

Thermogravimetric investigation of some chloro(pyridine) complexes of titanium(III)

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

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

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The thermogravimetric study of the compounds of the composition $TiCl_3L_n$ (where L is pyridine and its alkyl derivatives, and $n = 1-3$) showed the intermediate formation of pale yellow complex $TiCl_3(py)_2$. Each of the compounds decomposed, ultimately, to the solid black titanium(II) chloride and to volatile yellow adduct $TiCl_4L_2$.

Термогравиметрическое изучение соединений состава $TiCl_3L_n$ (где L пиридин и его алкилпроизводные, $n = 1-3$) показало образование промежуточного светло-желтого комплекса $TiCl_3(py)_2$. Каждое из соединений разлагалось с выделением твердого черного двуххлористого титана и летучего желтого аддукта $TiCl_4L_2$.

Previous workers [1-18] have prepared and investigated a number of complexes of the stoichiometry $TiCl_3L_n$ where L is pyridine (py), α -picoline, β -picoline, or γ -picoline (pic), and $n = 1, 2$, or 3 and have reported limited and sometimes conflicting data on their properties and reactivity in nonaqueous solutions and in the solid state. A green complex $TiCl_3(py)_3$ has been first described in patented reports [1-3]. It has been reported that by thermal treatment at 250-400°C, preferably under vacuum, all the pyridine is removed and the crystalline $TiCl_3$, having a higher catalytic activity, is recovered. Later, as a part of an investigation dealing with the catalytic polymerization of olefins by various solid amine adducts of titanium(III) chloride, Carrasi and Danielli [5] described the grey adduct $TiCl_3(py)$, while Pirogov and Chirkov [6] confirmed the existence of the violet adduct $TiCl_3(py)$ and the light yellow adduct $TiCl_3(py)_2$. Green complexes $TiCl_3(py)_3$ and $TiCl_3(\gamma\text{-pic})_3$, a green-blue adduct $TiCl_3(\alpha\text{-pic})_2$, and a brown solid product of the composition $TiCl_3(2,4\text{-lutidine})$ have been examined by Fowles and Hoodless [4].

Little is known about whether such adduct formation is maintained in green and red-brown solutions of titanium(III) chloride in pyridine [4, 9, 16-18]. The reaction of titanium(III) chloride with *n*-hexane solution of pyridine has been studied by Takashi [10]. Results of the chemical analysis and physical investigations indicated

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

that only the solid $\text{TiCl}_3(\text{py})_3$ complex was formed. On the other hand, *Collins and Drew* [15] following the method of *Ref.* [4] have prepared crystals of the adduct $\text{TiCl}_3(\text{py})_3 \cdot \text{py}$ with one solvent molecule of pyridine per complex having *mer*-configuration according to the crystal structure determination.

In previous papers [7–9], the authors of the present study have shown that it was possible to obtain the range of solid products by sampling a solid phase of titanium(III) chloride with *n*-hexane containing various amounts of pyridine. The composition of the non-stoichiometric intermediates was found to vary according to the reaction conditions. As the reaction proceeded the colour of the solid phase changed from the violet colour attributable to the monopyridine adduct to the green of the trispyridine complex.

Continuing our studies on the influence of the chemical composition and structure of compounds of titanium(III) chloride with pyridine and its alkyl derivatives on their chemical properties, we have investigated, by thermogravimetric (TG) method, the thermal decomposition of reaction products prepared as described in [7–9].

Experimental

Because of the titanium(III) complexes react rapidly with oxygen and moisture, it was necessary to carry out the syntheses in special all-glass equipment. All transfer operations and chemical reactions were conducted in an atmosphere of nitrogen to prevent hydrolysis and oxidation. Nitrogen was dried and deoxygenated by passing through columns of zeolite molecular sieves 4 A (Nalsit 4), activated copper and liquid nitrogen bath.

Reagents and solvents were the best commercially available and were purified and dried by appropriate methods. The methods of synthesis were similar as reported earlier [21]. Previous workers [4, 10] have reported that only the complex $\text{TiCl}_3(\text{py})_3$ was formed in the reaction between titanium(III) chloride and pyridine. In view of this, we have repeated our preparation, obtaining once more the series of solid intermediates between

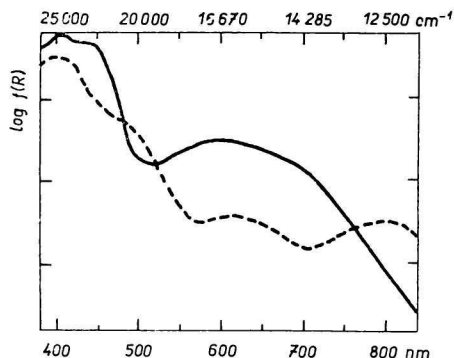


Fig. 1. Diffuse reflectance spectra of $\text{TiCl}_3(\text{py})_3$ (—) and $\text{TiCl}_3(\text{py})_2$ (- -).

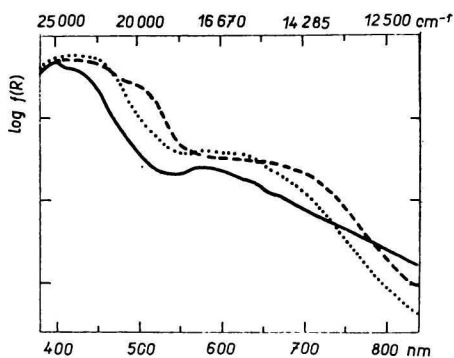


Fig. 2. Diffuse reflectance spectra of $\text{TiCl}_3(\alpha\text{-pic})_3$ (—), $\text{TiCl}_3(\beta\text{-pic})_3$ (- -), and $\text{TiCl}_3(\gamma\text{-pic})_3$ (· ·).

TiCl_3 and $\text{TiCl}_3(\text{py})_3$. A comparison of the two sets of results indicates adequate agreement within experimental error. Identical composition TiCl_3L_3 of the final products and almost identical colours and analogous diffuse reflectance spectra are obtained if α -picoline, β -picoline, γ -picoline, and 4-ethylpyridine are used instead of pyridine (Figs. 1 and 2).

The effect of diluting the pyridine and picolines solutions with *n*-hexane was studied in order to monitor the stoichiometry of the solid products formed. Three new pale brown adducts of the average stoichiometry $\text{TiCl}_3\text{L}_{3.3}$ where L is pyridine, β -picoline, or γ -picoline were synthesized. The method of preparation was very similar in all the cases; the following is the typical example: 5 grams of titanium(III) chloride were treated with 700 g of the hexane solution containing 30 g of pyridine. The suspension was stirred for 4 hrs. The resulting pale brown compound, which was slightly soluble in the parent solution, was filtered, washed with dry hexane and dried under reduced pressure. If the initial reaction mixture was allowed to stand at room temperature overnight, green precipitate $\text{TiCl}_3(\text{py})_3$ formed. We have been unable to isolate $\text{TiCl}_3(\text{py})_3 \cdot \text{py}$ adduct [15]. The composition of the adducts of the general formula $\text{TiCl}_3\text{L}_{3.3}$ was found to vary according to the conditions of handling. Because of the poor mulling properties of the adduct $\text{TiCl}_3(\text{py})_{3.3}$ its infrared spectrum and Nujol visible absorption spectrum can be interpreted in a qualitative way only (Fig. 3). Hence, it was impossible to differentiate between the coordinated and the solvate bound pyridine.

The pale yellow complex $\text{TiCl}_3(\text{py})_2$ (Fig. 1) has been prepared by the thermal decomposition of $\text{TiCl}_3(\text{py})_3$ *in vacuo* at 90°C for 1 hr.

Apparatus and equipment

Thermogravimetric curves have been determined for synthesized and previously reported compounds. Thermogravimetric experiments were performed under reduced pressure (10^{-1} Torr) using helical spring recording balance described in paper [19]. Approximately 50 mg samples were heated at a rate of 4°C min^{-1} .

The diffuse reflectance spectra were recorded on Optica Milano Model CF-4 spectrophotometer, furnished with the standard reflectance attachment for the range $38\,000$ to $15\,000\text{ cm}^{-1}$, modified to make it suitable for measurements in inert atmosphere [20], and on VEB Zeiss Spekol spectrophotometer which is equipped with the reflectance attachment Model Rd/0 for the range $27\,000$ – $12\,000\text{ cm}^{-1}$ using special all-glass vessel for obtaining spectra of the air-sensitive samples.

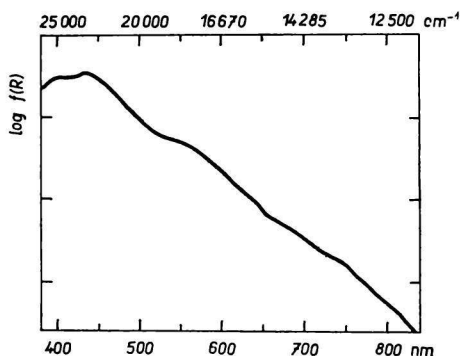


Fig. 3. Diffuse reflectance spectrum of $\text{TiCl}_3(\text{py})_{3.3}$.

Results and discussion

Examination of the thermograms of complexes of $TiCl_3L_3$ type (Figs. 4 and 5) indicates three steps in the decomposition. The first weight loss in the temperature range of $50-100^\circ C$ is the decomposition corresponding to the reaction

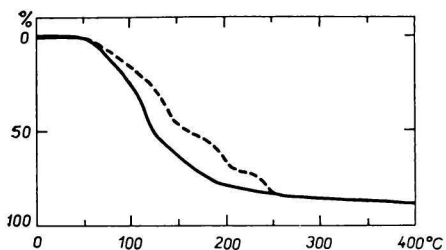


Fig. 4. Thermogravimetric curves of $TiCl_3(py)_{3.3}$ (—) and $TiCl_3(py)_3$ (- -).

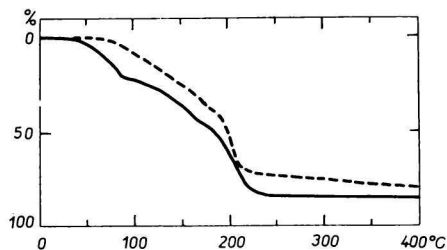


Fig. 5. Thermogravimetric curves of $TiCl_3(\alpha\text{-pic})_3$ (—) and $TiCl_3(\alpha\text{-pic})_2$ (- -).

The second weight loss corresponds to the release of the second ligand molecule, L, and leads to the very unstable intermediate $TiCl_3L$



The final weight loss is the disproportionation of the intermediate $TiCl_3L$ (probably with chlorine-bridged polymeric structure) leading to a residue whose weight loss corresponds (within the experimental errors due with the simultaneous presence of the low-volatile $TiCl_4(py)_2$ adduct) to that of titanium(II) chloride. The temperature range of $TiCl_3L$ disproportionation (about $200^\circ C$) is several hundred degrees below the disproportionation of uncomplexed titanium(III) chloride.

It is probable that other thermal decompositions reported here (Figs. 6—9) could proceed by a similar route but the thermograms were insufficiently well-resolved to confirm this suggestion.

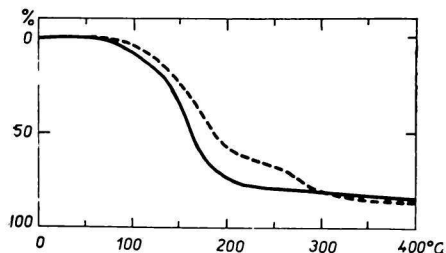


Fig. 6. Thermogravimetric curves of $TiCl_3(\beta\text{-pic})_3$ (—) and $TiCl_3(\beta\text{-pic})_{3.3}$ (- -).

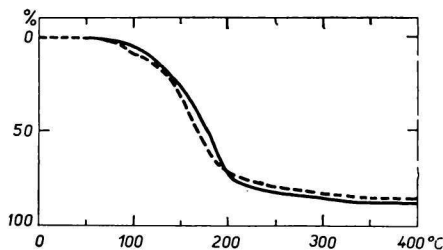


Fig. 7. Thermogravimetric curves of $TiCl_3(\gamma\text{-pic})_{3.3}$ (—) and $TiCl_3(\gamma\text{-pic})_3$ (- -).

The thermal stability of species under investigation is usually low and appears to be rather insensitive to steric and electronic effects of the alkyl groups on the pyridine ring. The course of thermal decomposition of stoichiometric complexes of the type $TiCl_3L_3$ (Figs. 4–7) is generally analogous to that of adducts $TiCl_3L_{3.3}$ (Figs. 4, 6, 7) and non-stoichiometric solid intermediates in the reaction between titanium(III) chloride and pyridine and its alkyl derivatives, respectively (Figs. 8, 9). The experiments shown in Figs. 8 and 9 indicates the non-existence of unreacted titanium(III) chloride in the investigated samples.

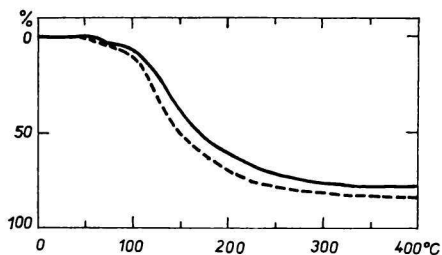


Fig. 8. Thermogravimetric curves of $TiCl_3(4-EtPy)_{1.5}$ (—) and $TiCl_3(2,4-lut)_{1.5}$ (- - -).

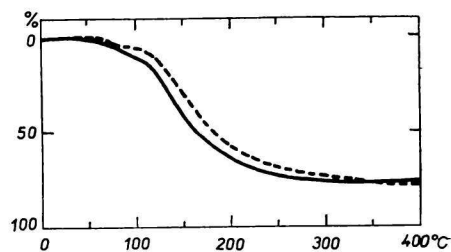


Fig. 9. Thermogravimetric curves of $TiCl_3(\alpha-pic)$ (—) and $TiCl_3(4-EtPy)$ (- - -).

The thermal decomposition of complexes of the type $TiCl_3L_3$ (where L is pyridine and its alkyl derivatives) leads only rarely to the formation of less or more stable intermediate products. The pale yellow complex $TiCl_3(py)_2$ can be prepared by heating of the *mer*-trichloro-tris(pyridine)titanium(III), $TiCl_3(py)_3$, at 90°C under reduced pressure. From the stereochemistry of its parent compound [15] and also from the fact that the two distinct *d-d* transitions were found in the visible region of its diffuse reflectance spectrum (Fig. 1), it seems very probable that $TiCl_3(py)_2$ has the trigonal-bipyramidal coordination [13].

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