Innersphere redox reactions of iron(II) halogeno complexes containing π-acceptor ligands

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The paper presents the results of the study of spontaneous redox reactions occurring in the systems of Fe(II) iodo complexes in acetone. The influence of halogenide, pseudohalogenide, and ligands of σ-donor and π-acceptor ability on the formation of conditions for innercomplex redox reactions of high-spin Fe(II) complexes containing the above-mentioned ligands is discussed. The results are interpreted on the basis of the phenomenon of the mutual influence of ligands through the central atom.

В работе приводятся результаты исследования самопроизвольных окислительно-восстановительных реакций, протекающих в системе иодных комплексов Fe(II) в ацетоне. Обсуждается влияние галогенидов, псевдогалогенидов и лигандов с σ-донорными и π-акцепторными свойствами на создание условий для внутрикомплексных окислительно-восстановительных реакций высокоспиновых комплексов Fe(II) с этими лигандами. Результаты интерпретируются с точки зрения явления межлигандного взаимодействия через центральный атом.

The study of the course of spontaneous redox reactions of Cu(II) chloro and bromo complexes in nonaqueous media resulted in the formulation of conclusion [1] that the reduction of Cu(II) to Cu(I) accompanied by the oxidation of halogenide X^- was conditioned by simultaneous presence of X^- and π-acceptor ligand within the coordination sphere of Cu(II) complex. The interpretation of the mechanism of these reactions was based on the assumption of mutual interaction of ligands in the coordination sphere of Cu(II) complex mediated by the central atom electronic system.

In the systems of Fe(II) complexes having the coordination sphere composition such as with Cu(II) complexes (X⁻ ligands and π-acceptor ligands, such as acetone [2], other ketones [3], acetonitrile [4]) spontaneous oxidation of Fe(II) to Fe(III) accompanied by reduction of π-acceptor ligand proceeds [5, 6]. It has been found that spontaneous redox reactions occur only in the presence of π-acceptor ligand within the coordination sphere of complex (Fe(II) chloro or bromo complexes in methanol are redox stable). It is evident from the experiments that only complexes with certain σ-donor ligands undergo spontaneous oxidation of Fe(II) (complexes $[Fe(NO_3)_x(AC)_y]^{(2-x)+}$ and $[Fe(AC)_x(MeOH)_y]^{2+}$, where AC and MeOH denote acetone and methanol, respectively, do not undergo spontaneous redox processes in the absence of dioxygen [7]).

In order to contribute to elucidation of the problem, which of the properties of σ-donor ligand determines the ability of Fe(II) to be oxidized and of π-acceptor ligand to be reduced, the behaviour of Fe(II) iodo and isothiocyanato complexes was followed in acetone and/or methanol. Both results and the formulation of the conclusion concerning the influence of σ-donor ligand on the redox properties of Fe(II) complexes are the topic of this paper.

Experimental

Methanol, anal. grade (Lachema, Brno) and acetone, spectrograde quality (Lachema, Brno) were deprived of water and dioxygen before the use [5, 6]. Tetramethylammonium thiocyanate [(CH₃)₄N]NCS and tetramethylammonium tetraisothiocyanatoferrate [(CH₃)₄N]₂[Fe(NCS)₄] were prepared according to the published procedure [8]. Contents of C, N, H, and Fe were correspondent to the assumed composition. Anhydrous iron(II) iodide FeI₂ (Cerac Pure, Inc.), tetramethylammonium iodide [(CH₃)₄N]I (BDH Reagent), and 2,2'-bipyridine, anal. grade (Lachema, Brno) were used as received. Fe(II)-containing solutions were prepared and kept in argon atmosphere, in red light and at the temperature of 15.0 ± 0.1 °C.

The concentration of Fe(II) was determined spectrophotometrically after addition of solid 2,2'-bipyridine into solution under investigation, $\varepsilon([Fe(bpy)_3]^{2+}, \lambda = 520$ nm$) = 8000$ mol⁻¹ dm³ cm⁻¹ [9]; the concentration of I_3^- anion likewise found spectrophotometrically, $\varepsilon(I_3^-, \lambda = 362$ nm$) = 25\,000$ mol⁻¹ dm³ cm⁻¹ [10].

The electronic absorption spectra were scanned on a Specord UV VIS apparatus (Zeiss, Jena). Iodo derivatives of acetone were analyzed after passing the studied solutions through a strongly acidic cation-exchange resin Duolit C 25 D by gas chromatography on a Chrom 4 apparatus equipped with a column packed with stationary phase Squalan.

Results

The spectral properties of oxygen-free solutions of FeI₂ in methanol and methanolic solution of [(CH₃)₄N]I with $c = 1.0 \times 10^{-2}$ mol dm⁻³, respectively, as well as Fe(II) concen-

tration do not change when in the dark during 30 h after preparation. By influence of light and/or dioxygen FeI_2 decomposes into iron and iodine.

Without dioxygen and light radiation the concentration of Fe(II) does not exhibit any change with time, the concentration of I_3^- anion first increases, then it becomes stable at a certain constant value (denoted as $c_{max}(I_3^-)$), and decreases at last.

A plot of I_3^- concentration on time for solution of FeI_2 with $c(Fe(II)) = 3.2 \times 10^{-5}$ mol dm^{-3} is shown in Fig. 1. The concentrations $c_{max}(I_3^-)$ for acetone solutions of FeI_2 depend on Fe(II) concentration; the data are summarized in Table 1.
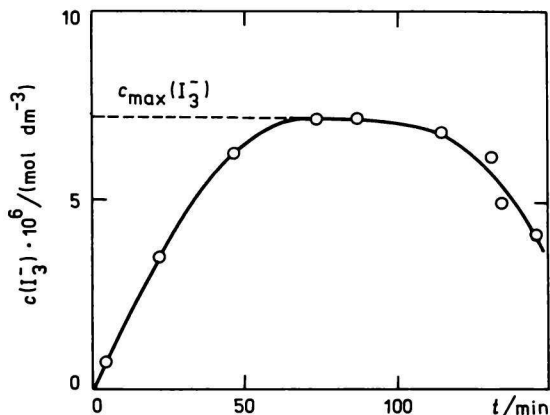

Fig. 1. Time dependence of the concentration of I_3^- ion in the system FeI_2—acetone.
$c(Fe(II)) = 3.2 \times 10^{-5}$ mol dm^{-3}, $\theta = (15.0 \pm 0.1)$ °C, atmosphere of argon.

Table 1

Values of the concentration $c(Fe(II))$ and $c_{max}(I_3^-)$ for the systems FeI_2—acetone
$\theta = (15.0 \pm 0.1)$ °C, atmosphere of argon

$c(Fe(II)) \cdot 10^5/(\text{mol dm}^{-3})$	1.4	3.2	3.3	11.2	15.6
$c_{max}(I_3^-) \cdot 10^6/(\text{mol dm}^{-3})$	1.44	7.20	6.40	28.0	56.0

In acetone solutions of FeI_2 containing $[(CH_3)_4N]I$ with $c = 1.0 \times 10^{-2}$ mol dm^{-3} was observed an unceased growth of concentration of I_3^- anion during 30 h. The concentration of Fe(II) does not change with time. For these solutions, the values of concentration of I_3^- ions measured 5 h after preparation of solutions, as well as the values of Fe(II) concentration are given in Table 2.

Table 2

Values of the concentration $c(Fe(II))$ and $c(I_3^-)$ for the systems FeI_2—$[(CH_3)_4N]I$—acetone 5 h after preparation of solutions
$\theta = (15.0 \pm 0.1)$ °C, atmosphere of argon, $c([(CH_3)_4N]I) = 0.01$ mol dm^{-3}

$c(Fe(II)) \cdot 10^5/(mol\ dm^{-3})$	2.3	3.3	8.7	9.5	15.0
$c(I_3^-) \cdot 10^5/(mol\ dm^{-3})$	4.6	6.6	9.2	8.9	11.0

Spectral properties and concentration of Fe(II) in systems of $[(CH_3)_4N]_2[Fe(NCS)_4]$ in acetone, methanol and in their solutions $[(CH_3)_4N]NCS$ with $c = 1.0 \times 10^{-2}$ mol dm^{-3} do not exhibit any change with time during 30 h after their preparation.

Discussion

From the decreased proton affinity values of halogenide ions in the following order Cl^-, Br^-, I^- as well as from the decrease of binding energies of electrons in the $3d$-like orbitals of iron atom bonded in $FeCl_2$, $FeBr_2$, and FeI_2 [11, 12] it results that the increased electron density on iron atom in the above-mentioned order of compounds is a consequence of the growing π-donor ability of halogenide passing from Cl^- to I^-

From the binding energy differences of coordinated and free N-donor ligands with diverse bonding abilities (σ-donor NH_3, σ-donor and π-acceptor N_2, NCS^- ion [13—16]) a conclusion can be drawn: σ-donor and π-acceptor bondings take place at N-coordination of NCS^- ion on the central atom of the first-row transition elements, *i.e.* unlike halogenide, NCS^- ion is not a ligand with π-donor ability.

When postulating internal conditions for redox decomposition of Fe(II) complexes, the bonding properties of ligands I^-, NCS^-, molecules of AC and MeOH can be taken as a starting point. Complexes of Fe(II) with methanol as a ligand (which does not possess the vacant π^*-orbital), and I^- or NCS^- ligands, respectively, do not undergo spontaneous redox reactions because they do not contain a reducible ligand.

Owing to the mutual interaction of π-orbitals localized on I^- and AC ligands, as well as central atom in Fe(II) iodo complexes having AC in the coordination sphere, such an electron density transfer to antibonding orbital of acetone takes place (according to the scheme)

$$I^- \overset{\pi}{\underset{\sigma}{\rightrightarrows}} Fe(II) \overset{\pi}{\underset{\sigma}{\rightleftharpoons}} AC \qquad (A)$$

that in the case of suitable collision with environmental particles AC^- anion can be released (which recombines to pinacol identified by gas chromatography [5, 6]) from the coordination sphere and Fe(III) can be formed

$$I^- \text{---} Fe(II) \text{---} Ac \; \rightarrow \; I^- \text{---} Fe(III) + AC^- \qquad (B)$$

(only fragments of complexes are introduced due to the existence of several complexes containing various number of X^- ligands and solvent molecules in equilibrium in solutions of halogeno and isothiocyanato complexes of Fe(II)). Thermodynamically stable, spectrally detectable I_3^- ion is formed in the system, Fe(III) being reduced in the presence of I^- ions

$$2Fe(III) + 3I^- \; \rightarrow \; 2Fe(II) + I_3^- \qquad (C)$$
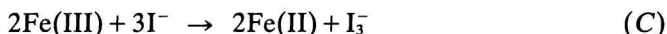
In the systems of chloro and bromo complexes spontaneous reduction of Fe(III) does not take place. Redox cycles including the oxidation of Fe(II) by acetone and the reduction of Fe(III) by I^- ions are repeated in the systems leading to the continuous growth of I_3^- ion concentration. Comprehensively, processes occurring in the solution can be expressed by the equation

$$3FeI_2 + 4AC \; \rightarrow \; 3Fe^{2+} + 4AC^- + 2I_3^- \qquad (D)$$

From eqn (D) it follows that maximum obtainable concentration of I_3^- ions is equal to 2/3 value of Fe(II) concentration in the system. It is obvious, extracting the data in Table 1, that such a concentration of I_3^- ions was not reached in any system under investigation. This is connected with the consumption of above-mentioned anions in their reactions with acetone (pinacol).

After the time interval during which the rate of formation and decomposition of I_3^- ions is equal, the decrease of the concentration of these ions with time takes place. Due to the course of some other reactions (formation of complexes with pinacol or its anion, changes of distribution of individual Fe(II) iodo complexes as a consequence of changes in concentration ratio of Fe(II) and I^-, *etc.*) the detailed kinetic analysis of reactions occurring in solutions of Fe(II) in acetone is not possible till now.

In systems containing $[(CH_3)_4N]I$ the equilibrium of Fe(II) complexes is shifted to the formation of iodo complexes with greater number of iodo ligands, as it is in FeI_2 solutions. In such a system, the I_3^- ion concentration is greater than the 2/3 value of Fe(II) concentration even after some hours and it is continuously growing with time. This means that in such systems a greater number of redox cycles takes place resulting in the formation and accumulation of I_3^- ions (Table 2).

The processes can be described by the equation of the oxidation of I^- ion by acetone catalyzed in the presence of Fe(II)

$$3I^- + 2AC \xrightarrow{\text{Fe(II)}} I_3^- + 2AC^- \qquad (E)$$

Comparison of the chromatographs of I_3^- solutions in acetone (prepared by dissolving iodine in acetone solution of $[(CH_3)_4N]I$) with chromatographs of the

studied systems has shown that organic iodo derivatives formed in these systems are equal.

The influence of π-acceptor NCS$^-$ ion coordinated to Fe(II) in acetone solutions leads to decrease of the electron density (orbital energies) on the central atom of Fe(II) and in that way (in comparison with halogeno complexes) to lowering the electron density transfer to antibonding π^*-orbital localized on the acetone molecule. In these complexes the intrinsic conditions for redox decomposition are not formed and oxidation of Fe(II) does not take place.

For the cations of the first-row transition elements methanol is a stronger Lewis base than acetone [17] and in the systems of Fe(II) halogeno complexes containing more than 60 vol. % of methanol, coordination of acetone molecule to Fe(II) practically does not occur. In such systems the complexes $[FeX_x(MeOH)_y]^{(2-x)+}$ are present. The fact that in those systems the spontaneous oxidation of Fe(II) does not proceed (despite of that they contain halogenide and acetone) documents that the realization of spontaneous, redox processes in the studied systems is a consequence of innercomplex electron transfer from the central atom of Fe(II) to π-acceptor ligand and of the decomposition in the following step but it is not a consequence of outersphere electron transfer between Fe(II) complex and free (noncoordinated) acetone molecule.

The results obtained so far [2—7] and those presented in this paper can be summarized as follows:

— complexes $[FeX_x(L_\pi)_y]^{(2-x)+}$ (where X = Cl, Br, and I, respectively, L_π = ligand of π-acceptor ability) undergo innercomplex spontaneous redox reactions owing to which Fe(II) is oxidized while L_π is reduced;

— complexes $[FeX_x(AC)_y]^{(2-x)+}$ (where X denotes NCS or NO$_3$, respectively, and complexes $[Fe(MeOH)_x(AC)_y]^{2+}$ do not undergo spontaneous redox processes;

— complexes $[FeX_x(MeOH)_y]^{(2-x)+}$ (where X = Cl, Br, I, NCS, or NO$_3$) do not yield spontaneous redox changes.

On the basis of the cited results the conclusion can be drawn: only Fe(II) complexes containing reducible ligands of σ-donor and π-acceptor nature as well as ligands of σ- and π-donor character simultaneously in their coordination sphere (which by means of their effect help to effective electron density transfer to antibonding π^*-orbital of σ-donor and π-acceptor ligand) can undergo innercomplex spontaneous redox reactions.

The above-mentioned conclusion is in harmony with up-to-present-time knowledge of the consequences of mutual interactions of ligands present in coordination sphere of complex mediated by electronic system of the central atom [1]. The comparison of properties of Cu(II) and Fe(II) complexes at the same time documents the influence of electronic structure of the central atom on the consequences of mutual influence of the ligands.

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