

862. Complexes of Titanium and Zirconium Halides with Organic Ligands.

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Complexes of titanium tetrafluoride, tetrachloride, tetrabromide, and tetraiodide and of zirconium tetrachloride and tetrabromide with various organic ligands have been prepared. Those of titanium tetraiodide are least readily formed. Dissociation pressures at 80—130° for complexes with selected ligands under comparable conditions diminish in the order fluoride > iodide > bromide > chloride and, for a given ligand and halide, are higher for the zirconium salt than for that of titanium. The difficulties in relating these measurements to the true heats of formation of the complexes are discussed.

FEW complexes of titanium tetra-fluoride, -bromide, and -iodide with organic ligands have been described, although for titanium tetrachloride the number is considerable.¹ The present experiments were made to determine if these three halides form compounds similar to those for the tetrachloride and to attempt to determine their relative stabilities from dissociation pressures. A number of compounds of zirconium tetrachloride and tetrabromide with organic ligands were also made and their dissociation pressures are recorded.

The known complexes of titanium tetrachloride include a number with simple inorganic molecules such as ammonia, hydrogen sulphide, nitrosyl chloride, thionyl chloride, and phosphorus halides and oxyhalides. There is virtually no information on the reaction of titanium tetraiodide with these substances. Titanium tetrabromide forms adducts with a few, of formulæ similar to those for titanium tetrachloride (*e.g.*, $\text{TiBr}_4 \cdot 8\text{NH}_3$; $\text{TiBr}_4 \cdot 2\text{H}_2\text{S}$; $2\text{TiBr}_4 \cdot \text{SO}_2$; $\text{TiBr}_4 \cdot 2\text{PH}_3$), but only the ammoniates of titanium tetrafluoride are known. The organic ligands which form adducts with the tetrachloride include ethers, sulphides, thiols, esters, acid chlorides, nitriles, amines, and amides whereas titanium tetrabromide forms adducts only with ethers² and with several aromatic amines.³ No pure addition compounds of the tetraiodide with ethers could be isolated,² presumably because of their low stability. The only compounds of titanium tetrafluoride with organic ligands are a 1 : 1 compound with ethyl alcohol, which is of interest because the tetrachloride forms alkoxides, and a 1 : 1 pyridine adduct.⁴ Zirconium tetrachloride forms addition compounds with much the same range of organic molecules as does titanium tetrachloride, and the tetrabromide is known to form adducts only with ammonia, pyridine, ethylamine, and aniline.

Our preparative work shows that titanium tetrafluoride and tetrabromide form much the same range of addition compounds as does the tetrachloride (see analyses, Tables 3—5). The same is true of the two zirconium halides. Only for titanium tetraiodide is there evidence that the organic ligands may be weakly held. In general, however, the preparations fail to give any indication of the relative stabilities of the products from the metal fluorides, chlorides, and bromides. Three organic compounds, phenol, 2-naphthol, and piperidine, reacted with titanium tetrabromide. This parallels exactly the behaviour of the tetrachloride. The extent of replacement of the halogen is presumably determined both by the conditions and the reactant. Thus, with phenol all four bromine atoms are replaced whereas with 2-naphthol under mild conditions, only two bromine atoms react. Probably these reactive substances would form addition compounds at lower temperatures but the point has not been studied.

Most of the compounds prepared contain two molecules of ligand per molecule of

¹ See Gmelin's "Handbuch der anorg. Chemie," 1951, No. 41. Titan. See also Ref. 5.

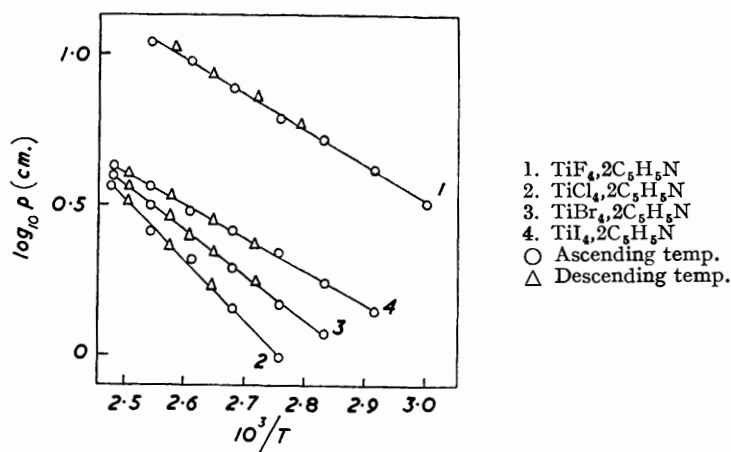
² Rolsten and Sisler, *J. Amer. Chem. Soc.*, 1957, **79**, 1068.

³ Prasad and Tripathi, *J. Indian Chem. Soc.*, 1956, **33**, 837.

⁴ Ruff and Ipsen, *Ber.*, 1903, **36**, 1777.

titanium halide. As excess of ligand was used, the experiments might not show the existence of a 1 : 1 compound. For titanium tetrachloride there are a number of cases in which both the 1 : 1 and 1 : 2 adducts are known (*e.g.*, with diethyl ether and ethane-thiol). In a few cases a 1 : 1 adduct only has been described (*e.g.*, $\text{TiCl}_4 \cdot \text{CH}_3 \cdot \text{COCl}$; $\text{TiCl}_3 \cdot \text{CH}_3 \cdot \text{NO}_2$; $\text{TiCl}_4 \cdot \text{C}_2\text{H}_5 \cdot \text{NO}_2$), and similar derivatives were obtained from the tetrabromide. With titanium tetrafluoride it is probably significant that in each case, apart from pyridine, only a 1 : 1 compound was obtained. With pyridine, however, Ruff and Ipsen isolated a 1 : 1 compound⁴ whereas the present work gave a 1 : 2 compound. Nothing is known about the structures of the compounds with organic ligands except that the majority would have octahedral configurations. All were readily decomposed by water and soluble in organic solvents such as carbon tetrachloride.

Dissociation pressures of selected complexes were measured with an isoteniscope in which a small mercury manometer was used as a null instrument. Attack on the mercury was slight and satisfactory reproducibility was obtained for ascending and descending



temperatures in the range 80—130°. Typical data are given in the Figure for the 1 : 2 pyridine adducts of the four titanium halides. In each case the plot of $\log p$ against $1/T$ was approximately linear.

The data are summarised in Table I, which gives the constants of the equation $\log_{10} p(\text{cm.}) = C - A/T$.

TABLE I.

Compound	A	C	Compound	A	C	Compound	A	C
$\text{TiF}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$	1200	4.10	$\text{TiCl}_4 \cdot 2\text{CH}_3 \cdot \text{CN}$	2700	7.92	$\text{ZrBr}_4 \cdot 2\text{C}_6\text{H}_5 \cdot \text{CN}$	840	3.33
$\text{TiCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$	2075	5.70	$\text{TiBr}_4 \cdot 2\text{CH}_3 \cdot \text{CN}$	2230	6.96	$\text{TiF}_4 \cdot 2\text{C}_6\text{H}_5 \cdot \text{CN}$	1500	4.68
$\text{TiBr}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$	1360	3.99	$\text{ZrCl}_4 \cdot 2\text{CH}_3 \cdot \text{CN}$	1500	4.77	$\text{TiCl}_4 \cdot 2\text{C}_6\text{H}_5 \cdot \text{CN}$	2130	5.92
$\text{TiI}_4 \cdot 2\text{C}_5\text{H}_5\text{N} \dots$	1010	3.14	$\text{ZrBr}_4 \cdot 2\text{CH}_3 \cdot \text{CN}$	1205	4.09	$\text{TiBr}_4 \cdot 2\text{C}_6\text{H}_5 \cdot \text{CN}$	1420	4.21
$\text{ZrCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$	1890	5.65	$\text{TiCl}_4 \cdot 2\text{C}_6\text{H}_5 \cdot \text{CN}$	2430	7.12	$\text{ZrCl}_4 \cdot 2\text{C}_6\text{H}_5 \cdot \text{CN}$	890	2.79
$\text{ZrBr}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$	1720	5.14	$\text{TiBr}_4 \cdot 2\text{C}_6\text{H}_5 \cdot \text{CN}$	1840	5.71	$\text{ZrBr}_4 \cdot 2\text{C}_6\text{H}_5 \cdot \text{CN}$	760	2.49
$\text{ZrBr}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$	1720	5.14	$\text{ZrCl}_4 \cdot 2\text{C}_2\text{H}_5 \cdot \text{CN}$	1010	3.76			
$\text{TiF}_4 \cdot \text{CH}_3 \cdot \text{CN}$	1650	5.41						

The pyridine adducts of the four titanium halides, which are similarly constituted, have dissociation pressures in the order fluoride > iodide > bromide > chloride. The same order is observed for acetonitrile and benzonitrile adducts of the fluoride, chloride, and bromide, notwithstanding that the fluoride forms only a 1 : 1 compound. The significance of this anomalous position of the fluoride is discussed below. The dissociation pressure curves of the adducts of zirconium tetrabromide adducts were also above those for the tetrachloride, and, for a given halogen and ligand, were higher for zirconium than for titanium. The infrared spectra of most of the compounds were recorded⁵ but no

⁵ Complete data are given in the Ph.D. Thesis of G. S. Rao (Cambridge University, 1957).

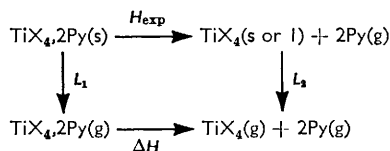
correlation could be found between the small changes in the characteristic frequencies of the ligand molecules resulting from co-ordination and the apparent relative stabilities of the compounds.

Thermodynamic functions can only be derived from these data on certain major assumptions, the first of which is that the complexes are fully dissociated in the vapour phase. The complex $\text{TiCl}_4 \cdot 2\text{POCl}_3$ was shown by Payne to be completely dissociated at 80° .⁶ Calculation of equilibrium constants is possible only if the dissociation products are in a definite state. Titanium tetraiodide and zirconium tetrachloride and tetrabromide have very small vapour pressures at the maximum temperatures used in the dissociation-pressure measurements and may be treated as solid dissociation products of zero vapour pressure. The vapour pressure of titanium tetrafluoride (b. p. 284°) was <3 mm. at 100° and this has also been assumed to condense completely. The dissociation of the pyridine adduct of titanium tetrafluoride and of the other 1 : 2 adducts of these halides is therefore of the type $\text{AB}_2(\text{s}) \rightleftharpoons \text{A}(\text{s}) + 2\text{B}(\text{g})$ and the equilibrium constants are given by $K_p = \frac{1}{4}p^2$, where p is the measured dissociation pressure. Titanium tetrachloride and tetrabromide (b. p. 136° and 230°) are assumed to remain in the gas phase. Vapour pressures for the latter have been measured recently.⁷ In this case the dissociation equilibrium is of the type $\text{AB}_2(\text{s}) = \text{A}(\text{g}) + 2\text{B}(\text{g})$ and $K_p = (4/27)p^3$. Variation of K_p with temperature is then given by $\log_{10} K_p = C' - A'/T$. Values of A' and C' , and of the derived value of ΔH , ΔG , and ΔS , for the series of pyridine adducts are given in Table 2. Values of K_p are in atmospheres.

TABLE 2.

Compound	A'	C'	ΔH_{exp} (kcal. mole ⁻¹)	ΔG_{298° (kcal. mole ⁻¹)	ΔS (cal. deg. ⁻¹ mole ⁻¹)
$\text{TiF}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$	2400	3.84	11	5.8	18
$\text{TiCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$	6225	10.64	28	14	49
$\text{TiBr}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$	4090	5.50	19	11	25
$\text{TiI}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$	2030	1.91	9	6.8	8
$\text{ZrCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$	3780	6.93	17	7.9	32
$\text{ZrBr}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$	3430	5.92	16	7.6	27

The values of ΔH_{exp} , the measured enthalpy, again show the anomalous position of the titanium tetrafluoride complex. The relationship between ΔH_{exp} , and ΔH , the enthalpy of formation of the complex in the gas phase, is shown by the annexed Hess's law cycle, L_1 and L_2 being the latent heats of sublimation of the complex and the tetrahalide, respectively. It follows that $\Delta H = \Delta H_{\text{exp}} + L_2 - L_1$. It is reasonable to assume that L_1 is approximately the same for the four octahedrally co-ordinated complexes.



The latent heats of sublimation (kcal. mole⁻¹) are known for all the titanium tetrahalides and are: TiF_4 22,⁸ TiCl_4 11,^{9,10} TiBr_4 12,⁷ TiI_4 14.¹¹ Values of $\Delta H_{\text{theoretical}}$ then become $33 - L_1$, $39 - L_1$, $31 - L_1$, and $23 - L_1$, in the order fluoride to iodide, and it is seen that the tetrafluoride complex has a lower heat of formation than the tetrachloride.

It seems impossible at present, particularly in the absence of structural data, to be

⁶ Payne, *Rec. Trav. chim.*, 1956, **75**, 620.

⁷ Hall, Blocher, and Campbell, *J. Electrochem. Soc.*, 1958, **105**, 271.

⁸ *Idem, ibid.*, 1958, **105**, 275.

⁹ Kelley, U.S. Bureau of Mines Bulletin No. 393, 1936.

¹⁰ *Idem, ibid.*, No. 383, 1936.

¹¹ Blocher and Campbell, *J. Amer. Chem. Soc.*, 1947, **69**, 2100.

more precise in the interpretation of such values. The differences cannot be directly related to the energy of the Ti-N bond in this set of complexes since this takes no account of the deformation energies of the donor and acceptor molecules involved in complex formation.

EXPERIMENTAL

Titanium tetrafluoride, prepared by passing fluorine (10 g. per hr.) over titanium turnings (20 g.) in a nickel boat in a nickel tube at 300°, was purified by vacuum sublimation in dry Pyrex at 200–250° (Found: F, 60.5; Ti, 38.9. Calc. for F_4Ti : F, 61.3; Ti, 38.7%). Titanium tetrachloride was purified by fractional distillation *in vacuo* (Found: Cl, 74.4; Ti, 25.4. Calc. for Cl_4Ti : Cl, 74.7; Ti, 25.3%). Titanium tetrabromide, prepared by passing bromine vapour in a stream of nitrogen over a mixture of titanium dioxide and sugar charcoal at 600°, was purified by vacuum distillation (Found: Br, 86.7; Ti, 13.3. Calc. for Br_4Ti : Br, 87.0; Ti, 13.0%). Titanium tetraiodide was prepared by Blocher and Campbell's method¹¹ (Found: I, 90.7; Ti, 8.8. Calc. for I_4Ti : I, 91.4; Ti, 8.6%). Zirconium tetrachloride and tetrabromide were prepared by passing chlorine, or bromine vapour in pure nitrogen, over a heated mixture of zirconium dioxide and sugar charcoal at 580–600° (Found: Cl, 60.5; Zr, 39.3. Calc. for Cl_4Zr : Cl, 60.9; Zr, 39.1%. Found: Br, 77.5; Zr, 22.4. Calc. for Br_4Zr : Br, 77.8; Zr, 22.2%). All organic ligands and solvents were "AnalaR" or were purified by standard methods. They were dried and distilled *in vacuo* just before use.

Complexes of titanium tetrachloride were made by distilling the halide and a moderate excess of the organic ligand in turn *in vacuo* into a weighed reaction flask cooled in liquid nitrogen. After reaction at 20° the excess of ligand was distilled off, and dry nitrogen was admitted to the flask, which was opened and handled subsequently in a dry-box. Titanium tetrabromide and tetraiodide were introduced into the weighed reaction flask in carbon tetrachloride solution, the solvent being pumped away before reweighing. Most of the organic ligands were again distilled directly on to the halide. A few which were of low volatility were added in an organic solvent. In these cases the excess of ligand was washed away with a solvent in which the adduct did not dissolve appreciably (*e.g.*, benzene). Samples for analysis were taken in the dry-box and decomposed by alkali, the metals being estimated as their dioxides, fluoride as calcium fluoride, the other halides by the Volhard method, and carbon and hydrogen by micro-combustion.

Complexes of Titanium Tetrafluoride.—Analyses of the compounds are in Table 3. They did not have definite m. p.s but most showed signs of decomposition between 80° and 200°.

TABLE 3.

Compound	Found (%)				Required (%)			
	C	H	F	Ti	C	H	F	Ti
$TiF_4 \cdot 2C_2H_5N$	42.9	4.0	26.6	17.3	42.6	3.5	27.0	17.0
$TiF_4 \cdot CH_3 \cdot CN$	14.6	1.8	45.7	29.5	14.5	1.8	46.1	29.1
$TiF_4 \cdot C_2H_5 \cdot CN$...	20.0	3.0	41.3	27.0	20.1	2.8	42.5	26.8
$TiF_4 \cdot C_6H_5 \cdot CN$...	37.0	2.3	33.0	21.5	37.0	2.2	33.5	21.2
$TiF_4 \cdot CH_3 \cdot NH_2$...	7.9	3.3	48.2	31.4	7.7	3.3	49.0	31.0
$TiF_4 \cdot C_2H_5 \cdot NH_2$...	14.1	3.9	44.4	28.8	14.2	4.1	45.0	28.4
$TiF_4 \cdot C_6H_5 \cdot NH_2$...	36.9	3.7	34.0	21.9	33.2	3.2	34.9	22.1
$TiF_4 \cdot CH_3 \cdot CHO$...	13.1	2.8	44.6	29.1	14.3	2.4	45.2	28.6
$TiF_4 \cdot C_6H_5 \cdot CHO$...	36.5	2.6	32.5	21.3	36.5	2.2	33.1	20.9
$TiF_4 \cdot (C_2H_5)_2CO$...	28.6	4.5	35.6	23.4	28.6	4.8	36.2	22.9
$TiF_4 \cdot CH_3 \cdot NO_2$...	6.6	1.5	40.5	26.5	6.5	1.6	41.1	25.9
$TiF_4 \cdot C_6H_5 \cdot NO_2$...	29.2	2.2	30.1	20.3	29.2	2.0	30.8	19.5

Dipyridinium Hexafluorotitanate.—The dipyridine complex of titanium tetrafluoride (0.8 g.) was dissolved in 40% hydrofluoric acid (15 ml.), and the solution evaporated at 20° and treated with pyridine (2 ml.) and ether (10 ml.). The white crystalline *dipyridinium hexafluorotitanate* was washed with ether and dried *in vacuo* (Found: F, 35.0; Ti, 15.3. $C_{10}H_{12}N_2F_6Ti$ requires F, 35.4; Ti, 14.9%).

Complexes of Titanium Tetrachloride and Tetrabromide.—Analyses of the compounds, are in Table 4.

Substitution Compounds of Titanium Tetrabromide.—(a) *With phenol.* Titanium tetrabromide (1.57 g.) in benzene (10 ml.) and phenol (2.0 g.) in benzene (15 ml.) were mixed in a

dry-box. The red precipitate was washed with benzene and dried *in vacuo* (Found: Br, 15.7; Ti, 9.9. Calc. for $C_{24}H_{21}O_4BrTi$: Br, 16.0; Ti, 9.6%). After prolonged pumping in a high vacuum hydrogen bromide was lost (Found: Ti, 11.7. $C_{24}H_{20}O_4Ti$ requires Ti, 11.4%).

(b) *With 2-naphthol*. The tetrabromide (1.61 g.) and 2-naphthol (4.0 g.) similarly gave a deep-red solid which was washed with benzene (Found: Br, 32.0; Ti, 9.9. $C_{20}H_{14}O_2Br_2Ti$ requires Br, 32.4; Ti, 9.7%).

(c) *With piperidine*. Piperidine (3.32 g.) was distilled *in vacuo* on to titanium tetrabromide (1.60 g.) cooled in liquid nitrogen. On gradual warming the colour changed from brown to green, yellow, and finally to white. The *product* was washed with carbon tetrachloride, benzene

TABLE 4.

Compound	Found (%)		Required (%)		M. p.
	Cl or Br	Ti	Cl or Br	Ti	
$TiCl_4 \cdot 2C_5H_5N$	40.4	14.2	40.8	13.8	190° (decomp.)
$TiCl_4 \cdot 2CH_3 \cdot CN$	51.8	17.9	52.2	17.6	Subl. 80°
$TiCl_4 \cdot 2C_2H_5 \cdot CN$	47.2	16.1	47.3	16.0	104°
$TiCl_4 \cdot 2C_6H_5 \cdot CN$	35.6	12.4	35.9	12.1	—
$TiBr_4 \cdot 2C_5H_5N$	60.4	9.4	60.8	9.1	206° (decomp.)
$TiBr_4 \cdot 2CH_3 \cdot CN$	69.6	11.0	71.1	10.7	112—114°
$TiBr_4 \cdot 2C_2H_5 \cdot CN$	66.7	10.2	67.0	10.0	118—121°
$TiBr_4 \cdot 2C_6H_5 \cdot CN$	55.4	8.5	55.7	8.4	190—191° (decomp.)
$TiBr_4 \cdot CH_3 \cdot NO_2$	74.1	11.3	74.6	11.2	57—59°
$TiBr_4 \cdot C_6H_5 \cdot NO_2$	64.9	9.9	65.2	9.8	86—88°
$TiBr_4 \cdot CH_3 \cdot COCl$	79.1	11.0	79.5	10.8	50—51°
$TiBr_4 \cdot C_6H_5 \cdot COCl$	69.5	9.6	69.8	9.4	80—81°
$TiBr_4 \cdot C_6H_4(CO_2 \cdot CH_3)_2$	56.5	9.0	56.7	8.7	150—152°
$TiBr_4 \cdot (C_6H_5)_2NH$	59.2	9.2	59.6	8.9	—

and light petroleum (b. p. 60—70°) (Found: C, 62.7; H, 10.7; Ti, 12.3. $C_{20}H_{40}N_4Ti$ requires C, 62.5; H, 10.4; Ti, 12.5%). The product was fairly stable in the atmosphere.

Complexes of Titanium Tetraiodide.—The compound $TiI_4 \cdot 2C_5H_5N$, prepared as already described, was a deep brown solid (Found: I, 70.8; Ti, 6.9. $C_{10}H_{10}N_2I_4Ti$ requires I, 71.2; Ti, 6.7%). In the attempted preparation of solid complexes with acetonitrile, nitromethane, and acetyl chloride, analyses are consistent with the loss of adduct during the removal of excess of uncombined adduct *in vacuo* (Found: I, 87.5; Ti, 8.2. Calc. for $TiI_4 \cdot 2CH_3 \cdot CN$: I, 79.6; Ti, 7.5%. Found: I, 86.3; Ti, 8.4. Calc. for $TiI_4 \cdot CH_3 \cdot NO_2$: I, 82.3; Ti, 7.8. Found: I, 82.3; Ti, 8.4. Calc. for $TiI_4 \cdot 2CH_3 \cdot COCl$: I, 80.0; Ti, 7.7%). Benzonitrile, nitrobenzene, and benzoyl chloride gave gums which were not analysed.

Pyridinium Hexaiodotitanate.—The pyridine adduct of titanium tetraiodide (1.5 g.) was dissolved in 10 ml. of "AnalaR" hydriodic acid. Dark brown crystals were deposited slowly. They were washed with benzene and light petroleum (Found: C, 13.5; H, 1.4; I, 77.7; Ti, 5.35. Calc. for $C_{10}H_{12}N_2I_6Ti$: C, 12.4; H, 1.2; I, 78.6; Ti, 5.0%).

Complexes of Zirconium Tetrachloride and Tetrabromide.—Analyses of the compounds are in Table 5.

TABLE 5.

Compound	Found (%)		Required (%)		Compound	Found (%)		Required (%)	
	Cl	Zr	Cl	Zr		Br	Zr	Br	Zr
$ZrCl_4 \cdot 2C_5H_5N$...	36.0	23.6	36.3	23.2	$ZrBr_4 \cdot 2C_5H_5N$...	56.1	16.2	56.3	16.0
$ZrCl_4 \cdot 2CH_3 \cdot CN$...	45.0	29.2	45.1	29.0	$ZrBr_4 \cdot 2CH_3 \cdot CN$...	64.7	18.7	64.9	18.5
$ZrCl_4 \cdot 2C_2H_5 \cdot CN$...	41.2	26.8	41.4	26.6	$ZrBr_4 \cdot 2C_2H_5 \cdot CN$...	60.8	17.7	61.4	17.5
$ZrCl_4 \cdot 2C_6H_5 \cdot CN$...	31.9	20.9	32.3	20.8	$ZrBr_4 \cdot 2C_6H_5 \cdot CN$...	51.3	14.9	51.9	14.8

Reaction of Titanium Tetrafluoride with Carbon Halides.—Titanium tetrafluoride (1.48 g.) when refluxed with carbon tetrachloride (8.6 g.) for 3 hr. gave trichlorofluoromethane (0.071 g.) (Found: *M*, 132. Calc. for $CFCl_3$: *M*, 137.5). No other volatile product was formed. Titanium tetrafluoride (1.10 g.) was refluxed with carbon tetrabromide (4.12 g.) at 120—125° for 4 hr. The volatile products were dibromodifluoromethane (0.21 g.) (Found: *M*, 200.

Calc. for CF_2Br_2 : M , 210), bromotrifluoromethane (0.18 g.) (Found: M , 153. Calc. for CF_3Br : M , 149), and bromine (0.23 g.). Titanium tetrafluoride (1.0 g.) and carbon tetraiodide (5.1 g.) at 120° for 3 hr. gave trifluoroiodomethane (0.31 g.) (Found: M , 187. Calc. for CF_3I : M , 196), iodine pentafluoride (0.092 g.) (Found: $\text{I} : \text{F} = 1 : 4.85$), and carbon tetrafluoride (0.08 g.) (Found: M , 92. Calc. for CF_4 : M , 88). When titanium tetrafluoride (1.6 g.) and carbon tetraiodide (5.2 g.) were refluxed with carbon tetrachloride (20 g.) the main volatile product was trifluoroiodomethane (Found: M , 191. Calc. for CF_3I : M , 196). The residue was extracted with carbon tetrachloride and benzene and the extract evaporated and hydrolysed with 2N-sodium hydroxide. Analysis of the hydrolysate showed the formation of the *fluoroiodide* TiFI_3 (Found: F , 4.2; I , 84.3; Ti , 9.6. FI_3Ti requires F , 4.3; I , 85.0; Ti , 10.7%).

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