Electronic supplementary materials *Mendeleev Commun.*, 2014, **24**, 334−335

Effect of a sacrificial anode material on the electrochemical generation of phosphane oxide (H_3PO)

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Experimental

All reactions and manipulations were carried out under dry, pure nitrogen using standard Schlenk apparatus. Ethanol was purified by distillation over sodium ethylate and stored under an atmosphere of dry nitrogen. The hydrochloric acid (37%) is commercially available (Sigma-Aldrich) and was used without additional purification.

The ^{31}P NMR spectra were recorded at 25 °C on a Bruker Avance III 400 MHz spectrometer operating at 161.9 MHz.

Cyclic voltammograms were recorded with a glassy carbon electrode (working surface 3.14 mm^2) in a thermostatically controlled (T = 20 °C) three-electrode electrochemical cell under N_2 in the presence of $(NBu_4)BF_4$ (0.1 M). A silver electrode $Ag/AgNO_3$ (0.01 $mol \cdot l^{-1}$ solution in CH_3CN) was used as a reference electrode and a platinum wire served as an auxiliary electrode. Curves were recorded at a constant potential scan rate of 50 mV s^{-1} at 20 °C using a potentiostat/galvanostat model PI-50-1 (USSR). A saturated solution of PH_3, prepared by bubbling of the electrochemically generated from P_4 in pure ethanol phosphane, was used for investigation of the electrochemical properties of PH_3.[1]

The macroscale electrolyses were carried out at room temperature in galvanostatic conditions [the potential of the electrochemically soluble anode was in the region +0.5 to +1.5 V vs $Ag/AgNO_3$ (0.01 $mol \cdot l^{-1}$ solution in MeCN)]. The electrolyses were performed in a single electrochemical cell (three-electrode cell, 40 ml)[2] without separation of anodic and cathodic compartments supplied with lead cylindrical electrode with a surface area of 60 cm^2 served as the cathode and Al, Cd, Co, Mg, Ni, Nb, Sn or Zn rods used as the anode.

Electrochemical reduction of white phosphorus (generation of phosphane oxide H_3PO). A solution for electrolysis was prepared by suspending of 0.07 g (0.56 mmol) of white phosphorus P_4 in 30 ml of ethanol/water (2:1 by volume) mixture. 0.5 ml of 2N HCl (water solution) has been added to the reaction mixture before the electrolysis started. After that constant current of 150 mA was passed through the resulting mixture for 30 min. The cell voltage was in the range 10-20 V for Al, Cd, Co, Mg, Ni and Zn anodes. In case of niobium and tin anodes the electric current was limited by 50 mA and the cell voltage was increased up to 40 V due to relatively high electric resistivity of the used metals.[3] After the electrolysis was completed, the resulting solution was analysed by ^{31}P NMR spectroscopy.

References

1 D. G. Yakhvarov, E. V. Gorbachuk and O. G. Sinyashin, *Eur. J. Inorg. Chem.*, 2013, 4709.

2 D. G. Yakhvarov, E. A. Trofimova and O. G. Sinyashin, *Russ. Pat. 85903*, C25B3/12, 2009. Priority 09.04.2009; Publ. 20.08.2009.

3 See for the details: http://www.webelements.com.