The thermal decomposition of 1,4-dioxan complexes of titanium(III) chloride

M. ZIKMUND, A. VALENT*, and K. HRNČIAROVÁ

Institute of Inorganic Chemistry, Slovak Academy of Sciences, 809 34 Bratislava

Received 29 December 1974

Accepted for publication 25 August 1975

The thermal decomposition reactions of $TiCl_3(C_4H_8O_2)_3$, $TiCl_3(C_4H_8O_2)_2$, and $TiCl_3(C_4H_8O_2)$ have been studied by thermogravimetric method in nitrogen atmosphere and under reduced pressure. The intermediates have been isolated and characterized.

Термогравиметрическим методом изучены реакции термического разложения $TiCl_3(C_4H_8O_2)_3$, $TiCl_3(C_4H_8O_2)_2$ и $TiCl_3(C_4H_8O_2)$ при пониженном давлении и в атмосфере азота. Были выделены и охарактеризованы промежуточные продукты.

The reactions between titanium(III) chloride and various organic ligands and characterization of the resulting complexes have attracted a great deal of attention. However, there is relatively little known about 1,4-dioxan (D) complexes of titanium(III) although *Rolsten* and *Sisler* [1] and *Clark et al.* [3] have rep.orted the preparation of the complex of the stoichiometry $TiCl_3 \cdot 2D$ and *Fowles et al* [4] have synthesized the species $TiCl_3 \cdot D$, $TiCl_3 \cdot 2D$, and $TiCl_3 \cdot 3D$. These compounds have been characterized in some details by studying their magnetic properties [2, 5—7, 9, 10], visible absorption and diffuse reflectance spectra [2, 4, 10], and infrared spectra [1—4, 8], but little work has been done with investigation of their chemical properties in the solid state because of the experimental difficulties in their pre paration and characterization. This paper reports the results obtained from an examination of the thermal decomposition of the above-mentioned type of adducts.

Experimental

Reactions were carried out in all-glass equipment connected to a nitrogen manifold under an overpressure of about 10 Torr to prevent oxidation, hydrolysis and decomposition of synthesized complexes under reduced pressure. Nitrogen was dried and deoxygenated by passing through columns of zeolite molecular sieves 4 A (commercial mark Nalsit), activated copper, as well as through freezing traps cooled with liquid nitrogen. Solvents and reagents used were purified and dried by appropriate methods.

* *Present address:* Department of Inorganic and Organic Chemistry, Faculty of Pharmacy, Komenský University, 880 34 Bratislava.

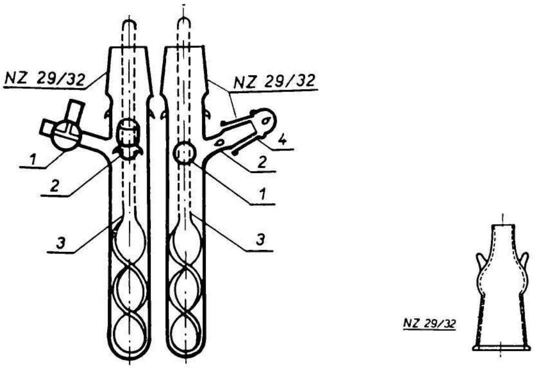

Fig. 1. Tube for thermal decomposition of solid samples in inert atmosphere or under reduced pressure.

The complex $TiCl_3 \cdot 2D$ was prepared by a method given in literature [3, 4]. The powdered adduct $TiCl_3 \cdot 3D$ was obtained by adding of an excess of *n*-hexane to the saturated solution of $TiCl_3 \cdot 2D$ in 1,4-dioxan. The intermediate product $TiCl_3 \cdot D$ was prepared by heating of $TiCl_3 \cdot 2D$ in flowing nitrogen atmosphere at 150°C under stirring in special glass tube (Fig. 1) dipped in an oil bath. The synthesized compounds were checked by chemical analysis and diffuse reflectance spectra. Fig. 2 shows the reflectance spectra of the synthesized triadduct and diadduct superimposed of that of the intermediate monoadduct. The observed spectra of complexes under investigation are consistent with those described in previous papers [2, 4, 10].

Thermogravimetric measurements were performed with all the complexes under two different experimental conditions: in dynamic atmosphere of dry nitrogen ($1\ l\ h^{-1}$) and under reduced pressure (10^{-1} Torr) using helical spring recording balance described in paper [11].

The diffuse reflectance spectra were recorded on VEB Zeiss Spekol spectrophotometer which is equipped with the reflectance attachment Model Rd/0 using special all-glass vessel for obtaining spectra in an inert atmosphere.

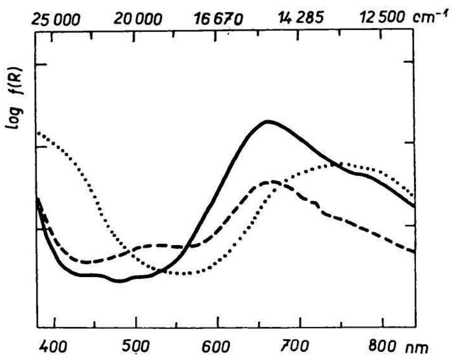

Fig. 2. Diffuse reflectance spectra of $TiCl_3 \cdot 3D$ (——), $TiCl_3 \cdot 2D$ (- - -), and $TiCl_3 \cdot D$ (· · ·).

Results and discussion

The complex $TiCl_3 \cdot 3D$ is thermally stable under nitrogen atmosphere to about 70°C (Fig. 3). Over this temperature, as far as to about 100°C it follows the splitting off of two molecules of 1,4-dioxan. Next, over 200°C, it follows the disproportionation of a complex $TiCl_3 \cdot D$, yielding titanium(II) chloride. On the contrary, the thermal decomposition of the same compound under reduced pressure proceeds quite differently. When heated over about 40°C *in vacuo*, the thermal decomposition of the complex $TiCl_3 \cdot 3D$ was found to proceed in one step only. Thus it is not possible to prepare the complex $TiCl_3 \cdot D$. The final product in the curve illustrated corresponds to the titanium(II) chloride, too.

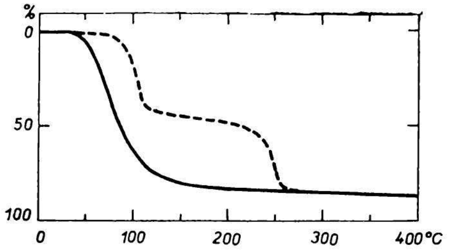

Fig. 3. Thermogravimetric curves of $TiCl_3 \cdot 3D$ in nitrogen atmosphere (- - - -) and under reduced pressure (——).

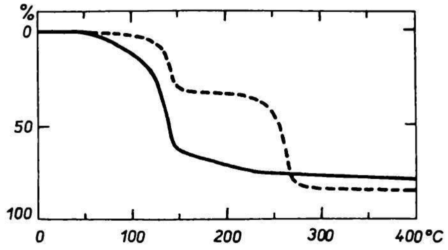

Fig. 4. Thermogravimetric curve of $TiCl_3 \cdot 2D$ in nitrogen atmosphere (- - - -) and that of $TiCl_3 \cdot D$ under reduced pressure (——).

Analysis of the thermogram of the complex $TiCl_3 \cdot 2D$ (Fig. 4) indicates two steps in the decomposition under nitrogen atmosphere. The first one corresponds approximately to the weight loss of one ligand. The intermediate exists within the temperature interval between 150 and 200°C. In the temperature range about 230—280°C the disproportionation of $TiCl_3 \cdot D$ occurs leading to stable solid titanium(II) chloride. The compound $TiCl_3 \cdot D$, when decomposes thermally under vacuum, disproportionates to titanium(II) chloride in the temperature range about 100—150°C.

References

1. Rolsten, R. F. and Sisler, H. H., *J. Amer. Chem. Soc.* ***79***, 1068 (1957).
2. Hendra, P. J. and Powell, D. B., *J. Chem. Soc.* ***1960***, 5105.
3. Clark, R. J. H., Lewis, J., Machin, D. J., and Nyholm, R. S., *J. Chem. Soc.* ***1963***, 379.
4. Fowles, G. W. A., Hoodless, R. A., and Walton, R. A., *J. Chem. Soc.* ***1963***, 5873.
5. Machin, D. J., Murray, K. S., and Walton, R. A., *J. Chem. Soc., A*, ***1968***, 195.
6. Fowles, G. W. A. and Walton, R. A., *J. Chem. Soc.* ***1964***, 4953.
7. Schläfer, H. L. and Götz, R., *Z. Phys. Chem.* (Frankfurt) ***41***, 97 (1964).
8. Alyea, E. C. and Torrible, E. G., *Can. J. Chem.* ***43***, 3468 (1965).
9. Udachin, Y. M., Belova, V. I., and Dyatkina, M. E., *Zh. Strukt. Khim.* ***8***, 366 (1967).
10. Hoff, G. R. and Brubaker, C. H., *Inorg. Chem.* ***10***, 2063 (1971).
11. Zikmund, M., Štepničková, L., and Hrnčiarová, K., *Chem. Zvesti* ***22***, 917 (1968).

Translated by M. Zikmund