

Oxidation of triphenylphosphine by dioxygen in the presence of iron(III) perchlorate

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In the presence of iron(III) perchlorate triphenylphosphine is oxidized by dioxygen under mild conditions in acetonitrile solution to yield triphenylphosphine oxide. At the same time, Fe(III) is reduced to Fe(II) and a ferrous complex of composition $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ comes into existence. Perchloric acid is formed as a side product. The reaction exhibits stoichiometric course and the oxidation of triphenylphosphine proceeds as far as the mole ratio $n(\text{PPh}_3) : n(\text{Fe}) = 4$ is reached. The cause why the generated Fe(II) complex does not act as a catalyst of the oxidation of triphenylphosphine is discussed in this paper.

Under common conditions triphenylphosphine (PPh_3) is only slightly oxidized by molecular oxygen to triphenylphosphine oxide (OPPh_3) and this oxidation necessitates to use stronger oxidants. Some complexes of transition elements are able to transfer oxygen to PPh_3 under mild conditions [1—6]. These stoichiometric reactions frequently play an important role in catalytic oxidation of PPh_3 to OPPh_3 . One of the conditions of this catalytic reaction is the postulate that the arising OPPh_3 must easily be liberated from the coordination sphere of the central atom [3—5]. It is known that an exchange of ligands takes place during the catalytic cycle and the catalyst itself is subjected to reversible redox transformations [5—9]. However, the catalytic oxidation is not observed if excess PPh_3 produces inhibition of the oxidation of triphenylphosphine [10] or the active complex undergoes a consecutive reaction with solvent or the formed OPPh_3 is firmly fixed to the central atom to give a stable complex [11].

We have shown in our preceding papers that the triphenylphosphine oxide complexes $\text{FeX}_3(\text{OPPh}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{or NCS}$) and $\text{Fe}(\text{OPPh}_3)_4(\text{I}_3)_2$ function as catalysts of the oxidation of PPh_3 by dioxygen at slightly increased temperature [12, 13]. The object of this study has been to elucidate the influence of iron(III) and iron(II) perchlorate and of the pertinent triphenylphosphine oxide complexes on the oxidation of PPh_3 by dioxygen.

Experimental

Triphenylphosphine (Jansen Chimica, Belgium) was recrystallized from ethanol in the presence of activated carbon. Triphenylphosphine oxide was prepared by catalytic oxidation of PPh_3 [13]. Acetonitrile (Apolda, GDR) was rectified and the fraction obtained at 81.5°C was used. Iron(III) perchlorate was made by dissolving fresh precipitated $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ in 70 % perchloric acid. After concentration *in vacuo*, colourless crystals crystallized from the solution [14]. The iron content in $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ ($M_r = 516.33$) was $w_i(\text{calc.})$: 10.81 % Fe; $w_i(\text{found})$: 10.65 % Fe. Iron(II) perchlorate was prepared by using the reaction of powdered iron with hot 70 % perchloric acid [14]. After concentrating and cooling the separated light blue crystals were filtered. The content of iron in $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($M_r = 362.84$) was $w_i(\text{calc.})$: 15.39 % Fe; $w_i(\text{found})$: 15.13 % Fe. Tetrakis(triphenylphosphine oxide)iron(III) perchlorate $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$ (yellow) was obtained by mixing hot ethanolic solution of $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ with OPPh_3 in the mole ratio 1 : 4 [15]. Tetrakis(triphenylphosphine oxide)iron(II) perchlorate $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ (violet) was prepared by using the direct reaction of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with OPPh_3 in hot ethanol, the mole ratio being 1 : 4 [16]. The results of analysis of both complexes are in agreement with literature.

The infrared spectra of the solid substances in nujol suspension were measured in the region of $\tilde{\nu} = 400\text{--}4000\text{ cm}^{-1}$ on a spectrophotometer Specord M-80 (Zeiss, Jena). The electronic absorption spectra of acetonitrile solutions of the above-mentioned complex compounds were taken on a spectrophotometer Specord M-40 (Zeiss, Jena). The pH values of aqueous solutions of HClO_4 were measured by the use of a laboratory digital pH-meter OP 211/1 (Radelkis, Budapest) equipped with a combined electrode. The oxidation of PPh_3 was investigated in an apparatus designed for measuring the consumption of dioxygen [17].

The samples were subjected to decomposition with nitric acid and the content of iron was determined complexometrically by using Chelaton 3. The content of carbon and hydrogen was determined by elemental analysis. The presence of HClO_4 was detected in aqueous solution by measuring pH or with methylene blue after separation of the poorly soluble KClO_4 .

Indirect synthesis of $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$

Acetonitrile (10 cm^3) was added into two thermostated vessels ($T = 323\text{ K}$) containing $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ (0.129 g; 0.25 mmol) and PPh_3 (0.262 g; 1 mmol) and under constant stirring dioxygen was introduced in both vessels till all PPh_3 was oxidized (about one day). The end of the oxidation of PPh_3 to OPPh_3 was ascertained by comparing the electronic absorption spectrum of the reaction mixture in acetonitrile solution with the spectrum of pure OPPh_3 which exhibits four absorption bands at $\lambda = 254, 260, 265,$ and 272 nm . The oxidation finished, acetonitrile was removed from both reaction systems and thus dry reaction mixture was obtained. The violet complex $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ obtained in the first reaction system was purified with ether. The positions of bands in the infrared spectra of the complex $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ prepared by direct synthesis [16] as well as by

the described indirect synthesis are equal. In both cases, it holds $\tilde{\nu}(\nu(\text{P}=\text{O})) = 1147 \text{ cm}^{-1}$ for the coordinated OPPh_3 [16]. For $\text{C}_{72}\text{H}_{60}\text{O}_{12}\text{P}_4\text{Cl}_2\text{Fe}$ ($M_r = 1367.91$) $w_i(\text{calc.}): 63.22\% \text{ C}, 4.42\% \text{ H}, 4.08\% \text{ Fe}$; $w_i(\text{found}): 62.15\% \text{ C}, 4.66\% \text{ H}, 4.30\% \text{ Fe}$. The presence of HClO_4 arising in the course of reaction (mentioned in discussion) was proved in the aqueous solution obtained by adding distilled water (15 cm^3) to the dry reaction mixture in the second vessel. This proof was achieved by measuring pH ($\text{pH} = 2.6$) and by using methylene blue after eliminating KClO_4 .

Results and discussion

In the presence of some iron compounds, *e.g.* FeX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{NCS}$) or FeI_2 , triphenylphosphine is autocatalytically oxidized to triphenylphosphine oxide and the corresponding complexes $\text{FeX}_3(\text{OPPh}_3)_2$ or $\text{Fe}(\text{OPPh}_3)_4(\text{I}_3)_2$ are subsequently formed. If we use excess PPh_3 , *i.e.* for the mole ratios $n(\text{PPh}_3) : n(\text{Fe}) > 2$ in the case of FeX_3 ($\text{X} = \text{Cl}, \text{Br}$ or NCS) or $n(\text{PPh}_3) : n(\text{Fe}) > 4$ in the case of $\text{FeI}_2 + \text{I}^-$, free OPPh_3 is generated besides the corresponding triphenylphosphine oxide complex. Those complexes act as catalysts of the oxidation of PPh_3 by dioxygen at temperature of about 323 K [12, 13]. The rate of oxidation of triphenylphosphine in the system catalyst— PPh_3 — O_2 — CH_3CN depends on properties of the X^- anions bonded to triphenylphosphine oxide iron complexes and increases in the order $v(\text{Cl}) \ll v(\text{NCS}) < v(\text{Br}) \ll v(\text{I})$. The rate of oxidation is probably related with oxidizability of the X^- anions [17, 18].

It has been disclosed by measuring the consumption of O_2 in the systems containing perchlorate anions, *i.e.* $\text{Fe}(\text{ClO}_4)_2$, $\text{Fe}(\text{ClO}_4)_3$, $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$, and $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$ that PPh_3 is oxidized by dioxygen only in the presence of iron(III) perchlorate. In other cases, dioxygen was not consumed and triphenylphosphine oxide did not arise. In the above-mentioned case, the oxidation of PPh_3 is not catalytic but proceeds stoichiometrically up to the mole ratio $n(\text{PPh}_3) : n(\text{Fe}(\text{ClO}_4)_3) = 4$. At the same time, the reduction of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ takes place and the ferrous complex $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ comes into existence. This complex was separated and identified. Perchloric acid appears as by-product of the reaction of $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ with PPh_3 and O_2 in acetonitrile. The excess PPh_3 remains nonoxidized in the reaction mixture towards the end of the reaction. The infrared spectra of these reaction mixtures did not contain the band corresponding to free OPPh_3 .

It has been found by measuring the consumption of dioxygen in the $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ — PPh_3 — CH_3CN system at different concentrations of $\text{Fe}(\text{ClO}_4)_3$ (c_{Fe}) and PPh_3 (c_{PPh_3}) that the total consumption of O_2 for 1 mol of Fe reaches the value of 1.75, which means that the oxidation proceeds up to the mole ratio $n(\text{O}_2) : n(\text{Fe}) = 7 : 4$. Fig. 1 expressing three measurements of oxygen consumption at equal concentration c_{Fe} and different concentrations c_{PPh_3} shows that the

rate of oxidation decreases with increasing concentration of PPh_3 . On the basis of experimental data we can assume that the reaction obeys the following equation



The generation of perchloric acid is probably analogous to that of HX in the reaction of PPh_3 with CuX_2 ($\text{X} = \text{Cl}, \text{Br}$ or NO_3) where $\text{Cu}(\text{II})$ is reduced to $\text{Cu}(\text{I})$ to give Ph_3PX_2 which undergoes hydrolysis to yield HX and OPPh_3 [19].

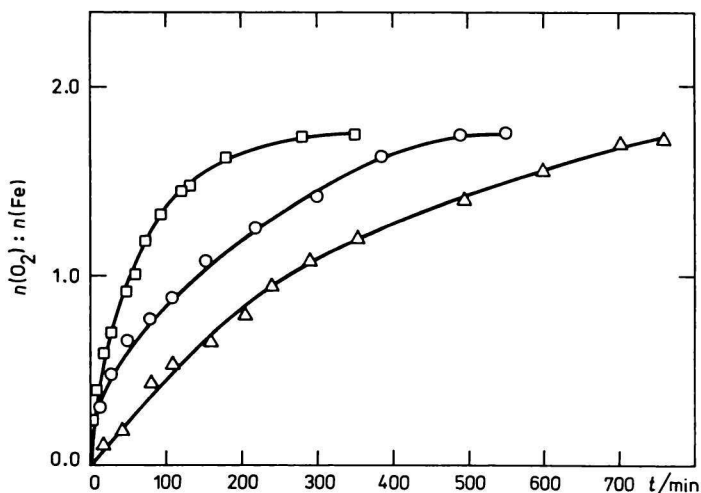


Fig. 1. Variation of dioxygen consumption with time for the $\text{Fe}(\text{ClO}_4)_3$ — PPh_3 — O_2 — CH_3CN system. $n(\text{PPh}_3)/n(\text{Fe})$: □ 4, ○ 6, △ 11. $[\text{Fe}] = 0.025 \text{ mol dm}^{-3}$; $T = 323 \text{ K}$.

The evidence that the catalytic oxidation of PPh_3 proceeds only in the presence of the X^- anions ($\text{X} = \text{Cl}, \text{Br}, \text{I}$, and NCS) is corroborated by the fact that all present triphenylphosphine was oxidized after adding *e.g.* the NCS^- anions into the $\text{Fe}(\text{ClO}_4)_3$ — PPh_3 — O_2 — CH_3CN system containing excess PPh_3 . The oxidation finished, free OPPh_3 was also present in the reaction mixture besides the coordinated OPPh_3 .

The reduction of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ sets in by the effect of PPh_3 on acetonitrile solution of the ferric complex $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$, but the reverse oxidation of $\text{Fe}(\text{II})$ does not take place. As to $\text{Fe}(\text{II})$ perchlorates, the presence of PPh_3 in acetonitrile solutions does not induce any redox transformations. The stoichiometric oxidation of PPh_3 in the presence of $\text{Fe}(\text{ClO}_4)_3$ at the mole ratio $n(\text{PPh}_3) : n(\text{Fe}) = 4$ proceeds as far as $\text{Fe}(\text{III})$ is reduced to $\text{Fe}(\text{II})$ and the stable ferrous complex $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ is formed by the reaction of $\text{Fe}(\text{II})$ with OPPh_3 and ClO_4^- . In contrast to this reaction, the reversible redox reaction

$\text{Fe(II)} \rightleftharpoons \text{Fe(III)}$ or $\text{I}_3^- \rightleftharpoons 3\text{I}^-$ [18, 20] takes place during the oxidation of PPh_3 catalyzed by the iron complex $\text{FeX}_3(\text{OPPh}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}$ or NCS) or $\text{Fe}(\text{OPPh}_3)_4(\text{I}_3)_2$.

The reversible redox reaction is a condition of catalytic course of the process not only in our investigated systems but also in many others. For instance, the fulfillment of conditions of reversible course of the redox reaction $\text{Fe(II)} \rightleftharpoons \text{Fe(III)}$ [8] plays an important role in the oxidation of PPh_3 catalyzed by iron phthalocyanines. Similarly, the redox process $\text{Fe(II)} \rightleftharpoons \text{Fe(IV)}$ proceeds in the oxidation of PPh_3 catalyzed by iron porphyrins [7]. The nitro(tetraphenylporphyrinato)Co(II) complexes can serve as another example. The nitro—Co(II) complex is reversibly reduced to nitrosyl—Co(II) complex in the course of catalytic oxidation [9].

In contrast to the catalytically active complexes $\text{FeX}_3(\text{OPPh}_3)_2$ and $\text{Fe}(\text{OPPh}_3)_4(\text{I}_3)_2$ [17, 18] the perchlorate compounds of iron are not catalysts of the oxidation of PPh_3 by O_2 . In the presence of iron perchlorates the condition of reversibility of the redox process as well as the condition of easy substitution of ligands in the coordination sphere of iron is not fulfilled. It results from this fact that the perchlorate anion is not liable to enter the coordination sphere of Fe and is not oxidizable when compared with the aniono ligands Cl^- , Br^- , I^- and NCS^- .

References

1. Ercolani, C., Gardini, M., Pennesi, G., and Rossi, G., *J. Chem. Soc., Chem. Commun.* 1983, 549.
2. Moyer, B. A., Sipe, B. K., and Meyer, T. J., *Inorg. Chem.* 20, 1475 (1981).
3. Graham, B. W., Laing, K. R., O'Connor, Ch. J., and Roper, W. R., *J. Chem. Soc., Dalton Trans.* 1972, 1237.
4. Van Vugt, B. H., Koole, N. J., Drenth, W., and Kuijpers, F. P. J., *Rec. Trav. Chim. Pays-Bas* 92, 1321 (1973).
5. Mimoun, H., *Rev. Inst. Fr. Pet.* 33, 259 (1978).
6. Taqui Khan, M. M., Siddiqui, M. R. H., Hussain, A., and Moiz, M. A., *Inorg. Chem.* 25, 2765 (1986).
7. Der-Hang Chin, La Mar, G. N., and Balch, A. L., *J. Am. Chem. Soc.* 102, 5947 (1980).
8. Ercolani, C., Gardini, M., Pennesi, G., and Rossi, G., *J. Mol. Catal.* 30, 135 (1985).
9. Yamamoto, K., *Polyhedron* 5, 913 (1986).
10. Geoffroy, G. L., Denton, D. A., and Eigenbrot, C. W., Jr., *Inorg. Chem.* 15, 2310 (1976).
11. Beagley, B., McAuliffe, Ch. A., Minten, K., and Pritchard, R. G., *J. Chem. Soc., Dalton Trans.* 1987, 1999.
12. Ondrejčková, I., Vančová, V., and Ondrejovič, G., *Collect. Czechoslov. Chem. Commun.* 48, 254 (1983).
13. Ondrejčková, I. and Ondrejovič, G., *Czechoslov.* 245541 (1987).
14. *Gmelins Handbuch*, Syst. No. 59, Part B, Vol. 2, p. 320. Verlag Chemie, Berlin, 1930.
15. Cotton, S. A. and Gibson, J. F., *J. Chem. Soc., A* 1971, 859.
16. Hunter, S. H., Nyholm, R. S., and Rodley, G. A., *Inorg. Chim. Acta* 3, 631 (1969).

17. Vančová, V., Ondrejkočičová, I., and Ondrejovič, G., *Chem. Zvesti* 38, 363 (1984).
18. Ondrejkočičová, I. and Ondrejovič, G., *Proc. 10th Conf. Coord. Chem.*, p. 303. Faculty of Chemical Technology, Slovak Technical University, Bratislava—Smolenice, 1985.
19. Makáňová, D., Ondrejovič, G., Valigura, D., and Gažo, J., *Chem. Zvesti* 28, 604 (1974).
20. Ondrejkočičová, I., Vančová, V., and Ondrejovič, G., *Proc. 9th Conf. Coord. Chem.*, p. 321. Faculty of Chemical Technology, Slovak Technical University, Bratislava—Smolenice, 1983.

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