

## The Oxidation of Titanium(III) Chloride by Chlorinated Alkyl Cyanides

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Monochloro-, dichloro-, and trichloro-acetonitrile and 1-cyano-1,1,2-trichloroethane oxidise titanium(III) chloride to yield titanium(IV) chloride-alkyl cyanide complexes. The organic reaction products were isolated from the reaction media. A mechanism for the oxidation and structures for the complexes are proposed.

THE reduction of certain transition-metal halides by alkyl cyanides has been extensively studied.<sup>1-8</sup> Recently the organic products from the reaction of rhodium(v) chloride<sup>4,5</sup> and vanadium(IV) chloride<sup>6</sup> with methyl cyanide have been isolated; it was proposed that the primary organic products arising from the reduction of vanadium(IV) chloride by methyl cyanide<sup>6</sup> was trichloroacetonitrile.

The formation of hydrogen halides by hydrogen abstraction from the ligand has been observed during the reduction of metal halides by nitriles,<sup>1,2,8</sup> aliphatic amines,<sup>9</sup> and heterocyclic amines.<sup>10</sup> Further studies of the variation of the facility for hydrogen abstraction and the associated redox changes have been made by investigation of the reactions of transition-metal halides with halogenated alkyl cyanides. Prior to our studies, the only related work was a patent report<sup>11</sup> of the oxidation by chlorinated nitriles of copper powder to copper(II) chloride and the associated polymerisation of the nitriles. In a preliminary communication<sup>12</sup> we reported the oxidation of titanium(III) chloride by trichloroacetonitrile; this is now described in more detail, together with an account of reaction of the trichloride with monochloro- and dichloro-acetonitrile and 1-cyano-1,1,2-trichloroethane.

### DISCUSSION

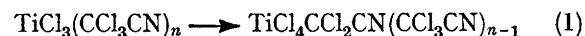
Titanium(III) chloride was oxidised by mono-, di-, and tri-chloroacetonitrile and 1-cyano-1,1,2-trichloroethane to yellow volatile complexes  $\text{TiCl}_4 \cdot 2\text{CH}_2\text{ClCN}$ ,  $\text{TiCl}_4 \cdot 2\text{CHCl}_2\text{CN}$ ,  $\text{TiCl}_4 \cdot \text{CCl}_3\text{CN}$ , and  $\text{TiCl}_4 \cdot \text{CH}_2\text{ClCCl}_2\text{CN}$  respectively. Adducts with identical infrared spectra were obtained from titanium(IV) chloride by reaction with the appropriate nitrile. In addition, compounds of similar stoichiometry to the titanium(IV) chloride complexes were obtained with zirconium(IV) chloride and mono- and tri-chloroacetonitrile.

These oxidations are of special interest as titanium(IV) chloride was not reduced when heated under reflux with acetonitrile.<sup>13</sup> Titanium(III) chloride and trichloroacetonitrile showed no visible signs of reaction when

shaken together for days at room temperature; however, the mixture formed the titanium(IV) adduct in 80% yield on warming to 35 °C for 12 h. In contrast, there was reaction between dichloroacetonitrile and titanium(III) chloride at room temperature, and over a period of six days the mixture turned brown and gave a 15% yield of  $\text{TiCl}_4 \cdot 2\text{CHCl}_2\text{CN}$ . The yield was increased to 45% when the reactants were heated to 35 °C for 24 h. Monochloroacetonitrile and titanium(III) chloride yielded a royal-blue compound  $\text{TiCl}_3 \cdot 3\text{CH}_2\text{ClCN}$  at room temperature, but when the mixture was heated to 35 °C for four days, there was a 6% yield of  $\text{TiCl}_4 \cdot 2\text{CH}_2\text{ClCN}$ .  $\text{TiCl}_4 \cdot \text{CH}_2\text{ClCCl}_2\text{CN}$  could only be obtained when titanium(III) chloride and 1-cyano-1,1,2-trichloroethane were heated at 60 °C for 10 days, when an 80% yield was obtained. Observations indicate that while co-ordination appears to be most rapid for the monochloroacetonitrile at room temperature, the oxidation (at 35 °C) occurs most readily with the trichloroacetonitrile.

The organic reaction products from the reaction of titanium(III) chloride and trichloroacetonitrile were examined, and tetrachlorosuccinonitrile and a polymer having the approximate composition  $(\text{Cl}_2\text{CCN})_n$  were isolated in low yield. Both of these compounds can be obtained from the species  $\text{CCl}_2\text{CN}$ , formed by the homolytic fission of a carbon-chlorine bond in trichloroacetonitrile.

Accordingly the most probable reaction scheme for the oxidation involves the transfer of a chlorine atom from a co-ordinated alkyl cyanide molecule to the metal: followed by expulsion of the  $\text{CCl}_2\text{CN}$  moiety.



Any reaction scheme involving the production of two radicals from trichloroacetonitrile by the breaking of a carbon-chlorine bond can be excluded as this reaction would have an activation energy<sup>14</sup> of the order of 78 kcal mol<sup>-1</sup> and so would not proceed at just above room temperature.

From the heat of formation of titanium(III)<sup>15,16</sup> and

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<sup>9</sup> G. W. A. Fowles and C. M. Pleas, *J. Chem. Soc.*, 1957, 1674.

<sup>10</sup> R. E. McCarley, B. G. Hughes, J. C. Boatman, and B. A. Torp, *Adv. Chem. Ser.*, 1963, **37**, 243.

<sup>11</sup> U.S.P. 3,231,523/1966.

<sup>12</sup> G. W. A. Fowles, D. A. Rice, N. Rolfe, and R. A. Walton, *Chem. Comm.*, 1970, 459.

<sup>13</sup> R. A. Walton, *Quart. Rev.*, 1965, **19**, 126.

<sup>14</sup> R. Walsh, personal communication.

<sup>15</sup> R. B. Head, *Austral. J. Chem.*, 1960, **13**, 332.

<sup>16</sup> D. G. Clifton and G. E. Maewood, *J. Phys. Chem.*, 1956, **60**, 309.

<sup>1</sup> M. W. Duckworth, G. W. A. Fowles, and R. A. Hoodless, *J. Chem. Soc.*, 1963, 5665.

<sup>2</sup> E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J. Chem. Soc.*, 1964, 4531.

<sup>3</sup> W. Schneider and A. v. Zelewsky, *Helv. Chim. Acta*, 1963, **46**, 1848.

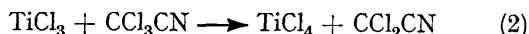
<sup>4</sup> G. Rouschias and G. Wilkinson, *Chem. Comm.*, 1967, 442.

<sup>5</sup> G. Rouschias and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 489.

<sup>6</sup> C. A. A. van Driel and W. L. Groeneveld, *Rec. Trav. chim.*, 1969, **88**, 891.

<sup>7</sup> A. P. Zuur, Thesis, Leiden, 1961.

titanium(IV)<sup>15</sup> chlorides, and assuming the carbon-chlorine bond strength in trichloroacetonitrile to be comparable to that in chloroform,<sup>14</sup> (78 kcal mol<sup>-1</sup>), an approximate value for the enthalpy of the oxidation reaction, (2), is 30 kcal mol<sup>-1</sup>.



This calculation does not take solvation energies into account and reaction, (2), differs from (1) in that the species  $\text{CCl}_3\text{CN}$  and  $\text{CCl}_2\text{CN}$  are not co-ordinated. However, these effects will cancel to a first approximation and so give a value of the activation energy close to 30 kcal mol<sup>-1</sup> which is *ca.* 5 kcal mol<sup>-1</sup> more than required to give a reasonable rate constant for reaction (1) at 35 °C.

The trimer  $(\text{CCl}_3\text{CN})_3$  was also isolated, but this most probably results from a separate polymerisation reaction rather than the oxidation as the same product can be obtained from trichloroacetonitrile by allowing it to react with aluminium(III) chloride.<sup>17</sup>

The chlorinated alkyl cyanide complexes all have infrared spectra in the region 3000–500 cm<sup>-1</sup> typical of co-ordinated chloroalkyl cyanides, and the expected shifts in the cyanide frequencies are observed (see Experimental section). Complexes of the same stoichiometry as  $\text{TiCl}_4 \cdot 2\text{CH}_2\text{ClCN}$ ,  $\text{TiCl}_4 \cdot 2\text{CHCl}_2\text{CN}$ , and  $\text{ZrCl}_4 \cdot 2\text{CH}_2\text{ClCN}$  are formed by the parent halide and acetonitrile.<sup>18</sup> The adducts formed by the chlorinated alkyl cyanides appear to be *cis*-pseudo-octahedral. Since all the

metal–chlorine stretching frequencies, this suggests  $C_{4v}$  symmetry (four  $\nu_{\text{M-Cl}}$ ) rather than  $D_{4h}$  (one  $\nu_{\text{M-Cl}}$ ).

The complexes  $\text{TiCl}_4 \cdot \text{CCl}_3\text{CN}$  and  $\text{ZrCl}_4 \cdot \text{CCl}_3\text{CN}$  are isomorphous (Table 2). A single-crystal X-ray study

TABLE 2

The X-ray powder diffraction data for  $\text{TiCl}_4 \cdot \text{CCl}_3\text{CN}$  and  $\text{ZrCl}_4 \cdot \text{CCl}_3\text{CN}$

<i>d</i> (Å)	Intensity	<i>d</i> (Å)	Intensity
4.33	6	4.36	9
2.67	4	2.73	4
2.09	5	2.13	5
2.01	10	2.03	5
1.970	7	1.931	6
1.727	3	1.709	7
1.427	4	1.387	4
1.361	5	1.361	3
1.273	7	1.247	10
1.200	6	1.200	4

Intensities were estimated visually.

of  $\text{TiCl}_4 \cdot \text{CCl}_3\text{CN}$ <sup>19</sup> showed the complex to be a chlorine-bridged dimer, each metal atom being six-co-ordinate.  $\text{TiCl}_4 \cdot \text{POCl}_3$ <sup>20</sup> and  $\text{TiCl}_4 \cdot \text{CH}_3\text{CO} \cdot \text{OEt}$ <sup>21</sup> have been shown to have similar structures.

The structures of these two complexes are centrosymmetric and thus there are no coincidences below 500 cm<sup>-1</sup> between the infrared and Raman absorptions (Table 1).  $\text{TiCl}_4 \cdot \text{CH}_2\text{ClCCl}_2\text{CN}$  has a low-frequency infrared spectrum (Table 1) which is not inconsistent with a dimeric bridged structure.

The electronic spectra are all charge-transfer in origin and are similar to the spectra of the titanium(IV) chloride-, and zirconium(IV) chloro-acetonitrile complexes.<sup>22</sup>

The royal-blue complex  $\text{TiCl}_3 \cdot 3\text{CH}_2\text{ClCN}$  has a magnetic moment of 1.8 B.M. at 298 K. The electronic spectra show two absorptions at 14,700 and 17,200 cm<sup>-1</sup>. Similar absorptions have been observed for  $\text{TiCl}_3 \cdot 3\text{CH}_3\text{CN}$ <sup>23</sup> and these have been assigned to  $^2A_{1g} \leftarrow ^2B_{2g}$  and  $^2B_{1g} \leftarrow ^2B_{2g}$  transitions.

The low-frequency infrared spectrum (Table 1) shows a number of bands assignable to metal–chlorine frequencies. A *cis*-octahedral configuration having approximately  $C_{3v}$  symmetry would give rise to two such infrared bands whereas a *trans*-species ( $C_{2v}$ ) would show three. Comparison with the published spectrum of  $\text{TiCl}_3 \cdot 3\text{THF}$ <sup>24</sup> which has been assigned a *trans*-structure reveals a considerable agreement, and accordingly a similar structure is assigned to  $\text{TiCl}_3 \cdot 3\text{CH}_2\text{ClCN}$ .

This study has shown that when chlorinated alkyl cyanides oxidise titanium(III) to titanium(IV), stable alkyl cyanides are formed; this is in contrast to the oxidation of tungsten(V) to tungsten(VI), where addition across the cyanide bond occurs.<sup>25</sup>

TABLE 1

Infrared spectra of the complexes in the region 500–200 cm<sup>-1</sup> and Raman spectra of  $\text{TiCl}_4 \cdot \text{CCl}_3\text{CN}$  and  $\text{ZrCl}_4 \cdot \text{CCl}_3\text{CN}$  500–80 cm<sup>-1</sup>

Complex		Absorption maxima
$\text{TiCl}_4 \cdot \text{CCl}_3\text{CN}$	I.r.	457mw, 440sh, 390vsbr, 380sh, 342mw, 272m, 256w, 243w
	Raman	440vs, 412s, 395ms, 353m, 288ms, 240mw, 220m, 168mw, 152s, 130s, 124sh, 115sh, 86w
$\text{ZrCl}_4 \cdot \text{CCl}_3\text{CN}$	I.r.	370svbr, 348sh, 285sh, 276sh, 264s, 222w
	Raman	396vs, 372ms, 364m, 349m, 273s, 207m, 156m, 137mw, 128vs, 116s, 104m, 80m
$\text{TiCl}_4 \cdot 2\text{CHCl}_2\text{CN}$		440m, 381vsbr, 361sh, 309m, 299mw, 277mw
$\text{TiCl}_4 \cdot 2\text{CH}_2\text{ClCN}$		440sh, 380vsbr, 325ms, 282w, 225w
$\text{ZrCl}_4 \cdot 2\text{CH}_2\text{ClCN}$		381sh, 368s, 347s, 321sh, 280w
$\text{TiCl}_3 \cdot 3\text{CH}_2\text{ClCN}$		392sh, 375s, 336sh, 302sh, 281m, 270sh, 243ms, 218w
		490s, 425m, 390vsbr, 360sh, 330sh, 270m
$\text{CCl}_3\text{CN}$		500vs, 327m, 314s, 264vs, 244sh
$\text{CHCl}_2\text{CN}$		502ms, 479ms, 286w, 233w
$\text{CH}_2\text{ClCN}$		500vs
$\text{CH}_2\text{ClCCl}_2\text{CN}$		500vs, 345ms, 320m

infrared spectra in the region 500–200 cm<sup>-1</sup> (Table 1) contain a number of bands that may be assigned to

<sup>17</sup> U.S.P. 2,525,714/1950.

<sup>18</sup> H. J. Emeleus and G. S. Rao, *J. Chem. Soc.*, 1958, 4245.

<sup>19</sup> M. G. B. Drew, personal communication.

<sup>20</sup> C. I. Bränden and I. Lindquist, *Acta Chem. Scand.*, 1960, **14**, 726.

<sup>21</sup> L. Brun, *Acta Cryst.*, 1966, **20**, 739.

<sup>22</sup> G. W. A. Fowles and R. A. Walton, *J. Chem. Soc.*, 1964, 2840.

<sup>23</sup> R. J. H. Clark, J. Lewis, D. J. Machin, and R. S. Nyholm, *J. Chem. Soc.*, 1963, 379.

<sup>24</sup> R. J. H. Clark, *Spectrochim. Acta*, 1965, **21**, 955.

<sup>25</sup> M. G. B. Drew, G. W. A. Fowles, D. A. Rice, and N. Rolfe, *Chem. Comm.*, 1971, 231.

## EXPERIMENTAL

All the chlorinated alkyl cyanides were obtained from commercial sources, and were dried under reflux over calcium hydride followed by distillation under reduced pressure onto phosphorus pentoxide. All reactants and products were handled under rigorously anhydrous conditions, standard vacuum-line and dry-box techniques being used.

**Physical Measurements.**—Diffuse-reflectance spectra were measured using a Unicam SP 700 spectrophotometer fitted with a reflectance attachment. Infrared spectra in the range  $4000\text{--}400\text{ cm}^{-1}$  were measured as mulls between KBr plates with a Perkin-Elmer 457 spectrophotometer. Spectra in the range  $500\text{--}200\text{ cm}^{-1}$  were obtained from mull samples between Polythene plates with a Grubb-Parsons D.M.4 instrument.

Magnetic measurements were made with a Gouy-type balance. Mass spectra were obtained with an A.E.I. M.S.12 spectrometer, and X-ray powder photographs were taken using 5.73 cm radius camera by the Debye-Scherrer technique.

**Analysis.**—Titanium and zirconium were determined by the ignition of complexes to the dioxide. Chloride was determined gravimetrically; C, H, and N analyses were determined in our own microanalytical laboratory.

**Preparation of the Complexes.**—(i) *Preparations using tetrachlorides.* The tetrachloride (2 g) was placed in an ampoule with the nitrile ( $30\text{ cm}^3$ ). All the nitriles, with the exception of monochloroacetonitrile, gave complexes which were insoluble in an excess of the nitrile and so the complexes were isolated by filtration, the excess nitrile being removed by a stream of dry nitrogen. The monochloroacetonitrile complexes were obtained by removal of excess of nitrile under reduced pressure.

(ii) *Oxidation reactions.* The titanium(III) chloride (2 g) was sealed in an ampoule with an excess ( $30\text{ cm}^3$ ) of the nitrile. The ampoules were heated to  $35^\circ\text{C}$  in the case of the chlorinated acetonitriles and  $60^\circ\text{C}$  with 1-cyano-1,1,2-trichloroethane. The reaction mixture was transferred to a vacuum line, and the excess of ligand and the volatile complex were distilled free from the other non-volatile reaction products. Yellow crystals of the adducts formed in the distillate and these were isolated by filtration and dried in a stream of dry nitrogen.

**$\text{TiCl}_4\cdot\text{CCl}_3\text{CN}$ .** (a) *Product from oxidation.* Yield 80% after 12 h at  $35^\circ\text{C}$ ; Found: Ti, 14.3; Cl, 42.7; C, 5.7; N, 3.0%.

(b) *Product from  $\text{TiCl}_4$  reaction.* Found: Ti, 14.4; Cl, 42.3; C, 7.2; N, 3.6%. Calc. for  $\text{TiCl}_4\cdot\text{CCl}_3\text{CN}$ : Ti, 14.3; Cl, 42.5; C, 7.2; N, 4.2%;  $\nu_{\text{max}}$  2298m ( $\text{C}\equiv\text{N}$  stretch), 1665w, 1652w, 1027s, 984s, 974sh, 798sh, 788vs, 720sh, 525sh, 511w, and 501s  $\text{cm}^{-1}$ .

**$\text{TiCl}_4\cdot 2\text{CHCl}_2\text{CN}$ .** (a) *Product from oxidation of  $\text{TiCl}_3$ .* Yield 45% after 24 h at  $35^\circ\text{C}$ . At room temperature there was a 15% yield after six days; Found: Ti, 11.5; Cl, 34.6%.

(b) *Product from  $\text{TiCl}_4$ .* Found: Ti, 11.5; Cl, 34.6. Calc. for  $\text{TiCl}_4\cdot 2\text{CHCl}_2\text{CN}$ : Ti, 11.7; Cl, 34.6%;  $\nu_{\text{max}}$

2481w, 2305s ( $\text{C}\equiv\text{N}$  stretch), 1596w, 1543w, 1310w, 1250s, 1186ms, 1150w, 1083w, 1025m, 990sh, 961vs, 938w, 818w, 776vs, 711s, 520s, and 507s  $\text{cm}^{-1}$ .

**$\text{TiCl}_4\cdot 2\text{CH}_2\text{ClCN}$ .** (a) *Product from oxidation of  $\text{TiCl}_3$ .* Yield 6% after 4 days at  $35^\circ\text{C}$ . The yield was increased to 70% on reaction at  $60^\circ$  for 12 h; Found: Ti, 13.8; Cl, 41.5%.

(b) *Product from  $\text{TiCl}_4$ .* Found: Ti, 13.9; Cl, 41.5. Calc. for  $\text{TiCl}_4\cdot 2\text{CH}_2\text{ClCN}$ : Ti, 14.1; Cl, 41.6%;  $\nu_{\text{max}}$  2453w, 2346w, 2308s ( $\text{C}\equiv\text{N}$  stretch), 2255w, 1658w, 1647m, 1545mw, 1413w, 1401s, 1345sh, 1306sh, 1268s, 1258sh, 1192mw, 1175w, 1085w, 1018w, 968sh, 944vs, 896m, 806s, 740s, and 515s  $\text{cm}^{-1}$ .

**$\text{TiCl}_4\cdot\text{CH}_2\text{ClCCl}_2\text{CN}$ .** (a) *Product from oxidation of  $\text{TiCl}_3$ .* At  $35^\circ\text{C}$  there was no oxidation, but after 10 days at  $60^\circ\text{C}$  there was an 80% yield; Found: Ti, 14.0; Cl, 40.3%.

(b) *Product from  $\text{TiCl}_4$ .* Found: Ti, 13.8; Cl, 40.0. Calc. for  $\text{TiCl}_4\cdot\text{CH}_2\text{ClCCl}_2\text{CN}$ : Ti, 13.8; Cl, 40.7%;  $\nu_{\text{max}}$  3005m, 2955m, 2293m ( $\text{C}\equiv\text{N}$  stretch), 1654m, 1540w, 1420s, 1375s, 1275m, 1257m, 1207s, 1072s, 1012w, 978m, 885w, 870m, 790s, 745s, and 615s  $\text{cm}^{-1}$ .

**$\text{ZrCl}_4\cdot\text{CCl}_3\text{CN}$ .** *Prepared from tetrachloride.* Found: Zr, 24.0; Cl, 37.6; C, 6.1; N, 2.7. Calc. for  $\text{ZrCl}_4\cdot\text{CCl}_3\text{CN}$ : Zr, 24.2; Cl, 37.6; C, 6.4; N, 3.7%;  $\nu_{\text{max}}$  2300ms ( $\text{C}\equiv\text{N}$  stretch), 1605m, 1598mw, 1031s, 985s, 978sh, 794vs, 782sh, 728sh, and 516  $\text{cm}^{-1}$ .

**$\text{ZrCl}_4\cdot 2\text{CH}_2\text{ClCN}$ .** *Prepared from tetrachloride.* Found: Zr, 23.5; Cl, 36.8. Calc. for  $\text{ZrCl}_4\cdot 2\text{CH}_2\text{ClCN}$ : Zr, 23.7; Cl, 36.9%;  $\nu_{\text{max}}$  2425w, 2340w, 2307s ( $\text{C}\equiv\text{N}$  stretch), 2256sh, 1650sh, 1630mw, 1600sh, 1404sh, 1400s, 1344sh, 1306w, 1256ms, 1174m, 1016w, 951w, 942vs, 896m, 743s, 582mw, and 520ms  $\text{cm}^{-1}$ .

**$\text{TiCl}_3\cdot 3\text{CH}_2\text{ClCN}$ .** This product was obtained by shaking together  $\text{TiCl}_3$  and  $\text{CH}_2\text{ClCN}$  in a sealed ampoule at room temperature. Found: Ti, 12.7; Cl, 27.9. Calc. for  $\text{TiCl}_3\cdot 3\text{CH}_2\text{ClCN}$ : Ti, 12.6; Cl, 27.9%;  $\nu_{\text{max}}$  2428w, 2346w, 2307s ( $\text{C}\equiv\text{N}$  stretch), 2252sb, 1408s, 1346sh, 1316sh, 1266ms, 1258s, 1180ms, 1177ms, 945vs, 909m, 897mw, 739s, and 519ms  $\text{cm}^{-1}$ .

**Isolation of the Organic Products from the Oxidation of Titanium(III) Chloride by Trichloroacetonitrile.**—Titanium(III) chloride and trichloroacetonitrile were heated *in vacuo* at  $35^\circ\text{C}$  for 24 h. The volatile products,  $\text{TiCl}_4\cdot\text{CCl}_3\text{CN}$  and the excess of trichloroacetonitrile were removed by distillation under reduced pressure. The residue, on extraction with dry isopentane, gave a black solid and a yellow extract. Evaporation of the extract gave a yellow wax from which crystals of tetrachlorosuccinonitrile were sublimed; the remainder of the wax was dissolved in isopentane to give a solution from which crystals of 1,3,5-trichloromethyltriazine were obtained. The black powder was shown to be a polymer based on  $\text{CCl}_2\text{CN}$  units having one titanium(IV) chloride molecule co-ordinated for every 5.5 units of  $\text{CCl}_2\text{CN}$ . The nature of the organic products was deduced by infrared and mass spectrometry. Melting points were compared with literature values.<sup>11,26</sup>

<sup>26</sup> K. Wakabayashi, M. Tsuruda, and Y. Suzuki, *Bull. Chem. Soc. Japan*, 1969, **42**, 2924.