

# Oxidation of triphenylphosphine in chloroiron(III) complexes

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Ferric chloride reacts with triphenylphosphine in acetonitrile and some other solvents in the presence of air oxygen to give  $\text{FeCl}_3(\text{OPPh}_3)_2$ . The air oxygen gradually oxidizes triphenylphosphine in the solid  $\text{FeCl}_3(\text{PPh}_3)_2$ , too, and  $\text{FeCl}_3(\text{OPPh}_3)_2$  arises. A complete oxidation of triphenylphosphine in the solid  $\text{FeCl}_3(\text{PPh}_3)_2$  takes place at  $80^\circ\text{C}$ .

Хлорид трехвалентного железа взаимодействует с трифенилфосфином в ацетонитриле и в некоторых других растворителях в присутствии кислорода воздуха с образованием  $\text{FeCl}_3(\text{OPPh}_3)_2$ . Кислород воздуха постепенно окисляет трифенилфосфин и в твердом  $\text{FeCl}_3(\text{PPh}_3)_2$  и образуется  $\text{FeCl}_3(\text{OPPh}_3)_2$ . Полное окисление трифенилфосфина в твердом  $\text{FeCl}_3(\text{PPh}_3)_2$  происходит при  $80^\circ\text{C}$ .

In some solvents such as acetone, acetonitrile, and acrylonitrile the chloroiron(III) complexes are subjected to spontaneous oxidation-reduction changes [1, 2, 4] while Fe(III) is reduced to Fe(II). The reaction is affected remarkably by light radiation. The solutions of chlorocopper(II) complexes in the above-mentioned solvents show similar properties as well [3, 4, 15]. This similarity results from analogous interactions between ligands in the halo complexes of Fe(III) and Cu(II) and is due to a possible formation of the dative  $\pi$  bonds between ligands (molecules of solvents) and the central atom [5, 6]. The reducing effects of triphenylphosphine on halocopper compounds are well known [16] and for this reason the halocopper(II) complexes with triphenylphosphine have not been hitherto prepared in the solid state. Triphenylphosphine, however, forms with  $\text{FeCl}_3$  the relatively stable complexes  $\text{FeCl}_3(\text{PPh}_3)_2$  [7] and  $\text{FeCl}_3(\text{PPh}_3)$  [8]. These striking differences stimulated us to a deeper study of the reaction between  $\text{FeCl}_3$  and triphenylphosphine in different solvents.

## Experimental

### *Chemicals and equipments*

The anhydrous  $\text{FeCl}_3$  was prepared by usual method [9]. The starting  $\text{PPh}_3$  (preparation of the practical grade) was twice recrystallized from ethanol.  $\text{OPPh}_3$  was prepared according to [10] and twice recrystallized from an aqueous solution of ethanol.

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#### *Abbreviations:*

$\text{OPPh}_3$  triphenylphosphine oxide.

$\text{PPh}_3$  triphenylphosphine.

ACN acetonitrile.

Acetonitrile (anal. grade) was dried by means of  $\text{CaH}_2$  and rectified. Iron was determined complexometrically with sulfosalicylic acid, carbon, hydrogen, and oxygen by elemental analysis, and chlorides argentometrically with potentiometric indication of the titration end point. Infrared spectra of solid substances were measured on a UR-20 (Zeiss, Jena) spectrophotometer using the Nujol mull technique. The magnetic susceptibilities were measured by the Gouy method at room temperature by means of a magnetic balance of original construction.

## Results and discussion

### *Oxidation of triphenylphosphine bonded in iron(III) complexes in non-aqueous solvents*

The reaction of anhydrous ferric chloride with triphenylphosphine in ether affords crystalline  $\text{FeCl}_3(\text{PPh}_3)_2$  [7]. However, if the ether solution of  $\text{FeCl}_3(\text{PPh}_3)_2$  is allowed to stand in air for a longer period of time (*ca* 24 hrs under laboratory condition) the yellow crystals of  $\text{FeCl}_3(\text{OPPh}_3)_2$  are separated from the solution. The oxidation may be accelerated by thorough bubbling of the solution with air. The reaction was also followed in other solvents. Anhydrous ferric chloride reacts with  $\text{PPh}_3$  in acetonitrile at elevated temperature (about  $80^\circ\text{C}$ ) in the presence of air oxygen to form a yellow crystalline substance the composition of which corresponds to  $\text{FeCl}_3(\text{OPPh}_3)_2$ .

For  $\text{C}_{36}\text{H}_{30}\text{P}_2\text{O}_2\text{FeCl}_3$  (718.78) calculated: 7.78% Fe, 14.79% Cl, 60.14% C, 4.20% H, 4.2% O; found: 7.72% Fe, 14.62% Cl, 60.40% C, 4.27% H, 4.10% O.

The data of chemical analysis, the magnetic moment  $\mu_{\text{eff}} = 5.89$  B.M., and the infrared spectra give proof that the substance is identical with the complex  $\text{FeCl}_3(\text{OPPh}_3)_2$  which was prepared by the synthesis of  $\text{FeCl}_3$  and  $\text{OPPh}_3$  in ethanol [11].

Ferric chloride dissolved in acetonitrile is reduced by the effect of light radiation [2]. The ferrous-ferric complex  $2\text{FeCl}_3 \cdot \text{FeCl}_2 \cdot 6\text{ACN}$  [12] crystallizes from this solution. In the presence of  $\text{PPh}_3$  ferric chloride does not undergo any reduction and the yellow species  $\text{FeCl}_3(\text{OPPh}_3)_2$  arises.

$\text{FeCl}_3(\text{PPh}_3)_2$  is oxidized analogically to  $\text{FeCl}_3(\text{OPPh}_3)_2$  even in ethanol, benzene, acetone, and ethyl acetate. Acetonitrile decomposes  $\text{FeCl}_3(\text{PPh}_3)_2$ , the crystalline  $\text{PPh}_3$  separates and Fe(III) remains in the form of chloro complexes in the mother liquor.

The problem whether  $\text{PPh}_3$  is oxidized inside or outside the complex was investigated by means of the reactions with different molar ratios of  $\text{FeCl}_3$  to  $\text{PPh}_3$ .  $\text{FeCl}_3(\text{OPPh}_3)_2$  is formed only at the molar ratio  $\text{FeCl}_3 : \text{PPh}_3 = 1 : 2$ . Provided  $\text{PPh}_3$  is present in excess ( $\text{FeCl}_3 : \text{PPh}_3 = 1 : 3-6$ ), the surplus  $\text{PPh}_3$  crystallizes first from the solution and subsequently  $\text{FeCl}_3(\text{OPPh}_3)_2$  but no formation of the free  $\text{OPPh}_3$  is to be observed.

### *Oxidation of triphenylphosphine in the solid $\text{FeCl}_3(\text{PPh}_3)_2$*

The crystalline  $\text{FeCl}_3(\text{PPh}_3)_2$  is oxidized to  $\text{FeCl}_3(\text{OPPh}_3)_2$  even in the solid state. The oxidation with air oxygen proceeds very slowly under laboratory conditions and the substance is oxidized only partially while the colour changes from original black into violet. By this procedure it is not possible to transform completely the substance into the oxidized form.

The gradual oxidation of  $\text{FeCl}_3(\text{PPh}_3)_2$  was investigated by means of infrared spectroscopy. It may be observed in the spectra that the band at  $1155\text{ cm}^{-1}$  corresponding to the

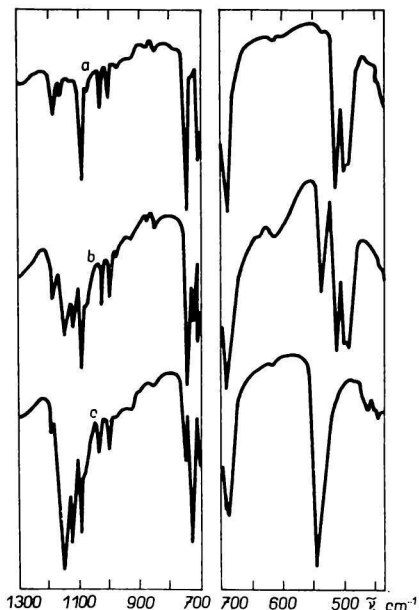


Fig. 1. Infrared spectra.  
 a) Spectrum of  $\text{FeCl}_3(\text{PPh}_3)_2$  immediately after preparation; b) spectrum of  $\text{FeCl}_3(\text{PPh}_3)_2$  after partial oxidation; c) spectrum of  $\text{FeCl}_3(\text{OPPh}_3)_2$ .

stretching vibrations of the P—O bond of the coordinated  $\text{OPPh}_3$  [13] increases. Simultaneously a band appears at  $545\text{ cm}^{-1}$  (this band is present in the spectrum of  $\text{OPPh}_3$  and its wavenumber is practically independent of coordination) and the intensity of the band at  $525\text{ cm}^{-1}$  corresponding to the stretching vibrations of the Fe—P bond [8] decreases. By the effect of oxygen on the solid dark complex  $\text{FeCl}_3(\text{PPh}_3)_2$  in a sealed test tube at  $80^\circ\text{C}$  a complete transformation into  $\text{FeCl}_3(\text{OPPh}_3)_2$  takes place in the time interval of five hours.

For  $\text{C}_{36}\text{H}_{30}\text{P}_2\text{O}_2\text{FeCl}_3$  (718.78) calculated: 7.78% Fe, 14.79% Cl, 60.14% C, 4.20% H; found: 7.72% Fe, 14.61% Cl, 61.3% C, 4.30% H.

From the chemical analysis and from the comparison of the band in infrared region at  $1155\text{ cm}^{-1}$  corresponding to the stretching P—O vibration it ensues that the substance formed is identical with the complex prepared by the direct synthesis of  $\text{FeCl}_3$  with  $\text{OPPh}_3$  (Fig. 1).

These experimental data demonstrate that triphenylphosphine is oxidized to triphenylphosphine oxide in acetonitrile solution only in the presence of Fe(III) and the phosphine oxide complex  $\text{FeCl}_3(\text{OPPh}_3)_2$  is formed as the final product. Triphenylphosphine bonded in complex is oxidized to triphenylphosphine oxide by air oxygen. Analogously  $\text{CoCl}_2(\text{PEt}_3)_2$  reacts with oxygen in solution to give a triethylphosphine oxide complex [14]. The formation of the phosphine oxide complex  $\text{FeCl}_3(\text{OPPh}_3)_2$  by the reaction of the chlorotriphenylphosphineiron(III) complexes in non-aqueous solutions or the solid  $\text{FeCl}_3(\text{PPh}_3)_2$  with oxygen is in contrast with the formation of the Cu(II) complexes of triphenylphosphine oxide.

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