Redox Reactions of Iron(III) Chloro and Isothiocyanato Complexes with Triphenylstibine and Triphenylbismuthine in Acetonitrile

V. VANČOVÁ and I. ONDREJKOVIČOVÁ

Department of Inorganic Chemistry, Faculty of Chemical Technology, Slovak Technical University, CS-812 37 Bratislava

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The reduction of Fe(III) to Fe(II) in the systems FeX₃—EPh₃—acetonitrile (X = Cl, NCS; E = Sb, Bi; Ph = phenyl) occurs at ambient temperature. Fe(II)—Fe(III) complexes of the composition [Fe(NCCH₃)₃][FeX₄]₂ are formed and the ligands EPh₃ are oxidized under formation of X₂EPh₃.

Investigation of the influence of ligands PPh₃, AsPh₃, SbPh₃, and BiPh₃ on the redox reactions of iron(III) chloro and isothiocyanato complexes showed that they depend not only on their properties but also on the nature of the solvent in which the reactions take place. Naldini [1] has found that anhydrous FeCl₃ reacts at ambient temperature with PPh₃ and AsPh₃ in ether and as a result of this reaction black insoluble compounds FeCl₃(PPh₃)₂ and FeCl₃(AsPh₃)₂ are formed. In methanol FeCl₃ and PPh₃ react under formation of the complex [PPh₃(CH₃)][FeCl₄]. Reaction of ethereal solution of Fe(SCN)₃ and PPh₃ gives a red solid substance Fe(SCN)₃(PPh₃)₂ at ambient temperature. On the other hand, in acetonitrile or in benzene the reaction of iron(III) chloro and isothiocyanato complexes with PPh₃ and AsPh₃ occurs so that the ligands are oxidized at elevated temperature of 50—70 °C by air oxygen to OPPH₃ and OAsPh₃, respectively. Phosphine oxide and arsine oxide complexes FeCl₃(OPPh₃)₂ [2], FeX₃(OAsPh₃)₂, and FeX₃(OAsPh₃)₁.₅ (X = Cl [3]; NCS [4]) crystallize from the solution.

At excess of the ligands, i.e. when n(PPh₃ resp. AsPh₃) : n(Fe(III)) > 2, PPh₃ and AsPh₃ are catalytically oxidized. In addition to the above-mentioned complexes also free OPPH₃ and OAsPh₃ precipitate. Presence of Fe(III) complexes as catalysts is necessary [5, 6]. However, the reactions of FeX₃ (X = Cl, NCS) with SbPh₃ and BiPh₃ in acetonitrile proceed in a very different way. We found that at a room temperature only one third of amount of substance of Fe(III) is reduced to Fe(II) and as a result of that iron(II)—iron(III) complex compound of the composition [Fe(NCCH₃)₃][FeX₄]₂ is formed. As a result of the oxidation of EPh₃ (E = Sb, Bi) X₂EPh₃ and X₃BiPh₃, respectively, were produced. These remarkable differences in behaviour of this class of substances attracted our interest to a more detailed investigation of the reactions of FeCl₃ and Fe(NCS)₃ with SbPh₃ and BiPh₃.

EXPERIMENTAL

Anhydrous FeCl₃ was prepared by the reaction of iron powder with chlorine. The product was resublimed in the stream of chlorine [7]. Acetonitrile solution of Fe(NCS)₃ was prepared by mixing of the acetonitrile solutions of FeCl₃ with KSCN in the mole ratio 1 3. KCl was separated by the filtration.

SbPh₃ and BiPh₃, pure (Jansen Chimica, Belgium) were further purified by recrystallization from acetone with the addition of active charcoal. Purity of the product was checked by determination of melting point and by the elemental analysis. The melting points of SbPh₃ and BiPh₃ were determined to be 52—53 °C and 78 °C, which is in good agreement with the values in Refs. [8] and [9], respectively. Acetonitrile of anal. grade (Apolda, Germany) was dried with CaH₂ and rectified. The fraction with b.p. = 81.5 °C was used.

[Fe(NCCH₃)₃][FeCl₄]₂ (yellow substance) was prepared by the reaction of iron powder with chlorine in acetonitrile [10]. The compound [Fe(NCCH₃)₃][Fe(NCS)₄]₂ was prepared by reaction of iron powder with solid (SCN)₂ (n(Fe) : n(SCN)₂ = 3 : 4) at a low temperature 0—5 °C in acetonitrile. The product consisted of fine dark-red crystals.

The content of Fe(III) in solid compounds was determined after their decomposition in concentrated nitric acid by the titration with chelatone 3 using sulfosalicylic acid as indicator. Content of Fe(II) was determined after dissolution of the compounds in acetonitrile and addition of 2,2'-bipyridine by spectrophotometry. For elemental analysis the apparatus Erba was used, chlorides were determined by the argentometric titration with potential-
metric determination of the end point.

IR spectra of complexes were determined on a spectrometer Specord M-80 in the range of $\tilde{\nu} = 200-4000\ \text{cm}^{-1}$ in nujol suspension, electronic spectra on a UV-VIS Specord in the range of $\tilde{\nu} = 11\ 000-30\ 000\ \text{cm}^{-1}$ in nujol suspension and acetonitrile solution.

**Reactions of FeCl_3 with EPH_3**

Mixture of anhydrous FeCl_3 and EPH_3 in acetonitrile of composition $n(\text{Fe(III)})/n(\text{EPh}_3) = 1/0.5$ was kept at a room temperature for 1—1.5 h. For yellow crystals of the composition Fe_3Cl_8 $\cdot$ 6CH_3CN $w(\text{calc.}): 20.66\ %\ C, 2.60\ %\ H, 12.05\ %\ N$; $w(\text{found}): 21.40\ %\ C, 2.83\ %\ H, 11.95\ %\ N$. For Fe_3Cl_8 $\cdot$ 6CH_3CN $w(\text{calc.}): 20.66\ %\ C, 2.60\ %\ H, 12.05\ %\ N$; $w(\text{found}): 21.40\ %\ C, 2.83\ %\ H, 11.95\ %\ N$. The crystals were further purified by recrystallization from acetone or methanol with addition of charcoal. For Fe_3SbPh_3 $w(\text{calc.}): 50.99\ %\ C, 3.57\ %\ H, 16.72\ %\ Cl$; $w(\text{found}): 51.92\ %\ C, 3.65\ %\ H, 16.85\ %\ Cl$. For Fe_3BiPh_3 $w(\text{calc.}): 42.29\ %\ C, 2.96\ %\ H, 13.87\ %\ Cl$; $w(\text{found}): 41.32\ %\ C, 2.89\ %\ H, 14.05\ %\ Cl$.

**RESULTS AND DISCUSSION**

FeCl_3 and Fe(NCS)_3 react with EPH_3 (E = Sb, Bi) in acetonitrile at ambient temperature under formation of complex compounds Fe_3Cl_8 $\cdot$ 6CH_3CN and Fe_3(NCS)_6 $\cdot$ 6CH_3CN which contain both Fe(III) and Fe(II). Ligands EPH_3 are reducing agents in these reactions and they are oxidized to Cl_2EPH_3 and (NCS)_2EPH_3, respectively. Course of the reduction of Fe(III) by ligands EPH_3 in the systems FeCl_3—EPH_3—acetonitrile (1) and Fe(NCS)_3—EPH_3—acetonitrile (2) was investigated spectrophotometrically in the visible region of the spectrum. Absorption band at $\tilde{\nu} = 27\ 480\ \text{cm}^{-1}$ corresponds to the charge transfer in iron(III) chloro complexes [11]. Intensity of this band decreases with time in the system 1 while the absorbance of the band at $\tilde{\nu} = 19\ 100\ \text{cm}^{-1}$ in the system 2 which corresponds to the charge transfer in the ion [Fe(bpyr)_3]^{2+} increases with time. This ion is formed after the addition of 2,2'-bipyridine and masking of NCS^- ions by mercury(II) chloride. The final stable value corresponds to absorbance of 2/3 of the system 1 and/or 1/3 of the system 2 according to the original amount of Fe(III) in the system. Excess of the ligands EPH_3 increases the rate of the reduction. However, it does not influence the final content of Fe(III).

The reduction of FeX_3 by ligands EPH_3 can be described by the equation (A) which contains all the components taking part in the reaction

$$6\ \text{FeX}_3 + \text{EPH}_3 + 12\ \text{CH}_3\text{CN} \rightarrow 2\ (2\text{FeX}_3 + \text{FeX}_2\ \cdot\ \text{6CH}_3\text{CN}) + X_2\text{EPH}_3 \quad \text{(A)}$$

As two thirds of the amount of substance of iron stay in the form of Fe(III), the amount of EPH_3 required for its reduction follows from the equation

$$2\ \text{FeX}_3 + \text{EPH}_3 \rightarrow 2\ \text{FeX}_2 + X_2\text{EPH}_3 \quad \text{(B)}$$

Thus for the reduction of Fe(III) to Fe(II) the ratio $n(\text{Fe(III)})/n(\text{EPH}_3) = 1/0.5$ is sufficient. If ligand is in surplus it does not react, which may complicate separation of the mixture.

On the basis of chemical analysis and comparison of the IR and electronic spectra of the prepared substance Fe_3Cl_8 $\cdot$ 6CH_3CN we assume that this substance is identical with [Fe(NCCH_3)_6][FeCl_2] structure which has been determined by Daran [12].

In the IR spectrum of compound Fe_3(NCS)_6 $\cdot$ 6CH_3CN there is a broad band with two maxima at $\tilde{\nu} = 2289$ and 2050 cm$^{-1}$. The first maximum can be identified with stretching vibration $\nu(\text{CN})$ of acetonitrile. Owing to the coordination of CH_3CN to the central atom Fe(II) the maximum is shifted from the value of $\tilde{\nu} = 2266.7\ \text{cm}^{-1}$ for noncoordinated acetonitrile [13] by 22.3 cm$^{-1}$ towards a higher value. The second band corresponds to the stretching vibration $\nu(\text{NC})$ of the isothiocyanate group [14].

At $\tilde{\nu} = 478\ \text{cm}^{-1}$ a bending vibration $\delta(\text{NCS})$ occurs [15]. From the position of this band and from the band at $\tilde{\nu} = 2050\ \text{cm}^{-1}$ one can assume that
the isothiocyanate group is bound to the central atom through nitrogen atom [14, 16]. The bands at $\tilde{v} = 339$ and 280 cm$^{-1}$ found in the range of 200—400 cm$^{-1}$ were assigned to $v$(Fe(III)—NCS) vibration [15], that at $\tilde{v} = 245$ cm$^{-1}$ was assigned to the vibration $v$(Fe(II)—N) and at $\tilde{v} = 202$ cm$^{-1}$ to the bending vibration $\delta$(Fe(II)—NC) [12].

The band in the region of $\tilde{v} = 11000—30000$ cm$^{-1}$ of electronic spectrum with maximum at $\tilde{v} = 21580$ cm$^{-1}$ corresponded to iron(III) isothiocyanate anion. It can be characterized as a charge-transfer band [17, 18].

REFERENCES


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