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SPECTROSCOPIC STUDY OF THE STATE OF TITANIUM(III)

IONS IN ALCOHOL-WATER SOLUTIONS

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Information on the state of titanium(III) ions in water and in alcohols is extremely limited [1-3], and nothing whatever is known of the nature of the compounds formed in alcoholwater solutions. Meanwhile, such data are needed, particularly in connection with studies of the photochemical activity of coordination compounds of titanium in the sensitization of oxidation of organic substrates [4-7] and in the reaction of water decomposition to generate molecular hydrogen [8]. The present work is addressed to the question of the state of titanium(III) ions in alcohol-water solutions.

EXPERIMENTAL

In this work we used double-distilled TiCl4, Grade kh.ch. ("chemically pure"); sodium hydroxide, Grade kh.ch.; lithium chloride, Grade kh.ch.; and HClO4, Grade ch.d.a. ("analytically pure"). The hydrogen chloride was obtained by procedures given in [9]. The titanium(III) compounds were obtained by a photochemical method involving UV irradiation of deaerated ethanol solutions of TiCl4 [5]. The absorption spectra were taken in Specord UV-VIS and SF-2D spectrophotometers. The ESR spectra were registered in an RÉ-1301 radiospectrometer. The g-factors of the signals were calculated relative to the signal of DPPH.

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Fig. 1

Fig. 2

Fig. 1. Effect of added water on the absorption spectrum of titanium(III) compounds in ethanol. $C_{\text{Ti}} = 4.6 \cdot 10^{-3}$ M; $C_{\text{H}_2\text{O}}$, M, as follows: 1)0; 2) 1; 3) 2.5; 4) 7. d = 7 cm.

Fig. 2. Changes in ESR spectra of titanium(III) compounds with increasing concentrations of water in alcohol—water solutions, at 77 K. $C_{Ti} = 1.4 \cdot 10^{-2}$ M; C_{H_2O} , M, as follows: 1) 0; 2) 0.5; 3) 1.0; 4) 1.4; 5) 3.0; 6) 7.6.

RESULTS AND DISCUSSION

Irradiated solutions of titanium tetrachloride in dry ethanol (Fig. 1, curve 1) are characterized by an asymmetric absorption band in the visible region of the spectrum ($\lambda_{max} = 595$ nm, shoulder at $\lambda = 700$ nm), which, according to [1, 2], corresponds to d-d transitions in octahedral complexes of titanium(III) of the [Ti(C₂H₅OH)₆]³⁺ type. Also present in the irradiated solutions are mixed chloride-alcoholate complexes [10], which are characterized by an anisotropic signal I in the ESR spectrum with $g_1 = 1.988$, $g_2 = 1.903$, and $g_3 = 1.833$ (Fig. 2, curve 1). The addition of water to ethanol solutions of titanium(III) leads to changes in the absorption spectra and ESR spectra. With small amounts of added water, the electronic spectrum shows a hypsochromic shift of the absorption band of the original titanium(III) complexes from 595 to 500 nm; also, a new band appears with $\lambda_{max} = 400$ nm (Fig. 1, curve 2 and 3). With higher concentrations of water, the intensity of the 400-nm band decreases, and a new band appears with a maximum in the 500-nm region (Fig. 1, curve 4), which, according to [1, 2], is characteristic for aqua complexes of titanium(III) [Ti• (H₂0)₆]³⁺.

The ESR spectrum of frozen (77 K) solutions of titanium(III) containing small amounts of added water (Fig. 2, curves 2 and 3) represents a superposition of several anisotropic signals: II $(g_{\parallel}=1,990, g_{\perp}=1,904)$, III $(g_{\perp}=1,961, g_{\parallel}=1,945)$ and IV $(g_{\parallel}=1,995, g_{\perp}=1,914)$. As the water concentration is increased, the relative intensity of signal II decreases, and signals III and IV increase. With higher concentrations of water, the intensity of signal III gradually decreases (Fig. 2, curves 4-6); and at $C_{\rm H_2O} = 7.6$ M, only signal IV is observed in the spectrum.

At room temperature, in the ESR spectrum of alcohol-water solutions of titanium(III), an isotropic signal is observed with an intense central line, due to even isotopes of titanium, and also low-intensity side lines, the appearance of which is due to the uneven isotopes ⁴⁷Ti and ⁴⁹Ti with respective nuclear spins of 5/2 and 7/2 [11, 12]. The isotropic HFS constant $A_0 = 16.4 \cdot 10^{-4}$ cm⁻¹. With small amounts of added water, the intensity of the isotropic signals increases with increasing concentration of water; but in the region of high concentrations of water ($C_1 \ge 2$ M), it drops off. The value found for the isotropic g-factor, $g_0 = 1.955$, is in good agreement with the value calculated on the basis of data for the anisotropic signal III ($g'_0 = (g_{\parallel} + 2g_{\perp})/3 = 1.956$). This indicates that the anisotropic signal III that is observed at 77 K and the isotropic signal that is observed at room temperature pertain to one and the same complex.

According to [2, 3], titanium(III) in aqueous solutions may form aqua complexes, and it is also subject to hydrolysis. Therefore, the spectral changes observed when water is added to alcohol solutions may be explained by replacement of the alcohol molecules and chloride ions by water molecules in the coordination sphere of alcoholate and chloride—alcoholate complexes of titanium(III), and also by the occurrence of a hydrolysis reaction. We have established that when small quantities of sodium hydroxide are added to alcohol—water solutions of titanium(III), an increase in intensity is observed for the absorption band with $\lambda_{max} = 400$ nm in the electronic spectrum (Fig. 3), and also increases in intensity of the isotropic (295 K) and anisotropic (77 K) signals III in the ESR spectrum. Consequently, the absorption band with $\lambda_{max} = 400$ nm and the indicated ESR signals correspond to hydroxo complexes of titanium(III). With higher concentrations of caustic, a yellow-brown precipitate of titanium(III) hydroxide is formed.

The basic character of the products responsible for the appearance of the band with λ_{max} = 400 nm and also for the appearance of the isotropic and anisotropic signal III in the ESR spectrum is indicated by the results obtained when an acid is added. The introduction of hydrogen chloride leads to the disappearance of the band with λ_{max} = 400 nm and to the appearance of a lower-intensity band in the 520-600 nm region, the position of the maximum depending on the concentrations of hydrogen chloride and water in the solution. In the room-temperature ESR spectrum, as the HCl concentration is increased, the signal intensity drops off; in the 77 K spectrum, the intensities of signals III and IV decrease, and the intensity of signal II increases.

Solutions containing added perchloric acid, after extended storage, do not give any ESR signals. The reason is that the titanium(III) compounds are oxidized by the ClO₄⁻ ions, which have a rather high oxidation potential [13]. However, immediately after adding the perchloric acid, ESR spectra of titanium(III) complexes can be registered. When the HClO₄ is present, the same as in the case of added hydrogen chloride, a decrease in the intensity of signal III is observed, but signal IV remains in the spectrum. This indicates neutralization of hydroxo complexes of titanium(III) and also indicates that the product responsible for the appearance of signal IV does not have a pronounced basic character.

The data that we have obtained show that the coordination sphere of hydroxo complexes of titanium(III) contain water molecules as well as OH groups. This is indicated by the fact that such compounds are formed in moist alcohol, and also by the fact that when sodium hydroxide is added to a solution of titanium(III) in anhydrous ethanol, a signal with considerably less anisotropy is observed (Fig. 4). This means that the alcohol molecules distort the coordination sphere of the complex to a smaller degree than to the more polar water molecules.

On the basis of these results, we can judge the structure of the hydroxo complexes of titanium(III). The ESR spectra of octahedral complexes of titanium(III), with either tetragonal [12, 14] or trigonal [15] distortion, are characterized by values $g_{\parallel} > g_{\perp}$. Such a relationship between the components of the g-factor is expected in the case of tetragonal distortion (compression) of a tetrahedral complex [14]. In contrast, we found in the present work the values $g_{\parallel}(1.945) < g_{\perp}(1.961)$. This can serve as an indication that the hydroxo complex of titanium(III) that is formed has the shape of a distorted (extended along the z-axis) tetrahedron, for which, as suggested in [14], $g_{\perp} > g_{\parallel}$. A tetrahedral structure of the hydroxo complex is further indicated by the longer times of spin-lattice relaxation, as a result of which an ESR signal can be registered at room temperature. Here the explanation is that in the case of distorted tetrahedral complexes, in contrast to octahedral, the ground state (state of an unpaired electron) interacts weakly with the nearest excited state [14]. For ions in a tetrahedral field, according to [13], the parameter of spectroscopic splitting is approximately "/, of the octahedral. And in fact, in the spectrum of alcohol-water solutions containing hydroxo complexes of titanium(III), we have detected in the near-IR region an absorption band with $v_{max} = 10,000 \text{ cm}^{-1}$, which is close to the expected value.









Fig. 3. Effect of added sodium hydroxide on absorption spectrum of compounds of titanium(III) in alcohol-water solution. $C_{Ti} = 6 \cdot 10^{-3} \text{ M}; C_{H_20} = 5 \cdot 10^{-1} \text{ M}; C_{NaOH}, \text{ M}, \text{ as follows: } 1) 4.3 \cdot 10^{-4}; 2) 2.5 \cdot 10^{-3}; 3) 6.6 \cdot 10^{-3};$ 4) 8.9 \cdot 10^{-3}. d = 7 cm.

Fig. 4. Changes in ESR spectra (77 K) of titanium(III) compounds in absolute ethanol, in relation to amount of added NaOH. $C_{Ti} = 7 \cdot 10^{-3}$ M; C_{NaOH} , M, as follows: 1) 0; 2) $3 \cdot 10^{-3}$; 3) $1 \cdot 10^{-2}$.

The titanium(III) complex that is responsible for the appearance of signal IV predominates in solutions with high concentrations of water. Hence we can assume that the coordination sphere of this complex consists mainly of water molecules. As already noted, such solutions are characterized by an absorption band in the 500-nm region, which, according to [1, 2], pertains to the aqua complex $[Ti(H_2O)_6]^{3+}$. This type of coordination compounds of elements with d¹ electronic configuration is characterized by short spin-lattice relaxation times, and hence their ESR signals cannot be registered even at 77 K [10, 14]. Therefore, we should assume that in addition to the aqua complex $[Ti(H_2O)_6]^{3+}$ that is registered in the optical absorption spectrum, the solution also contains another, less symmetric complex with a coordination sphere consisting mainly of water molecules. Another possibility is that the absorption bands of these two complexes overlap, and as a consequence, the experimentally registered band (Fig. 1, curve 4) is very broad. The distinct axial anisotropy of the ESR signal and also the ratio of the anisotropy parameters $(g_{\parallel} (1.995) > g_{\perp} (1.914))$ show that the complex has the structure of an axially distorted octahedron. Since signal IV is clearly manifested in the ESR spectrum after disappearance of the signal of the hydroxo complex, we can assume that its appearance is related to an aquation reaction $[Ti(H_2O)_3OH]^{2+}$ + $3H_20 \rightarrow Ti(H_20)_6^{3+} + 0H^-$, and also to the occurrence of the second state of hydrolysis $TiOH^2 \rightarrow$ TiO + H⁺. Apparently the presence of the titanyl group also leads to axial distortion of the coordination sphere. It should be noted that in the case of titanium(IV), the formation of hydrolysis products containing the TiO^{2+} group is the most thermodynamically favorable [16, 17]. For trivalent titanium, no direct data are available on the existence of titanyl complexes in solutions; however, information has been reported [3] on compounds containing the TiO⁺ group. A possible alternative assignment of signal IV to a mixed alcohol-water complex of titanium(III) apparently should be discarded, since such a complex exists over a broad range of water concentrations. In addition, water at C \geq 7 M apparently should displace alcohol molecules from the coordination sphere. The ESR signal with similar parameters that was described in [18] was assigned to the complex $Ti(H_20)_6^{3+}$, distorted because of the matrix; however, no evidence was given for this assignment.

We have assigned signal II, observed in alcohol-water solutions with moderate water contents, to a distorted octahedral complex of titanium(III) with a mixed coordination sphere, the composition of which changes depending on the concentrations of water and chloride ions in the solution. Such complexes are characterized by d-d bands in the 520-600 nm region; the position of the maximum is determined primarily by the contents of the complexes with one composition or another.

Thus, in ethanol containing even small amounts of added water (C < 0.5 M), trivalent titanium forms a series of labile coordination compounds. Here we refer to various products

of partial replacement of chloride ions or alcohol molecules by water in complexes [TiCl2. (ROH)4] and [Ti(ROH)6]³⁺, which are stable in absolute ethanol. Also formed are tetrahedral complexes with hydroxyl groups in their composition $[TiOH(ROH)_3]^+$ or $[TiOH(H_2O)_3]^+$. In solutions with sufficiently high water contents (C \geq 7 M), the titanium(III) ions exist mainly in the form of an aqua complex with the composition $[Ti(H_2O)_6]^{3+}$, and also possibly [TiO. $(H_2O)_5]^+$. There is no doubt that all of these compounds may differ substantially in light sensitivity, and this must be taken into account when selecting optimal conditions for carrying out the photocatalytic generation of hydrogen from water. It should also be noted that the results we have obtained indicate the possibility of regulating the composition of the solutions to be irradiated by adding various types of substances and thus creating conditions for the predominance of one particular coordination compound of trivalent titanium or another.

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