

# SYNTHESIS OF TRIPHENYLPHOSPHINE OXIDE BY OXIDATION OF TRIPHENYLPHOSPHINE BY OXYGEN UNDER THE CATALYTIC EFFECT OF IRON COMPOUNDS

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Triphenylphosphine oxide,  $OP(C_6H_5)_3$ , can be conveniently prepared by oxidation of triphenylphosphine,  $P(C_6H_5)_3$ , by oxygen under the catalytic effect of iron compounds such as  $FeX_3$ ,  $FeX_3[OP(C_6H_5)_3]_2$ , ( $X = Cl, Br, NCS$ ), or  $FeCl_3[P(C_6H_5)_3]_2$ . The highest catalytic effect was observed in the case of the complexes containing the bromo or thiocyanato ligands. The oxidation in acetonitrile solution is quantitative and selective at 30–70°C and atmospheric pressure of oxygen gas.

Triphenylphosphine oxide,  $OP(C_6H_5)_3$ , can be prepared in several ways. The non-catalytic procedure consists in the reaction of triphenylphosphine with bromine leading to dibromotriphenylphosphine, which is hydrolyzed in aqueous solution to give the desired product<sup>1</sup>. Drawbacks of this method are the relatively low degree of conversion, not exceeding 50–60%, and corrosion of the apparatus brought about by the bromine used.

Procedures can be also used in which the oxidation of triphenylphosphine is catalyzed by complexes of transition elements. Thus  $[M(PPh_3)_4]$  complexes ( $M = Ni, Pd, Pt$ ;  $Ph = phenyl$ ) catalyze the reaction in toluene solutions<sup>2,3</sup>. In the case of  $M = Ni$ , the oxidation takes place at temperatures about –35°C, 50 mol of the phosphine being oxidized with one mol of the catalyst. With  $M = Pd, Pt$ , 500 mol of triphenylphosphine is oxidized with one mol of catalyst at 90°C. Ruthenium complexes can also act as catalysts in the reaction. The most efficient are the  $[Ru(NCS)(CO)(PPh_3)_2]$  and  $[Ru(NCS)(NO)(PPh_3)_2(O_2)]$  complexes, whose catalytic effect has been examined<sup>4,5</sup> in xylene solutions at 50–80°C. Also efficient is the  $[RuCl_2(PPh_3)_3]$  complex, in the presence of which the oxidation proceeds in benzene at room temperature<sup>6</sup>. Of rhodium and iridium compounds, the  $[RhCl(PPh_3)_3]$  and  $[IrX(CO)(PPh_3)_2]$  complexes ( $X = Cl, Br, I$ ) catalyze the oxidation of triphenylphosphine in toluene or benzene solutions<sup>7,8</sup>.

As to other transition elements, cobalt and molybdenum complexes can be used in the catalytic oxidation; for instance,  $[Co(CN)_2(PMe_2Ph_3)]$  and  $[MoO_2(S_2CNR_2)_2]$  ( $Me = methyl$ ;  $R = ethyl, 1-propyl, isobutyl$ ) can serve as catalysts in nonaqueous solutions at slightly elevated temperature<sup>9,10</sup>. The catalytic oxidation of triphenylphosphine has been also studied in the presence of iron complexes<sup>11</sup>. The  $[(C_2H_5)_4N]_2[Fe(mnt)_3]$  and  $[(C_2H_5)_4N][Fe(mnt)_2]$  complexes ( $mnt = cis-1,2-dicyanoethylene-1,2-dithiolate$ ) were used in acetonitrile solutions; fifteen and ten mol of the phosphine were oxidized with one mol of the catalysts, respectively.

In the present paper we report on a laboratory-scale preparation of triphenylphosphine oxide by catalytic oxidation of triphenylphosphine by oxygen in the pre-

sence of iron compounds of the types  $\text{FeX}_3$ ,  $[\text{FeX}_3(\text{OPPh}_3)_2]$ , ( $\text{X} = \text{Cl}, \text{Br}, \text{NCS}$ ) and  $[\text{FeCl}_3(\text{PPh}_3)_2]$  as catalysts<sup>1,2</sup>.

## EXPERIMENTAL

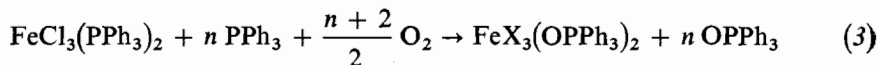
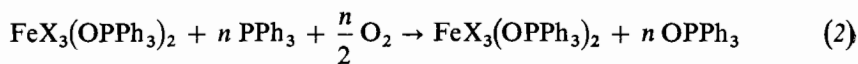
*Chemicals.* Triphenylphosphine *purum* was purified by recrystallization from acetone with an addition of activated carbon. Iron trichloride was prepared by reacting iron powder with chlorine<sup>13</sup>, iron tribromide was a commercial chemical of Cerac/Pure Inc., USA. Acetonitrile solution of iron(III) thiocyanate was prepared by mixing acetonitrile solutions of  $\text{FeCl}_3$  and  $\text{KSCN}$  in the molar ratio 1 : 3; the insoluble  $\text{KCl}$  formed during the reaction was removed after cooling. The  $[\text{FeX}_3(\text{OPPh}_3)_2]$  complexes with  $\text{X} = \text{Cl}, \text{Br}, \text{NCS}$  were obtained by reacting  $\text{FeX}_3$  with triphenylphosphine in the molar ratio 1 : 2 in the presence of  $\text{O}_2$  at 50–70°C;  $[\text{FeCl}_3 \cdot (\text{PPh}_3)_2]$  was prepared by reacting  $\text{FeCl}_3$  with  $\text{PPh}_3$  in ether<sup>14</sup>.

*Analytical procedures.* The purity of the compounds was checked by determining Fe(III) chelatometrically with Chelaton 3 using sulphosalicylic acid. Carbon, nitrogen, and hydrogen were determined by elemental analysis. The purity of the triphenylphosphine oxide prepared by catalytic oxidation was checked by elemental analysis and melting point measurements (m.p. 156°C, ref.<sup>15</sup>). For  $\text{C}_{18}\text{H}_{15}\text{OP}$  (278.3) calculated: 77.68% C, 5.43% H; found: 77.84% C, 5.30% H.

*Oxidation of triphenylphosphine.* 100 ml of 0.1M solution of catalyst was placed in a thermostated 250 ml reaction vessel, solid  $\text{PPh}_3$  was added in a molar ratio of 1 : 4 to 1 : 100 (the optimum ratio is 1 : 50), and the system was brought to the volume of 200 ml with acetonitrile. The mixture was stirred and oxygen was supplied continuously; during this process, triphenylphosphine oxidized slowly to triphenylphosphine oxide. The course of the reaction was monitored by comparing the UV spectrum of the product with that of pure  $\text{OPPh}_3$ , which in acetonitrile exhibits four absorption bands at 254, 260, 265, and 272 nm. When using the most efficient catalysts, *viz.* the bromo and thiocyanato complexes, in the molar ratio to triphenylphosphine 1 : 50, the oxidation took 10–15 hours.

## RESULTS AND DISCUSSION

The oxidation of triphenylphosphine by oxygen gas in the presence of a catalyst of the type  $\text{FeX}_3$ ,  $[\text{FeX}_3(\text{OPPh}_3)_2]$ , or  $[\text{FeCl}_3(\text{PPh}_3)_2]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{NCS}$ ;  $\text{Ph} =$  = phenyl) can be represented as



With one mol of catalyst, a maximum of 100 mol of triphenylphosphine can be oxidized in the homogeneous phase; the restriction arises from the solubilities of the phosphine and the product in acetonitrile. During the oxidation in  $\text{FeX}_3\text{-PPh}_3\text{-acetonitrile}$  systems ( $X = \text{Cl}, \text{Br}, \text{NCS}$ ) there are formed also  $\text{FeX}_3(\text{OPPh}_3)_2$  complexes (Eq. (1)), which themselves exhibit catalytic activity in the oxidation of triphenylphosphine by gaseous oxygen (Eq. (2)); thus the process in question is, in fact, an autocatalytic oxidation (Eqs (1) and (3)).

At the temperature  $50^\circ\text{C}$ , the catalyst concentration  $5 \cdot 10^{-2} \text{ mol l}^{-1}$ , and the iron-to-phosphine molar ratio 1 : 4, a 95% conversion to triphenylphosphine oxide using  $\text{FeBr}_3$ ,  $\text{Fe}(\text{NCS})_3$ , and  $\text{FeCl}_3$  was attained in 1.5, 3.5, and 36 h, respectively. No side products other than those given in Eqs (1)–(3) were detected.

From the point of view of the oxidation rate, the  $[\text{FeBr}_3(\text{OPPh}_3)_2]$  and  $[\text{Fe}(\text{NCS})_3 \cdot (\text{OPPh}_3)_2]$  complexes, or  $\text{FeBr}_3$  and  $\text{Fe}(\text{NCS})_3$ , appeared to suit best. The thiocyanate complex,  $[\text{Fe}(\text{NCS})_3(\text{OPPh}_3)_2]$ , has an additional advantage, namely, that it is readily prepared by reacting  $\text{Fe}(\text{NCS})_3$  with triphenylphosphine in the molar ratio 1 : 2 in acetonitrile in the presence of  $\text{O}_2$ , and purified by recrystallization from benzene.

The advantage of the suggested procedure for the synthesis of triphenylphosphine oxide, as compared with the methods hitherto reported, consists in the fact that catalysts are used that are considerably easier to prepare and are based on rather inexpensive iron compounds.

Pure triphenylphosphine oxide can be obtained from the reaction mixture by evaporation of acetonitrile and dissolution of the solid in acetone in the presence of activated carbon. After filtration, the triphenylphosphine oxide is precipitated from the solution by addition of water. The substance, in a high purity, is obtained in a 80% yield. Triphenylphosphine oxide prepared in this manner can be employed for extraction of some transition elements (Cr, Mn, Fe, Co, Cu, Zn, Zr) from acidic solutions<sup>16</sup> and also for extraction<sup>17</sup>, involving a synergic effect, of  $^{237}\text{U}$ .

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