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

Vlasta VANČOVÁ and Iveta ONDREJKOVIČOVÁ

*Department of Inorganic Chemistry, Slovak Technical University, 812 37 Bratislava*

Received February 27, 1991
Accepted March 9, 1991

Triphenylarsine oxide can be prepared conveniently by reacting triphenylarsine with dioxygen in the presence of iron compounds of the type of $FeX_3$, $[FeX_3(OAsPh_3)_2]$ and $[Fe(OAsPh_3)_4].(I_3)_2$ (X = Br, SCN; Ph = $C_6H_5$), which act as catalysts. The last-mentioned compound was found most catalytically active. Conducted in acetonitrile solution at slightly elevated temperatures (60 to 70°C) and atmospheric pressure of dioxygen, the oxidation is selective and quantitative.

Triphenylarsine oxide $OAsPh_3$ (Ph = $C_6H_5$) can be prepared in several ways. Non-catalytic oxidation of $AsPh_3$ can be accomplished using rather strong oxidants such as 30% $H_2O_2$ in acetone solution[1]. The product can also be obtained by dehydration of $(OH)_2AsPh_3$, which is prepared by reacting $AsPh_3$ with $SCl_2$ in carbon disulfide[2]. Drawbacks of these methods include low degrees of conversion (50 to 60%) and the use of the toxic carbon disulfide. Triphenylarsine oxide can also be synthesized by using various catalysts. Triphenylarsine is easy to oxidize in the presence of the $[Ru(NO)(O_2)(NCS)(PPh_3)_2]$ complex[3]. The starting oxidation rate is appreciably high, in several minutes, however, it drops rapidly and in approximately 30 min the catalyst is inactive due to its decomposition.

The rhodium complex $[RhCl(PPh_3)_3]$ is an efficient catalyst in the oxidation of diarsines but it is less active in the oxidation of triphenylarsine[4]. At the catalyst-to--triphenylarsine weight ratio of 1 : 10 in toluene, triphenylarsine is oxidized at the boiling temperature in a time as long as 70 h. Catalytic oxidation of triphenylarsine has also been examined in the presence of iron complexes[5]. The $[Ph_4N][Fe(mnt)_2]$ complex ($mnt^{2-}$ is the *cis*-1,2-dicyanoethylene-1,2-dithiolate anion) was used in acetonitrile solution; at catalyst and triphenylarsine concentrations of 19·3 and 33 mmol/dm$^3$, respectively, half of the substrate present is oxidized with dioxygen in 36 h. In the absence of the above catalysts, oxidation of triphenylarsine does not occur.

The present paper proposes a laboratory method for the preparation of triphenylarsine oxide by catalytic oxidation of triphenylarsine by dioxygen in the presence of compounds of the type of $FeX_3$, $[FeX_3(OAsPh_3)_2]$ (X = Br, NCS) and $[Fe.(OAsPh_3)_4](I_3)_2$ as catalysts[6]. The assets of this method include the use of inexpensive and readily available catalysts, selectivity and quantitativeness of the process, and easy isolation of the product.

## EXPERIMENTAL

*Chemicals.* Triphenylarsine purum (Jansen Chimica) was purified by recrystallization from acetone with the use of activated carbon. Iron tribromide (Cerac/Pure Inc., U.S.A.) was used as received.

Acetonitrile solution of iron(III) thiocyanate was prepared by reacting acetonitrile solutions of $FeCl_3$ and KSCN in the reactant molar ratio 1 : 3. KCl, which is insoluble in acetonitrile, was filtered off after cooling.

Complexes of the $[FeX_3(OAsPh_3)_2]$ type were prepared by reacting $FeX_3$ with triphenylarsine in the molar ratio 1 : 2 in the presence of $O_2$ at 60°C in acetonitrile. They are obtained in a good purity by recrystallization from acetone or ethanol. $[Fe(OAsPh_3)_4](I_3)_2$ was obtained by reacting $FeI_2$, $OAsPh_3$ and $I_2$ in the molar ratio 1 : 4 : 2 in acetonitrile.

*Analytical procedures.* The purity of the compounds prepared was checked by determining iron(III) with Chelaton 3 using sulfosalicylic acid as the indicator. Carbon, nitrogen and hydrogen were determined by elemental analysis. The purity of the triphenylarsine oxide obtained by the catalytic oxidation was checked by elemental analysis and by determining the melting temperature, which was 193°C (ref.[7], 191–193°C). For $C_{18}H_{15}AsO$ (322·2) calculated: 67·09% C, 4·85% H; found: 66·50% C, 5·18% H.

*Synthesis of triphenylarsine oxide.* An amount of 100 $cm^3$ of acetonitrile solution of catalyst at $c = 100$ mmol/$dm^3$ is placed in a 250 $cm^3$ thermostatted reaction vessel, solid $AsPh_3$ is added in a molar ratio of 1 : 1 to 1 : 20, and the mixture is diluted with pure acetonitrile to 200 $cm^3$. The system is stirred constantly and dioxygen is fed in, and at 70°C, triphenylarsine is oxidized to triphenylarsine oxide. Termination of the oxidation is established by comparing the electronic spectrum of the product with that of pure $OAsPh_3$, which in acetonitrile solutions exhibits four absorption bands with maxima at 252, 259, 262 and 270 nm. When the most efficient catalyst, viz. $[Fe(OAsPh_3)_4](I_3)_2$, is used at the catalyst-to-triphenylarsine molar ratio of 1 : 10, the oxidation takes 15 to 18 h.

Pure triphenylarsine oxide can be reclaimed from the reaction mixture as follows. After the oxidation, the acetonitrile solution is poured into 800 $cm^3$ of water. The $OAsPh_3$ formed is precipitated together with the catalyst, filtered out, dissolved in a small volume of acetone, and boiled with a solution of NaOH (about 0·1 g of NaOH per gramme of $OAsPh_3$) and with a solution of $NaClO_3$ (about 0·004 g of $NaClO_3$ per gramme of $OAsPh_3$). Activated carbon is added, and the solution is heated under reflux for approximately 5 h. After filtration, the $OAsPh_3$ is precipitated again with water and dried in a drying oven at 105°C. The product is obtained in a yield of 85–87% as a high purity chemical.

## RESULTS

Oxidation of triphenylarsine by dioxygen in the presence of catalysts of the type of $FeX_3$, $[FeX_3(OAsPh_3)_2]$ and $[Fe(OAsPh_3)_4](I_3)_2$ in acetonitrile at elevated temperatures can be represented by Eqs (*A*)–(*C*):

$$\mathrm{FeX_3} + n\mathrm{AsPh_3} + (n/2)\mathrm{O_2} \rightarrow [\mathrm{FeX_3(OAsPh_3)_2}] + (n-2)\mathrm{OAsPh_3} \quad (A)$$

$$[\mathrm{FeX_3(OAsPh_3)_2}] + n\mathrm{AsPh_3} + (n/2)\mathrm{O_2} \rightarrow$$
$$\rightarrow [\mathrm{FeX_3(OAsPh_3)_2}] + n\mathrm{OAsPh_3} \quad (B)$$

$$[\mathrm{Fe(OAsPh_3)_4}](\mathrm{I_3})_2 + n\mathrm{AsPh_3} + (n/2)\mathrm{O_2} \rightarrow$$
$$\rightarrow [\mathrm{Fe(OAsPh_3)_4}](\mathrm{I_3})_2 + n\mathrm{OAsPh_3} \quad (C)$$

One mole of catalyst can be used to oxidize a maximum of 10 moles of $AsPh_3$ in the homogeneous phase. This limitation is associated with the solubility of triphenylarsine and of the oxidation products in acetonitrile. In the $FeX_3$–$AsPh_3$–$CH_3CN$ systems ($X = Br, SCN$), the $[FeX_3(OAsPh_3)_2]$ complexes are also formed (Eq. (*A*)), exhibiting a catalytic effect in the oxidation of triphenylarsine by dioxygen (Eq. (*B*)). Hence, the process is autocatalytic oxidation of $AsPh_3$ by dioxygen in the presence of iron complexes.

Using a catalyst concentration of 50 mmol/dm$^3$ and the Fe : $AsPh_3$ molar ratio 1 : 10 at 70°C, triphenylarsine oxide can be obtained in a 95% yield in 6, 15 and 7 h when employing $FeBr_3$, $Fe(SCN)_3$ and $[FeBr_3(OAsPh_3)_2]$, respectively. No side products in addition to those included in Eqs (*A*) and (*B*) were found.

With the use of the $[Fe(SCN)_3(OAsPh_3)_2]$ complex at the molar ratio of Fe : : $AsPh_3$ = 1 : 4 and a catalyst concentration of 50 mmol/dm$^3$, oxidation to $OAsPh_3$ with a 95% degree of conversion takes 8 h. In this case the catalyst concentration cannot be increased to above the reported values because of its low solubility.

With respect to the oxidation rate, the $[Fe(OAsPh_3)_4](I_3)_2$ complex emerged as the most convenient catalyst; at its concentration of 20 mmol/dm$^3$ and at the Fe : : $AsPh_3$ ratio 1 : 8, 95% conversion is attained in 4·5 h; 100% conversion is reached in 6 h.

## REFERENCES

1. Shriner R. Z., Wolf C. N.: Org. Synth., Coll. Vol. *3*, 911 (1967).
2. Zuckerkandl F., Sinai M.: Ber. Dtsch. Chem. Ges. *54*, 2484 (1921).
3. Graham B. W., Laing K. R., O'Connor C. J., Roper W. R.: J. Chem. Soc., Dalton Trans. *1972*, 1237.
4. Poddar R., Agarwala U.: Inorg. Nucl. Chem. Lett. *9*, 985 (1973).
5. Sutin N., Yandell J. K.: J. Am. Chem. Soc. *95*, 4847 (1973).
6. Vančová V., Ondrejkovičová I.: Czech. Appl. PV 6700 (1990).
7. Hicker W., Lipp A.: Chem. Ber. *92*, 2075 (1959).

Translated by P. Adámek.