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LETTERS TO THE EDITOR

Interaction of Titanium(IV) Chloride with Selected Ethers and Ketones

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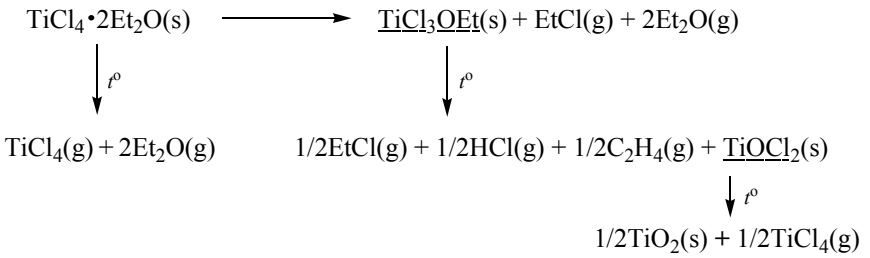
Titanium tetrachloride is a precursor of titanium dioxide, an important chemical for technological applications. $TiCl_4$ is usually transformed into TiO_2 via high-temperature gas-phase hydrolysis reactions (CVD process). Recently, aqueous-organic or pure oxygen-containing organic solvents (ethers or ketones) have been used in TiO_2 synthesis instead of water [1, 2]. In such systems, $TiCl_4$ acts as Lewis acid to form various complexes with the oxygen-containing donors [3]. The complexes vaporization is affected by the crystal structure type and the bonds energy [4].

Here we report on the influence of the donor type on the complex formation and vaporization in the mixtures of $TiCl_4$ with ethers (diethyl and diphenyl) and ketones (acetone and benzophenone). All complexes have been synthesized by direct interaction of components in whole glass apparatus under vacuum. The products were studied by NMR spectroscopy and mass spectrometry (70 eV, 120–320°C).

$TiCl_4$–Et_2O. The syntheses were performed at $TiCl_4 : Et_2O$ ratios of 1 : 2, 1 : 1, and 1 : 0.62. In the case of the 1:2 ratio, the $TiCl_4 \cdot 2Et_2O$ complex was formed, unstable at room temperature (the specimens were stored at –30°C). At the 1 : 1 ratio, the formed $TiCl_4 \cdot 2Et_2O$ complex was dissolved in the excess of $TiCl_4$. Within several months, colorless crystals precipitated from the so obtained solution; they were identified as $TiCl_3OEt$ by X-ray diffraction analysis. In view of that and taking into account the mass spectroscopy data of vapor composition over $TiCl_4 \cdot 2Et_2O$ and $TiCl_3OEt$, we suggested the following scheme of the processes in the $TiCl_4$–Et_2O system.



$TiCl_4$–Ph_2O. Independently of the components ratio (1.00 : 0.25 to 1.00 : 3.97), interaction of $TiCl_4$ with diphenyl ether yielded red solution without any solid phase. We failed to identify the dissolved complexes by ^1H and ^{13}C NMR spectroscopy. The vapor mass spectrum was a superposition of the initial components spectra. As no ions corresponding to possible complexes, chlorobenzene, or phenol were detected, we concluded that no reaction (complex formation or substitution) occurred in the gas phase in that system.

$TiCl_4$–Me_2CO. Irrespectively of the components ratio, synthesis in vacuum yielded the 1 : 1 solid complex which is unstable in the gas phase. The mass spectrum of the vapor phase revealed the following signals (along with the peaks assigned to $TiCl_4$ and acetone), *m*/*z*: 105 ($C_8H_9^+$ or $C_6H_5CO^+$), 120 ($C_9H_{12}^+$ or

$C_8H_8O^+$), and 134 ($C_{10}H_{14}^+$ or $C_9H_{10}O^+$), their intensity increasing with heating. Those signals suggested acetone polymerization upon heating.

$TiCl_4$–Ph_2CO. In that case, synthesis in vacuum yielded mixture of solid 1 : 1 and 1 : 2 complexes. Storing of the samples at room temperature led to steady transformation into the more stable 1 : 2 complex. Hence, the 1 : 1 complex could be prepared via precipitation from nonaqueous solvents exclusively. Mass spectra of the vapor phase confirmed that there is no complexes in the gas phase: the relative intensity of the MS signals are in good agreement with those for pure $TiCl_4$ and Ph_2CO data: upon heating, the complexes dissociated into the initial components.

To conclude, none of the studied complexes existed in the gas phase. The nature of the organic part determined the processes occurred upon the complexes heating: in the case of aromatic compounds, the complexes merely dissociated; in the case of aliphatic compounds, dissociation is accompanied by organic fragment transformation.

Stability of the complexes as determined in this work was in satisfactory agreement with the data on the proton affinity (E_H^+, kJ/mol) of the ligands [5].

Ph_2O	<	Et_2O	~	Me_2CO	<	Ph_2CO
–		828		812		882

Ether oxygen revealed weaker donor properties in the reactions with $TiCl_4$ that ketone oxygen.

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