

Catalytic Synthesis of the Esters of Phosphorus Acids from White Phosphorus and Aliphatic or Aromatic Alcohols

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Abstract

The various esters of the phosphoric and phosphorous acids have been obtained directly from white phosphorus and aliphatic (or aromatic) alcohols under aerobic atmosphere in the presence of the CuX_2 or FeX_3 ($X = \text{Cl}, \text{NO}_3, \text{C}_3\text{H}_7\text{CO}_2$) salts. Irrespective of the variable nature of the used alcohols and catalysts, trialkyl(aryl) phosphates and dialkyl phosphites are a major products, whereas trialkyl(aryl) phosphites and dialkyl phosphates are a minor products of the phosphorylation process. Thanks to the presence of catalysts, the possible side reaction route of the radical chain oxidation of white phosphorus by oxygen to phosphorus oxides has been precluded. A comparison between the catalytic properties of CuX_2 and FeX_3 has been done. Although both of them have been found an efficient catalysts for the syntheses, the Cu(II) salts are active at 50-65°C, whereas the Fe(III) based catalytic systems become competitive in terms of catalytic efficiency when reaction is carried out at 70-90°C. Aromatic alcohols are characterised by less reactivity in this catalytic reaction as compared with an aliphatic ones. The same coordinative redox mechanism of the oxidative P-O coupling of P_4 to ROH in the presence of both Cu(II) and Fe(III) catalysts has been proposed. Relevant steps of the catalytic cycle including the complexation of both white phosphorus and alcohol molecules to metal ion, the reduction of catalyst by white phosphorus, and the oxidation of reduced form of catalyst by oxygen have been also considered.

Introduction

White phosphorus, P_4 , is a precursor of many useful organophosphorus compounds including the esters of phosphorus acids that are produced in multiton amount and are widely employed in different technological areas as extractors of rare and radioactive elements, flame-retardants for plastic materials, additives for combustible and lubricating materials, bioactive substances for further elaboration in pharmaceutical and agricultural industries, etc. The traditional way for the synthesis of the esters is based on the preliminary oxidative chlorination of P_4 followed by the substitutive P-O coupling of phosphorus chlorides with alcohols or phenols [1]. This productive cycle demands consumption of toxic Cl_2 and causes the evolution of HCl, which has a negative influence on the product yield because may split the resulting organophosphorus compounds to undesired by-prod-

ucts. In consequence of neutralization, HCl is converted to inorganic chlorides, whose removal from waste may still cause problems in large-scale production plants. Moreover, the present methods of air purification do not secure a cheap and complete removal of both Cl_2 and HCl impurities from the technological workshops air. For the reasons, the search for an alternative technology, which does not use chlorine for the preparation of organophosphorus compounds, is attracting considerable industrial and environmental interest.

We have first proposed an original "chlorine-free" method of the oxidative alko(aro)xylation of white phosphorus under mild reaction conditions in the presence of CuX_2 or FeX_3 salts ($X = \text{Cl}, \text{Br}, \text{NO}_3, \text{CH}_3\text{CO}_2, \text{C}_3\text{H}_7\text{CO}_2, \text{C}_{17}\text{H}_{35}\text{CO}_2$) which uses dioxygen as a cheap and efficient oxidant [2-5]. The new catalytic protocol allows to remove both Cl_2 and HCl from the productive cycle and to incorporate into the catalytic cycle all the advantages of a homogeneous catalytic reac-

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