr_4 \cdot 4Me_2N \cdot NH_2$ two strong absorptions at 1600 and 1635 cm^{-1} replaced the absorption at 1623 cm^{-1} and a doublet also appeared, centred on 1256 cm^{-1} , in place of the single absorption in $Me_2NH \cdot NH_2Br$ at this wavelength.

Tensimetry and Thermal Decomposition of $TiCl_4 \cdot 4Me_2N \cdot NH_2$.—Whilst titanium(IV) chloride reacts violently with dimethylhydrazine, the product $TiCl_4 \cdot 4Me_2N \cdot NH_2$ (prepared in benzene) dissolves smoothly forming a yellow solution. The tetrabromide and tetraiodide, however, can

be dissolved in an excess of the hydrazine directly to give homogeneous solutions, the iodide being the most soluble halide. As the hydrazine is removed *in vacuo*, the solutions become viscous and equilibrium vapour-pressure measurements became very inaccurate. Because of this, many hours' evacuation were required at 15° before the composition $\text{TiCl}_4 \cdot 4\text{Me}_2\text{N} \cdot \text{NH}_2$ could be recovered. No stable higher hydrazinates were detected.

The thermal decomposition of $\text{TiCl}_4 \cdot 4\text{Me}_2\text{N} \cdot \text{NH}_2$ *in vacuo* was studied at temperatures up to 134°. The results (Table) show that one mole-ratio of dimethylhydrazine can be removed by 100° but further heating to 134° causes charring and evolution of ammonia.

Throughout the decomposition, traces of permanent gas and dimethylamine were also evolved. The residue had the composition C, 15.4; N, 18.1; H, 6.0%. The mixture melted at 61—77°; in a thermal decomposition of $\text{Me}_3\text{NH} \cdot \text{NH}_2\text{Cl}$, melting occurred at 81° but no decomposition occurred below 140°.

Thermal decomposition of $\text{TiCl}_4 \cdot 4\text{Me}_2\text{N} \cdot \text{NH}_2$.

Temp.	Residue composition ($\text{Me}_2\text{N} \cdot \text{NH}_2 / \text{TiCl}_4$)	Gaseous products (by i.r. spectra)
56°	3.83	$\text{Me}_2\text{N} \cdot \text{NH}_2$
61	3.71	„
77	3.36	„, trace NH_3
100	3.00	NH_3 , „
134	2.71	NH_3 , trace $\text{Me}_2\text{N} \cdot \text{NH}_2$

Ion-exchange of $\text{TiCl}_4 \cdot 4\text{Me}_2\text{N} \cdot \text{NH}_2$ in 1,1-Dimethylhydrazine.—Dry Amberlite I.R.A. 400 (Cl^- form) was prepared by evacuating a sample (200 g.) at 10^{-4} mm. for 2 days. This was then placed in the thimble of a Soxhlet extractor and any residual water removed by continually extracting the resin with dimethylhydrazine refluxing over crushed barium oxide. The swollen resin was tipped, under a dry nitrogen atmosphere, into an ion-exchange column and a dilute solution (yellow) of $\text{TiCl}_4 \cdot 4\text{Me}_2\text{N} \cdot \text{NH}_2$ in dimethylhydrazine was passed slowly down the column at 20°. A colourless eluant was obtained which on evaporation left white crystals. This solid contained no titanium but showed an i.r. red absorption spectrum identical to that of $\text{Me}_2^+\text{NH} \cdot \text{NH}_2\text{Cl}^-$.

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