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Photochromism as a Consequence of Redox Reactions of Iron Complexes

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Photochromism based on redox reactions has so far been uncommon in coordination chemistry [1] and until now it was observed only for dichalcogenocarbamates of nickel [2] and for some systems of the ruthenium trisbipyridyl complex [3].

Some of the possible mechanisms of photochemical and thermal redox reactions, which could be the reason for photochromic behaviour of complexes, are reported by Adamson [1].

Inoue and co-workers [4] found that on irradiation of solutions containing pale-green complex of Fe(III) chloride with pinacol in acetonitrile with ultra-violet light, the photoreduction of Fe(III) to Fe(II) was accompanied by the oxidation of pinacol to acetone which was the only oxidation product. Photoredox decomposition of pinacol occurred only in the case when pinacol was present in the coordination sphere of the Fe(III) complex.

These results, as well as the knowledge obtained by the study of spontaneous redox reactions of Fe(II) chlorocomplexes in acetone in which Fe(II) becomes oxidized to Fe(III) and the pinacol was identified as the reduction product [5], indicated the possible existence of photochromic properties of these systems.

This paper proved experimentally the justification of the above assumption.

Results

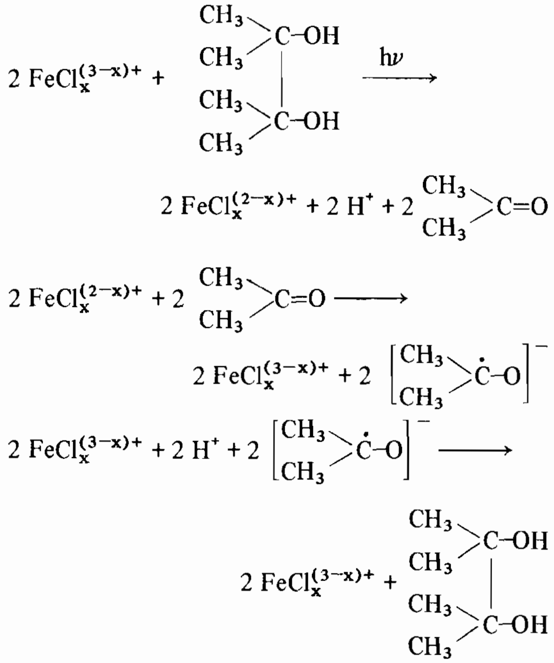
Pale-green solutions of anhydrous ferric chloride with pinacol in acetone in the molar ratios $[FeCl_3]$: [pinacol] = 1:5 and 1:20, respectively (for the shift of the equilibrium in the direction of the Fe(III) chlorocomplex formation with pinacol) were irradiated with a UV discharge lamp (Tesla RKV 125 W) for 12 hours, with a 1 cm layer of acetone used as filter. During this period the concentration of Fe(III) decreased from the original value of $4 \times 10^{-4} M$ to $2 \times 10^{-4} M$, and the absorbance of the system at 360 nm (the position of the absorption band maximum for the Fe(III) chlorocomplex with pinacol) also fell by 50%. After the completed irradiation Fe(II) became spontaneously oxidized to Fe(III) over 360 hours and the absorbance also reached its original value.

This cycle – photochemical reduction of Fe(III) to Fe(II) and the subsequent thermal oxidation of Fe(II) to Fe(III) – was repeated three times. The time needed for both the processes did not change by repeating the cycles nor did it depend on the ratio of $[FeCl_3]$: [pinacol]. Also the changes in the spectral properties of the systems were repeated.

After the last reoxidation of Fe(II) no secondary reaction products were identified in the systems using gas chromatography (Carlo Erba Fractowap 2350, 0.25% Carbowax 20M).

On irradiation of solutions of ferric chloride in acetone without adding pinacol, no redox reaction was observed.

Based on the above results the studied systems of Fe chlorocomplexes with pinacol in acetone may be considered to be photochromic due to the photochemical and thermal redox reactions of these complexes, and the photochromism of the systems can be expressed by the equations:



$$2\,FeCl_x^{(3-x)+} + (CH_3)_2C(OH){-}C(OH)(CH_3)_2 \xrightarrow{h\nu} 2\,FeCl_x^{(2-x)+} + 2\,H^+ + 2\,(CH_3)_2C{=}O$$

$$2\,FeCl_x^{(2-x)+} + 2\,(CH_3)_2C{=}O \longrightarrow 2\,FeCl_x^{(3-x)+} + 2\,[(CH_3)_2\dot{C}{-}O]^-$$

$$2\,FeCl_x^{(3-x)+} + 2\,H^+ + 2\,[(CH_3)_2\dot{C}{-}O]^- \longrightarrow 2\,FeCl_x^{(3-x)+} + (CH_3)_2C(OH){-}C(OH)(CH_3)_2$$

It should be noted that none of the mechanisms proposed by Adamson [1] for photochromic behaviour based on redox reactions of complexes applies to the systems investigated in this work.

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4 H. Inoue, N. Komakine and E. Imoto, *Bull. Chem. Soc. Japan, 41*, 2726 (1968).

5 J. Šima, E. Horváth, L. Jurík and J. Gažo, *Chem. Zvesti, 30*, 58 (1976).