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

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The highest yields of phosphane oxide in the title process were obtained in electrochemical cells supplied with aluminium (49%), tin (36%) or zinc (67%) anodes.

The phosphorous oxyacids are an important source for the production of pharmaceuticals, fertilizers, pesticides, herbicides, flame retardants, lubricants, *etc*.[1] Thus, new methods for the selective preparation of phosphorous compounds starting from elemental (white) phosphorus are of high practical interest. From synthetic viewpoint, reagents like phosphane (PH_3) and hypophosphorous (hypo) acid (H_3PO_2) are of considerable importance. The phosphane oxide H_3PO is a highly reactive intermediate between a reduced form of phosphorus hydride and hypo acid. According to the electronic structure of H_3PO, the oxygen atom carries a partial negative charge and phosphorus has a partial positive charge.[2] The high reactivity of this molecule is most likely due to its polarity, which converts phosphorus into an electrophile. The charge imbalance between the P and O atoms is considerable to make it unstable.[3] Note that this molecule can occur in its tautomeric form as phosphinous acid $H_2P(OH)$.[4]

Previously, it was considered that the phosphane oxide molecule H_3PO does not exist at room temperature. Some experimental observations of this molecule include the application of molecular beam sampling mass spectrometry[5] for monitoring the reaction of atomic oxygen with PH_3 in a discharge-flow system, IR spectroscopy of the photolysis products of the phosphane-ozone complex in a solid state,[6] the product of PH_3 oxidation by atomic oxygen in an argon matrix[7] and the microwave spectrum detection of the radical H_2PO[8] and the molecule H_3PO.[9] The matrix isolation and theoretical study of the photochemical reaction of PH_3 with $OVCl_3$ and $CrCl_2O_2$ were also described.[10]

Recently, we found that this compound can be easily generated in solution by the mild electrochemical oxidation of phosphane PH_3 generated *in situ* from white phosphorus (P_4).[11] Phosphane oxide was characterized by NMR spectroscopy as free species in solution and in a coordinated form as a ligand in water-soluble ruthenium complexes. The phosphane oxide molecule in our former experiments was generated in a single electrochemical cell supplied with a sacrificial zinc anode.

Here, we describe the effects of sacrificial anodes made from Al, Cd, Co, Mg, Ni, Nb, Sn and Zn on the electrochemical reduction of white phosphorus and generation of phosphane oxide.[†]

The reduction of white phosphorus is irreversible and proceeds through radical anion formation:[12] $P_4 + e \rightarrow P_4^{\bullet-}$.

The formed $P_4^{\bullet-}$ radical anion initiates the polymerization of white phosphorus leading to polyphosphorus compounds. The derivatives containing the P–H bond are formed in the presence of active proton donors which can protonate phosphide anions initially produced in the electrochemical process. Thus, in protic media, all P–P bonds in white phosphorus tetrahedrons and formed polyphosphorus intermediates are sequentially opened and phosphane PH_3 is formed as the main product of the electrochemical process: $P_4 + 12e + 12H^+ \rightarrow 4PH_3$.[13] From the viewpoint of electrochemical process efficiency, cathodes with high hydrogen overvoltage, like lead and mercury, have been used.[14,15]

According to the cyclic voltammetry data, the electrochemically produced phosphane PH_3 displays one irreversible peak of oxidation.[16,17] We were interested in the study of the products formed in the oxidation process and performed the electrochemical oxidation of PH_3 on different metal anodes in order to generate phosphane oxide H_3PO.

Thus, we carried out the *in situ* generation of PH_3 in acidic ethanol–water mixtures in a single electrochemical cell supplied with sacrificial anodes of Al, Cd, Co, Mg, Ni, Nb, Sn or Zn at a constant current density of 5 mA cm^{-2} (10–20 V cell voltage). In case of niobium and tin electrodes displaying relatively high electric resistivity,[18] the current density was limited by 1–2 mA cm^{-2} at a cell voltage increased up to 40 V.

The electrochemical reactions in the systems are shown in Scheme 1.

Cathode: $P_4 + 12H^+ + 12e \longrightarrow 4PH_3$

Anode: $M^0 \longrightarrow M^{n+} + ne$

$4PH_3 + 4H_2O \longrightarrow 4H_3PO + 8H^+ + 8e$

Summary: $P_4 + 4H_2O + M^0 + 4H^+ + 4e \longrightarrow 4H_3PO + M^{n+} + ne$

M = Sn, Zn (n = 2), Al (n = 3)

Scheme 1

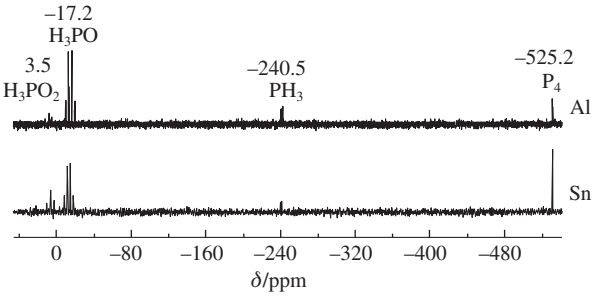

Figure 1 ^{31}P NMR spectra of an acidic EtOH–H_2O solution of P_4 after electrolysis (30 min) in an undivided electrochemical cell supplied with Al (top) and Sn (bottom) anodes.

[†] For experimental details, see Online Supplementary Materials.

Table 1 Distribution (%)[a] of phosphorous products in the reaction mixture after the electrolysis of the solution containing white phosphorus and standard electrode potentials (E^0) for the M^{n+}_{aq}/M^0 systems, where M = Cd, Co, Mg, Ni or Zn (n = 2) and Al or Nb (n = 3).

Entry	Anode	E^0/ (M^{n+}_{aq}/M^0)	P_4	PH_3	H_3PO	H_3PO_2
1	Al	–1.66	17	7	49	27
2	Cd	–0.40	traces	traces	traces	traces
3	Co	–0.28	traces	–	traces	–
4	Mg	–2.37	40	10	–	50
5	Nb	–1.10	8	–	–	–
6	Ni[b]	–0.25	–	–	–	–
7	Sn	–0.13	21	2	36	32
8	Zn[11]	–0.76	7	15	67	11

[a] Determined by the integral intensity of signals in the ^{31}P NMR spectra. [b] The ^{31}P NMR signals are not determined due to the presence of paramagnetic Ni^{2+} ions.

The highest yields of phosphane oxide were obtained with Al, Sn and Zn[11] anodes (Table 1). The reaction mixture after 30 min of electrolysis contained only the phosphorous products formed in the electrochemical process (Figure 1).

The lowest conversion of white phosphorus was observed with a Mg anode due to the low cell voltage that limited the cathodic process of P_4 electroreduction. However, at the same time, the formation of hypophosphorous acid H_3PO_2 proceeded with the highest yield. In principle, the potential of the system is sufficient for the oxidation of electrochemically generated phosphane PH_3 to phosphane oxide H_3PO, while a strong increase of the anodic potential can result in the formation of H_3PO_2 as the final product (Figure 2, Table 1).

The experimental data allow us to conclude that the nature of the metal anode has a crucial influence on the electrochemical generation of phosphane oxide. Nevertheless, although we did not observe the coordination of phosphane oxide to anodically generated Al^{3+}, Sn^{2+} and Zn^{2+} cations in our experiments, we cannot exclude the stabilization of H_3PO through coordination to these metals *via* the oxygen atom of phosphane oxide. Taking into account the standard electrode potentials determined in aqueous solutions, we believe that the formation of H_3PO is a more complicated process than a simple function of the standard electrode potentials of the metals used.

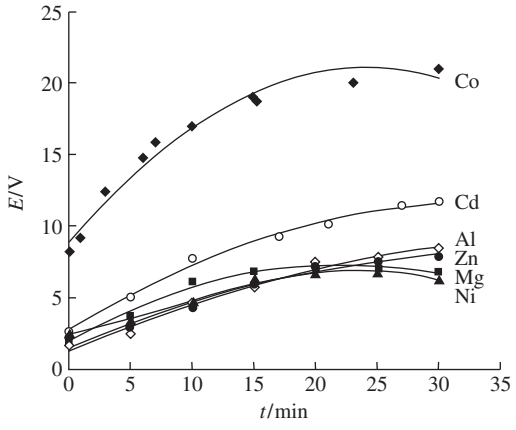

Figure 2 Cell voltage of the electroreduction of white phosphorus in acidic ethanol–water (1:2) solution with different sacrificial anodes: Zn, Mg, Al, Ni, Cd and Co.

Thus, we found that the illusive phosphane oxide molecule H_3PO can also be easily generated in an undivided electrochemical cell supplied with sacrificial aluminium and tin anodes. These results nicely supplement the data obtained using a sacrificial zinc anode.[11]

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2014.11.005.

References

1 D. E. C. Corbridge, *Studies in Inorganic Chemistry 20. Phosphorus. An Outline of its Chemistry, Biochemistry and Technology*, Elsevier, Amsterdam, 1995, p. 1208.
2 W. Kutzelnigg, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 272.
3 N. S. Nath, I. Bhattacharya, A. G. Tuck, D. I. Schlipalius and P. R. Ebert, *J. Toxicol*., 2011, **2011**, 1.
4 G. Manca, M. Caporali, A. Ienco, M. Peruzzini and C. Mealli, *J. Organomet. Chem*., 2014, **760**, 177.
5 P. A. Hamilton and T. P. Murrells, *J. Chem. Soc., Faraday Trans. 2*, 1985, **81**, 1531.
6 R. Withnall and L. Andrews, *J. Phys. Chem.*, 1987, **91**, 784.
7 R. Withnall and L. Andrews, *J. Phys. Chem*., 1988, **92**, 4610.
8 T. Hirao, S. Saito and H. Ozeki, *J. Chem. Phys*., 1996, **105**, 3450.
9 K. A. Imtiaz, H. Ozeki and S. Saito, *J. Chem. Phys*., 1999, **110**, 912.
10 D. A. Kayser and B. S. Ault, *J. Phys. Chem. A*, 2003, **107**, 6500.
11 D. Yakhvarov, M. Caporali, L. Gonsalvi, Sh. Latypov, V. Mirabello, I. Rizvanov, O. Sinyashin, P. Stoppioni, M. Peruzzini and W. Schipper, *Angew. Chem. Int. Ed*., 2011, **50**, 5370.
12 I. N. Brago and A. P. Tomilov, *Elektrokhimiya*, 1968, **4**, 697 (in Russian).
13 I. M. Osadchenko and A. P. Tomilov, *Zh. Prikl. Khim*., 1970, **43**, 1255 (in Russian).
14 N. Ya. Shandrinov and A. P. Tomilov, *Elektrokhimiya*, 1968, **4**, 237 (in Russian).
15 V. V. Turygin, M. K. Smirnov, A. V. Khudenko, S. V. Nikolashin, V. A. Fedorov and A. P. Tomilov, *Inorg. Mater*., 2009, **45**, 1388 (*Neorg. Mater.*, 2009, **45**, 1484).
16 D. G. Yakhvarov, E. V. Gorbachuk and O. G. Sinyashin, *Eur. J. Inorg. Chem*., 2013, 4709.
17 D. G. Yakhvarov, E. V. Gorbachuk, R. M. Kagirov and O. G. Sinyashin, *Russ. Chem. Bull., Int. Ed.*, 2012, **61**, 1300 (*Izv. Akad. Nauk, Ser. Khim*., 2012, 1285).
18 http://www.webelements.com.

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