788. *Titanium Tetrachloride as a Catalyst in the Friedel–Crafts Reaction. Part II.* Addition Compounds.*

By N. M. Cullinane, S. J. Chard, and D. M. Leyshon.

Titanium tetrachloride combines with acid chlorides, forming solid complexes of the general formula $TiCl_4,R{\cdot}COCl$. In some cases the results have been confirmed by thermal analysis. Similar products are formed by ketones and by anisole.

Thermal analysis indicates that the titanic salt forms with benzene the complex $3TiCl_4,C_6H_6$.

In Friedel–Crafts syntheses additive compounds derived from aluminium chloride and organic molecules have been frequently obtained. In the acylation processes already described (Cullinane, Chard, and Leyshon, Part I*), formation of compounds of similar types with titanium tetrachloride in place of aluminium chloride was also observed, and some examples of these are described in the present memoir.

A number of such complexes of titanic chloride have been previously reported; solid products have been isolated with nitro-compounds (cf. Hertel and Demmer, *Annalen*, 1932, **499**, 134; Reihlen and Hake, *Annalen*, 1927, **452**, 47; Pushin *et al.*, *ibid.*, 1942, **551**, 259; Hertel, *ibid.*, 1942, **553**, 286), nitroso-compounds (Reihlen and Hake, *loc. cit.*), nitriles (Hertel and Demmer, *loc. cit.*; Ulich, Hertel, and Nespital, *Z. physikal. Chem.*, 1932, *B*, **17**, 21; Pushin *et al.*, *Annalen*, 1942, **553**, 278), aldehydes (Scagliarini and Tartarini, *Atti R. Accad. Lincei*, 1926, **4**, 318), ethers (Demetrios and Ladikos, *Praktika Akad. Athenon*, 1930, **5**, 449), indoles (Schmidtz-Dumont and Motzkus, *Ber.*, 1929, **62**, 466).

Complexes prepared by the present authors include those formed by acid chlorides (cf. Bertrand, *Bull. Soc. chim.*, 1880, **33**, 403; 1881, **34**, 631); all were of the composition $TiCl_4,R{\cdot}COCl$ and their constitutions were confirmed in some cases by means of temperature–concentration diagrams.

Complexes with acetic or benzoic anhydride could not be obtained pure, probably because these substances react to some extent with the titanium halide forming the corresponding acid chlorides; a similar reaction takes place between aluminium chloride and acetic anhydride, as noted by Groggins and Nagel (*Ind. Eng. Chem.*, 1934, **26**, 1313; cf. Adrianowsky (*Bull. Soc. chim.*, 1879, **31**, 199). Scagliarini and Tartarini (*loc. cit.*; cf. Evard, *Compt. rend.*, 1933, **196**, 2007) obtained from titanium tetrachloride and benzophenone a product to which they assigned the formula $TiCl_4$, $COPh_2$, and Hertel and Demmer (*loc. cit.*) claimed to have prepared also the compound $TiCl_4,2COPh_2$. In the present work

---

* Part I, *J.*, 1952, 376.

we have isolated solid complexes of titanic chloride with *p*-methoxyacetophenone, acetophenone, and methyl, ethyl, and *n*-propyl *p*-tolyl ketone; all of these were 1 : 1 products.

A well-defined compound $TiCl_4$,PhOMe was obtained from anisole. The product formed with benzene had a low freezing point and was therefore subjected to thermal analysis (Figure); its composition corresponding to $3TiCl_4,C_6H_6$.

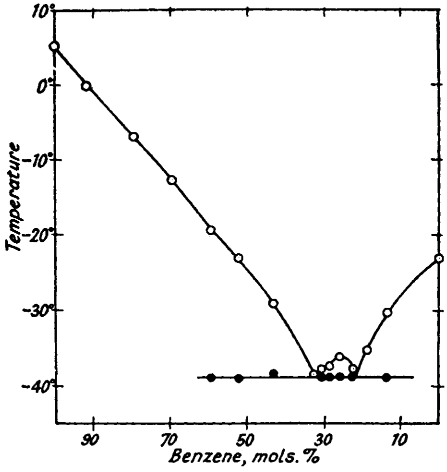
EXPERIMENTAL.

In all our experiments great care was taken to exclude moisture since all the products were hydrolysed at once by water.

Materials.—Titanium tetrachloride was boiled under reflux over copper turnings for 4 hours and then distilled, giving a water-white fraction, b. p. 136°.

" AnalaR " carbon disulphide was dried ($CaCl_2$) and fractionated; " thiophen-free " benzene and sulphur-free toluene were dried over sodium and distilled. The acid chlorides were boiled under reflux for an hour and then fractionated. " AnalaR " acetic anhydride was redistilled; benzoic anhydride, recrystallised from benzene–light petroleum, had m. p. 42°. Acetophenone (from B. D. H.) was dried ($CaCl_2$) and fractionated, then having m. p. 20°. Methyl (b. p. 224°), ethyl (b. p. 233°), and *n*-propyl (b. p. 250°) *p*-tolyl ketones (cf. Cullinane, Chard, and Leyshon, *loc. cit.*) were similarly treated. *p*-Methoxyacetophenone (m. p. 38°) and *p*-methoxybenzophenone (m. p. 62°) were recrystallised from alcohol and dried in a desiccator over phosphoric oxide.

Titanium tetrachloride–benzene.



Titanium was determined in the complexes by precipitation with ammonia solution and ignition to the dioxide, and chloride by precipitation with silver nitrate (cf. Cullinane *et al.*, *J. Soc. Chem. Ind.*, 1950, **69**, S 38).

Addition Compounds with Acid Chlorides.—In general the acid chloride was dissolved in dry carbondisulphide, and a solution containing an approximately equivalent amount of the titanium halide in the same solvent added. The precipitated complex was dissolved by careful heating, the solution cooled, and the supernatant liquid decanted from the crystals, which were washed with a little carbon disulphide and dried. With *n*- and *iso*-butyryl chlorides the procedure was modified somewhat; approximately equimolecular quantities of titanic chloride and acid chloride were mixed and placed in an ice-salt bath until partial solidification occurred, the mother-liquor was poured off, and the crystals were washed with a little cooled carbon disulphide, dried, and analysed. The following results were obtained: Titanium tetrachloride–acetyl chloride, small yellow plates, m. p. 19—20° (Found: Ti, 18·1; Cl 66·1. Calc. for $TiCl_4,CH_3\cdot COCl$: Ti, 17·9; Cl, 66·1%). Bertrand (*loc. cit.*) gives m. p. 25—30°.

Titanium tetrachloride–propionyl chloride, yellow prisms, m. p. 28·5° (Found: Ti, 16·9; Cl, 63·6. $TiCl_4,C_2H_5\cdot COCl$ requires Ti, 17·0; Cl, 62·9%).

*Titanium tetrachloride–*n*-butyryl chloride,* yellow needles, m. p. −4° (Found: Ti, 16·0; Cl, 59·7. $TiCl_4,C_3H_7\cdot COCl$ requires Ti, 16·2; Cl, 59·9%).

*Titanium tetrachloride–*iso*butyryl chloride,* yellow prisms, m. p. 11° (Found: Ti, 16·6; Cl, 59·6%).

Titanium tetrachloride–benzoyl chloride, small yellow needles, m. p. 63° (Found: Ti, 14·4; Cl, 53·9. Calc. for $TiCl_4,C_6H_5\cdot COCl$: Ti, 14·5; Cl, 53·7%). Bertrand (*loc. cit.*) gives m. p. 65°.

Addition Compounds with Ketones.—In the normal procedure an approximately equivalent amount of the titanium salt dissolved in toluene was added to a similar solution of the ketone. Finely divided crystals were gradually deposited at room temperature, and these were washed with a little toluene and dried.

Titanium tetrachloride–acetophenone, bright-yellow crystals which slowly darkened when heated and decomposed at 137—139° (Found: Ti, 16·0; Cl, 45·3. $TiCl_4,C_6H_5\cdot CO\cdot CH_3$ requires Ti, 15·7; Cl, 45·8%).

Titanium tetrachloride–methyl p-*tolyl ketone*, yellow needles, which darkened on heating and decomposed at about 120° (Found : Ti, 14·5; Cl, 43·4. $TiCl_4,CH_3{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3$ requires Ti, 14·8; Cl, 43·8%).

Titanium tetrachloride–ethyl p-*tolyl ketone*, orange plates, m. p. 65° (Found : Ti, 13·7; Cl, 41·4. $TiCl_4,CH_3{\cdot}C_6H_4{\cdot}CO{\cdot}C_2H_5$ requires Ti, 14·2; Cl, 42·0%).

*Titanium tetrachloride–*n-*propyl* p-*tolyl ketone*, bright yellow needles, darkening when heated and decomposing at about 110° (Found : Ti, 13·4; Cl, 39·8. $TiCl_4,CH_3{\cdot}C_6H_4{\cdot}CO{\cdot}C_3H_7$ requires Ti, 13·6; Cl, 40·3%).

*Titanium tetrachloride–*p-*methoxyacetophenone*, scarlet prisms, which darkened on heating and melted at 133° to a dark liquid which decomposed on further heating (Found : Ti, 14·6; Cl, 42·3. $TiCl_4,CH_3O{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3$ requires Ti, 14·1; Cl, 41·7%).

Other ketones gave reddish oils at the ordinary temperatures.

Titanium tetrachloride–Anisole.—The dark-red solution obtained by mixing the components in benzene deposited the *complex* as reddish-orange plates which were recrystallised from the same solvent and had m. p. 36° (Found: Ti, 15·8; Cl, 47·7. $TiCl_4,C_6H_5{\cdot}OCH_3$ requires Ti, 16·1; Cl, 47·6%).

Thermal Analyses.—In certain cases thermometric analyses were carried out by the cooling curve method. The apparatus consisted of a jacketed tube into which the components were distilled immediately before use, all essential precautions being taken to exclude moisture. The tube was fitted with a stirrer and immersed in a suitable bath; for lower temperatures a freezing mixture of ether and solid carbon dioxide contained in an unsilvered Dewar vessel was suitable. Temperatures were recorded on a standardized pentane thermometer. Fresh mixtures were made up for each freezing-point determination. The data are tabulated (eutectic temperatures are in parentheses).

Titanium tetrachloride–benzene.

Benzene, mols. % ...	100	91·9	79·5	69·6	59·5	52·2
F. p.	5·5°	0·0°	−6·8°	−12·6°	−19·3° (−38·7°)	−23·0° (−38·9°)
Benzene, mols. % ...	43·3	32·9	28·6	25·9		
F. p.	−29·0° (−38·4°)	−38·3°	−37·3° (−38·7°)	−36·0° (−38·7°)		
Benzene, mols. % ...	22·6	18·7	13·7	0		
F. p.	−37·7° (−38·7°)	−35·1° (−38·7°)	−30·2°	−23·1°		

The system indicates a compound $3TiCl_4,C_6H_6$, with a congruent m. p. of −36·0° and two eutectics both at about −38·7°, corresponding to 31·5 and 21·5 mols. % of benzene respectively.

Titanium tetrachloride–acetyl chloride.

Acetyl chloride, mols. %	100	97·1	93·7	85·3	79·5	63·4	53·0	42·7
F. p.	−112°	−28·1°	−7·0°	8·8°	15·1°	18·5°	19·3°	19·1°
Acetyl chloride, mols. %	33·3	22·5	15·5	6·6	4·7	0·0		
F. p.	18·3°	15·1°	11·9° (−28·4°)	2·1° (−28·6°)	−0·8°	−23·1°		

The system reveals a compound $TiCl_4,CH_3{\cdot}COCl$, with a congruent m. p. of 19·3°. One eutectic was at −28·5°, corresponding to 1·3 mols. % of acetyl chloride, the other was too low to be determined

Titanium tetrachloride–benzoyl chloride.

Benzoyl chloride, mols. %	100	97·4	95·5	86·3	82·4	67·6	
F. p.	−1·2°	−3·5° (−3·8°)	1·1° (−4·0°)	36·5°	47·1°	56·6°	
Benzoyl chloride, mols. %	52·3	39·8	27·2	18·9	8·4	3·7	0·0
F. p.	61·7°	62·4°	59·3°	56·2°	45·2°	35·0° (−24·5°)	−23·1°

A compound $TiCl_4,C_6H_5{\cdot}COCl$ is indicated, its congruent m. p. being 62·5°. The eutectics were at −3·9° and −24·5°, corresponding to 98 and 1 mol. % of benzoyl chloride respectively.

We thank Messrs. Peter Spence and Sons, Ltd., for gifts of titanium tetrachloride and the Department of Scientific and Industrial Research for a Maintenance Grant to one of us (D. M. L.).

THE TATEM LABORATORIES, UNIVERSITY COLLEGE,
CARDIFF.

[*Received, June 28th,* 1952.]