

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

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The reduction of Fe(III) to Fe(II) in the systems  $\text{FeX}_3\text{—EPh}_3\text{—acetonitrile}$  ( $\text{X} = \text{Cl, NCS}$ ;  $\text{E} = \text{Sb, Bi}$ ;  $\text{Ph} = \text{phenyl}$ ) occurs at ambient temperature. Fe(II)—Fe(III) complexes of the composition  $[\text{Fe}(\text{NCCH}_3)_6][\text{FeX}_4]_2$  are formed and the ligands  $\text{EPh}_3$  are oxidized under formation of  $\text{X}_2\text{EPh}_3$ .

Investigation of the influence of ligands  $\text{PPh}_3$ ,  $\text{AsPh}_3$ ,  $\text{SbPh}_3$ , and  $\text{BiPh}_3$  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  $\text{FeCl}_3$  reacts at ambient temperature with  $\text{PPh}_3$  and  $\text{AsPh}_3$  in ether and as a result of this reaction black insoluble compounds  $\text{FeCl}_3(\text{PPh}_3)_2$  and  $\text{FeCl}_3(\text{AsPh}_3)_2$  are formed. In methanol  $\text{FeCl}_3$  and  $\text{PPh}_3$  react under formation of the complex  $[\text{PPh}_3(\text{CH}_3)][\text{FeCl}_4]$ . Reaction of ethereal solution of  $\text{Fe}(\text{SCN})_3$  and  $\text{PPh}_3$  gives a red solid substance  $\text{Fe}(\text{SCN})_3(\text{PPh}_3)_2$  at ambient temperature. On the other hand, in acetonitrile or in benzene the reaction of iron(III) chloro and isothiocyanato complexes with  $\text{PPh}_3$  and  $\text{AsPh}_3$  occurs so that the ligands are oxidized at elevated temperature of 50–70 °C by air oxygen to  $\text{OPPh}_3$  and  $\text{OAsPh}_3$ , respectively. Phosphine oxide and arsine oxide complexes  $\text{FeCl}_3(\text{OPPh}_3)_2$  [2],  $\text{FeX}_3(\text{OAsPh}_3)_2$ , and  $\text{FeX}_3(\text{OAsPh}_3)_{1.5}$  ( $\text{X} = \text{Cl}$  [3];  $\text{NCS}$  [4]) crystallize from the solution.

At excess of the ligands, i.e. when  $n(\text{PPh}_3 \text{ resp. } \text{AsPh}_3) : n(\text{Fe(III)}) > 2$ ,  $\text{PPh}_3$  and  $\text{AsPh}_3$  are catalytically oxidized. In addition to the above-mentioned complexes also free  $\text{OPPh}_3$  and  $\text{OAsPh}_3$  precipitate. Presence of Fe(III) complexes as catalysts is necessary [5, 6].

However, the reactions of  $\text{FeX}_3$  ( $\text{X} = \text{Cl, NCS}$ ) with  $\text{SbPh}_3$  and  $\text{BiPh}_3$  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  $[\text{Fe}(\text{NCCH}_3)_6][\text{FeX}_4]_2$  is formed. As a result of the oxidation of  $\text{EPh}_3$  ( $\text{E} = \text{Sb, Bi}$ )  $\text{X}_2\text{SbPh}_3$  and  $\text{X}_2\text{BiPh}_3$ , respectively, were produced. These remarkable differences in behaviour of this class of substances attracted our interest to a more de-

tailed investigation of the reactions of  $\text{FeCl}_3$  and  $\text{Fe}(\text{NCS})_3$  with  $\text{SbPh}_3$  and  $\text{BiPh}_3$ .

## EXPERIMENTAL

Anhydrous  $\text{FeCl}_3$  was prepared by the reaction of iron powder with chlorine. The product was resublimed in the stream of chlorine [7]. Acetonitrile solution of  $\text{Fe}(\text{NCS})_3$  was prepared by mixing of the acetonitrile solutions of  $\text{FeCl}_3$  with  $\text{KSCN}$  in the mole ratio 1 : 3.  $\text{KCl}$  was separated by the filtration.

$\text{SbPh}_3$  and  $\text{BiPh}_3$ , 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  $\text{SbPh}_3$  and  $\text{BiPh}_3$  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  $\text{CaH}_2$  and rectified. The fraction with b.p. = 81.5 °C was used.

$[\text{Fe}(\text{NCCH}_3)_6][\text{FeCl}_4]_2$  (yellow substance) was prepared by the reaction of iron powder with chlorine in acetonitrile [10]. The compound  $[\text{Fe}(\text{NCCH}_3)_6][\text{Fe}(\text{NCS})_4]_2$  was prepared by reaction of iron powder with solid  $(\text{SCN})_2$  ( $n(\text{Fe}) : n(\text{SCN})_2 = 3 : 4$ ) 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 chelator 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 potenti-

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 $\text{FeCl}_3$ with $\text{EPh}_3$

Mixture of anhydrous  $\text{FeCl}_3$  and  $\text{EPh}_3$  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  $\text{Fe}_3\text{Cl}_8 \cdot 6\text{CH}_3\text{CN}$   $w_i(\text{calc.})$ : 20.66 % C, 2.60 % H, 12.05 % N, 40.66 % Cl, 8.01 % Fe(II), 24.02 % Fe(total);  $w_i(\text{found})$ : 21.40 % C, 2.83 % H, 11.95 % N, 40.87 % Cl, 7.98 % Fe(II), 24.03 % Fe(total).

After vacuum thickening of the filtrate white crystals of the composition  $\text{Cl}_2\text{EPh}_3$  were obtained. These crystals were further purified by recrystallization from acetone or methanol with addition of charcoal. For  $\text{Cl}_2\text{SbPh}_3$   $w_i(\text{calc.})$ : 50.99 % C, 3.57 % H, 16.72 % Cl;  $w_i(\text{found})$ : 51.92 % C, 3.65 % H, 16.85 % Cl. For  $\text{Cl}_2\text{BiPh}_3$   $w_i(\text{calc.})$ : 42.29 % C, 2.96 % H, 13.87 % Cl;  $w_i(\text{found})$ : 41.32 % C, 2.89 % H, 14.05 % Cl.

### Reactions of $\text{Fe(NCS)}_3$ with $\text{EPh}_3$

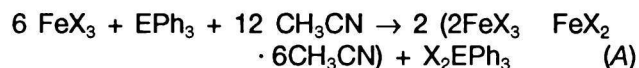
Mixture of  $\text{Fe(NCS)}_3$  and  $\text{EPh}_3$  in acetonitrile of composition  $n(\text{Fe(III)}) : n(\text{EPh}_3) = 1 : 0.5$  was kept at a room temperature for 2 h. Dark-red and white crystals corresponding to  $\text{Fe}_3(\text{SCN})_8 \cdot 6\text{CH}_3\text{CN}$  and  $(\text{NCS})_2\text{EPh}_3$ , respectively, were obtained from the solution. The crystals can be separated on the basis of different solubility in ether. While the white crystals were soluble, the red ones were insoluble in ether. The white crystals were purified by dissolution in acetone with suspended charcoal and in the next step by their precipitation with water. For  $\text{Fe}_3(\text{SCN})_8 \cdot 6\text{CH}_3\text{CN}$   $w_i(\text{calc.})$ : 27.34 % C, 2.06 % H, 22.32 % N, 6.36 % Fe(II), 19.07 % Fe(total);  $w_i(\text{found})$ : 28.25 % C, 2.21 % H, 21.80 % N, 6.28 % Fe(II), 18.70 % Fe(total). For  $(\text{NCS})_2\text{SbPh}_3$   $w_i(\text{calc.})$ : 51.19 % C, 3.22 % H, 5.97 % N;  $w_i(\text{found})$ : 52.50 % C, 3.32 % H, 5.89 % N. For  $(\text{NCS})_2\text{BiPh}_3$   $w_i(\text{calc.})$ : 43.20 % C, 2.72 % H, 5.04 % N;  $w_i(\text{found})$ : 42.85 % C, 2.80 % H, 4.96 % N.

## RESULTS AND DISCUSSION

$\text{FeCl}_3$  and  $\text{Fe(NCS)}_3$  react with  $\text{EPh}_3$  ( $\text{E} = \text{Sb}, \text{Bi}$ ) in acetonitrile at ambient temperature under for-

mation of complex compounds  $\text{Fe}_3\text{Cl}_8 \cdot 6\text{CH}_3\text{CN}$  and  $\text{Fe}_3(\text{SCN})_8 \cdot 6\text{CH}_3\text{CN}$  which contain both Fe(III) and Fe(II). Ligands  $\text{EPh}_3$  are reducing agents in these reactions and they are oxidized to  $\text{Cl}_2\text{EPh}_3$  and  $(\text{NCS})_2\text{EPh}_3$ , respectively. Course of the reduction of Fe(III) by ligands  $\text{EPh}_3$  in the systems  $\text{FeCl}_3\text{—EPh}_3\text{—acetonitrile}$  (1) and  $\text{Fe(NCS)}_3\text{—EPh}_3\text{—acetonitrile}$  (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  $[\text{Fe}(\text{bpyr})_3]^{2+}$  increases with time. This ion is formed after the addition of 2,2'-bipyridine and masking of  $\text{NCS}^-$  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  $\text{EPh}_3$  increases the rate of the reduction. However, it does not influence the final content of Fe(III).

The reduction of  $\text{FeX}_3$  by ligands  $\text{EPh}_3$  can be described by the equation (A) which contains all the components taking part in the reaction



As two thirds of the amount of substance of iron stay in the form of Fe(III), the amount of  $\text{EPh}_3$  required for its reduction follows from the equation



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  $\text{Fe}_3\text{Cl}_8 \cdot 6\text{CH}_3\text{CN}$  we assume that this substance is identical with  $[\text{Fe}(\text{NCCH}_3)_6][\text{FeCl}_4]_2$  structure which has been determined by *Daran* [12].

In the IR spectrum of compound  $\text{Fe}_3(\text{SCN})_8 \cdot 6\text{CH}_3\text{CN}$  there is a broad band with two maxima at  $\tilde{\nu} = 2289$  and  $2050\text{ cm}^{-1}$ . The first maximum can be identified with stretching vibration  $\nu(\text{CN})$  of acetonitrile. Owing to the coordination of  $\text{CH}_3\text{CN}$  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  $22.3\text{ cm}^{-1}$  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  $\tilde{\nu} = 339$  and  $280\text{ cm}^{-1}$  found in the range of  $200\text{--}400\text{ cm}^{-1}$  were assigned to  $\nu(\text{Fe(III)—NCS})$  vibration [15], that at  $\tilde{\nu} = 245\text{ cm}^{-1}$  was assigned to the vibration  $\nu(\text{Fe(II)—N})$  and at  $\tilde{\nu} = 202\text{ cm}^{-1}$  to the bending vibration  $\delta(\text{Fe(II)—NC})$  [12].

The band in the region of  $\tilde{\nu} = 11\,000\text{--}30\,000\text{ cm}^{-1}$  of electronic spectrum with maximum at  $\tilde{\nu} = 21\,580\text{ cm}^{-1}$  corresponded to iron(III) isothiocyanate anion. It can be characterized as a charge-transfer band [17, 18].

## REFERENCES

1. Naldini, L., *Gazz. Chim. Ital.* **90**, 1231 (1960).
2. Vančová, V., Ondrejovič, G., and Gažo, J., *Chem. Zvesti* **30**, 86 (1976).
3. Vančová, V., Melník, M., Ondrejovič, G., and Gažo, J., *Z. Anorg. Allg. Chem.* **455**, 93 (1979).
4. Vančová, V. and Melník, M., *Chem. Papers* **42**, 641 (1988).
5. Vančová, V. and Ondrejkočičová, I., *Collect. Czech. Chem. Commun.* **56**, 2869 (1991).
6. Vančová, V., Ondrejkočičová, I., and Ondrejovič, G., *Chem. Papers* **38**, 363 (1984).
7. Kľučnikov, N. G., *Průručka anorganických syntéz*. (Reference Book of Inorganic Syntheses.) P. 158. SVTL (Publishers of Technical Literature), Bratislava, 1957.
8. Vanino, L., *Handbuch der präparativen Chemie*. P. 731. Enke, Stuttgart, 1937.
9. Pfeiffer, P., *Chem. Ber.* **37**, 4620 (1904).
10. Hathaway, B. J. and Holah, D. G., *J. Chem. Soc.* **1964**, 2408.
11. Day, P. and Jørgensen, C. K., *J. Chem. Soc.* **1964**, 6226.
12. Daran, J. C., *Thesis*. P. 58. L'Université Paul Sabatier de Toulouse, Toulouse, 1973.
13. Horák, M. and Papoušek, D., *Infračervená spektra a struktura molekul*. (IR Spectra and Structure of Molecules.) P. 537. Academia, Prague, 1976.
14. Norbury, A. H., *Adv. Inorg. Chem. Radiochem.* **17**, 231 (1975).
15. Cotton, S. A. and Gibson, J. F., *J. Chem. Soc., A* **1971**, 859.
16. Lewis, J., Nyholm, R. S., and Smith, P. W., *J. Chem. Soc., A* **1961**, 4590.
17. Foster, D. and Goodgame, D. M. L., *J. Chem. Soc.* **1965**, 268.
18. Yano, Y., Fairhurst, M. T., and Swadle, T. W., *Inorg. Chem.* **19**, 3267 (1980).

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