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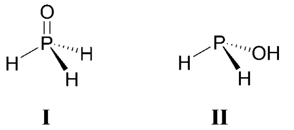
Phosphorus Chemistry

Experimental Evidence of Phosphine Oxide Generation in Solution and Trapping by Ruthenium Complexes**

Dmitry Yakhvarov, Maria Caporali, Luca Gonsalvi, Shamil Latypov, Vincenzo Mirabello, Ildar Rizvanov, Oleg Sinyashin, Piero Stoppioni, and Maurizio Peruzzini**

In memory of Massimo Di Vaira

Phosphorus oxides, oxyacids, and their esters are important chemicals for industry. Apart from playing a role in most organisms in ruling their energy transformations, they find wide and diverse applications, such as fertilizers, pesticides, herbicides, lubricants, flame retardants, additives for special plastics and materials, and drugs for different diseases.[1] Little attention has however been paid to lower-oxidation-state species, such as PO, HPO, and P_2O, for which synthetic isolation procedures and even direct evidence of their existence are scarce.[2] One of the most elusive species in this regard is phosphine oxide, H_3PO (**I**; Scheme 1). This molecule was first observed by reacting atomic oxygen with PH_3 using a discharge–flow system equipped with molecular-beam sampling mass spectrometry.[3] Alternatively, red-light photolysis of co-deposited PH_3/O_3 onto an argon matrix at 12–18 K was used to generate and trap **I** in a very diluted concentration together with its tautomer phosphinous acid $H_2P(OH)$ (**II**), which was identified by FTIR.[4] Finally, Ault and Kayser observed the formation of H_3PO in argon matrices after photochemical irradiation of a mixture of $VOCl_3$, CrO_2Cl_2, and PH_3.[5]



Scheme 1. Phosphine oxide (I) and its tautomer, phosphinous acid (II).

Both molecules have been studied by theoretical methods.[6] Application of an adequate phosphorus basis set has recently shown that, in contrast with previous ab initio studies,[7] **I** is more stable than **II** by only about 1 kcal mol^{-1} in the gas phase.[8] In contrast, computational analysis in aqueous solution showed that upon solvation **I** is largely preferred by about 10 kcal mol^{-1} owing to stronger hydrogen bonding with the highly polar $P^{\delta+}\rightarrow O^{\delta-}$ bond.[8] The possible involvement of H_3PO in the oxidative polymerization of phosphine to give polyhydride phosphorus P_xH_y polymers has been also proposed.[9]

Herein we show that the previously unknown P^{-1} species H_3PO (**I**) can be easily generated in solution by electrochemical methods, and we provide evidence of its solution stability, its characterization by conventional NMR spectroscopy, and its trapping as a ligand in the coordination sphere of hydrosoluble ruthenium complexes after tautomerization to **II**.

The electrochemical generation of H_3PO was performed in a single electrochemical cell with a lead cathode and a sacrificial zinc anode using P_4 melted in a slightly acidic water/ethanol solution (2:1 volume ratio, water acidified with HCl, 2 M) at 60 °C (Supporting Information, Figures S1, S2). The overall electrochemical process may be divided in two parts. In the first step, the electrochemical generation of PH_3 on the lead cathode takes place as previously described,[10,11] while in the second step, mild oxidation of PH_3 to H_3PO occurs at the anodic surface of the zinc electrode. In agreement with cyclic voltammetry experiments showing an irreversible oxidation wave, PH_3 is electrochemically active in the anodic potential range +0.80–1.25 V (vs. $Ag/AgNO_3$, 0.01 M in $CHCN_3$) and can be therefore oxidized in acidic water/ethanol 2:1 solution to H_3PO (Supporting Information, Figure S3). Scheme 2 shows the overall electrochemical process resulting in the cathodic reduction of P_4 to PH_3 and anodic oxidation of PH_3 to H_3PO ($E = +1.24$ V vs. $Ag/AgNO_3$, 0.01 M in $CHCN_3$).

Different working conditions were investigated to optimize the production of H_3PO. The best performance was

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[*] Dr. D. Yakhvarov, Dr. S. Latypov, Dr. I. Rizvanov, Prof. O. Sinyashin
A.E. Arbuzov Institute of Organic and Physical Chemistry
Russian Academy of Sciences
Arbuzov str., 8, 420088 Kazan (Russian Federation)
Fax: (+7) 843-273-2253
E-mail: yakhvar@iopc.ru
Prof. P. Stoppioni
Dipartimento Chimica, Università degli Studi di Firenze
Via della Lastruccia, 3-50019 Sesto Fiorentino (Italy)
Dr. M. Caporali, Dr. L. Gonsalvi, V. Mirabello, Dr. M. Peruzzini
Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici (ICCOM CNR)
Via Madonna del Piano 10, 50019 Sesto Fiorentino (Italy)
Fax: (+39) 055-522-5203
E-mail: mperuzzini@iccom.cnr.it
Homepage: http://www.iccom.cnr.it

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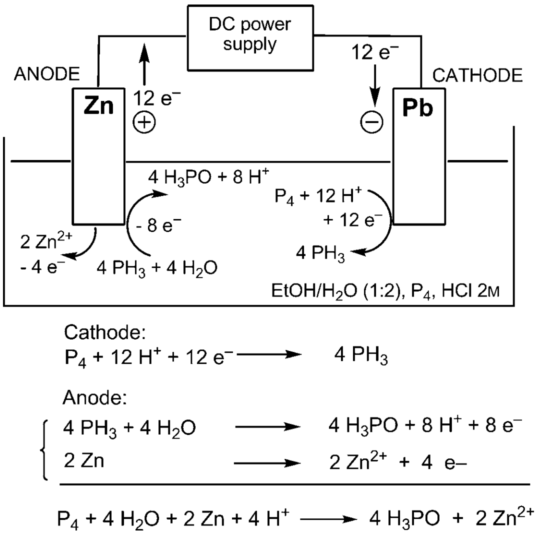


$$P_4 + 12\,H^+ + 12\,e^- \longrightarrow 4\,PH_3$$

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

$$2\,Zn \longrightarrow 2\,Zn^{2+} + 4\,e^-$$

$$P_4 + 4\,H_2O + 2\,Zn + 4\,H^+ \longrightarrow 4\,H_3PO + 2\,Zn^{2+}$$

Scheme 2. Electrochemical generation of H_3PO in acidic H_2O/EtOH solution from P_4.

obtained by dissolving 70 mg of solid P_4 in 30 mL of a mixture of water and ethanol 2:1 in the electrochemical cell heated to 60 °C. A current of 150 mA was applied for 30 min, and during this time HCl (2 mL, 2 M) was added. The presence of water played a crucial role: in pure ethanol, only the reduction of P_4 to PH_3 was observed, in keeping with a previous report from Tomilov.[10]

The optimized process (see the Supporting Information) resulted in the complete conversion of P_4 to three products identified by $^{31}P\{^1H\}$ NMR signals at $\delta = -243.05$ ppm and $\delta = 4.97$ ppm (Figure 1 a), which were easily attributed to phosphine (PH_3, 15.1 %) and (H_3PO_2, 16.1 %) respectively, while the singlet at $\delta = -17.55$ ppm was assigned to phosphine oxide, H_3PO (68.8 %). Turning off the ^1H decoupler (Figure 1 b) converted the latter singlet into a quartet, as expected for three protons directly bonded to phosphorus ($^1J_{PH} = 512.2$ Hz).[12] Moreover, the presence of a clear cross-peak in the $^{31}P\{^1H\},^1H$ HMQC 2D NMR spectrum (Figure 2) showed unambiguously direct bonding between the nuclei giving rise to the ^{31}P resonance attributed to H_3PO with the doublet centered at $\delta = 7.00$ ppm ($^1J_{PH} = 512.2$ Hz).[13]

Solutions of electrogenerated H_3PO slowly disproportionate to PH_3 and H_3PO_2 [Equation (1)]. At −30 °C, the process is rather slow, and after 20 days at −20 °C the concentration of H_3PO is about half of the original value. At room temperature, the transformation is much faster ($t_{1/2} \approx 345$ min) and a complete disproportionation to PH_3 and H_3PO_2 occurs in about two days.

$$2\,H_3PO \rightarrow PH_3 + H_3PO_2 \qquad (1)$$

Attempts to isolate the phosphine oxide in pure form from the water/ethanol solution were unsuccessful. Removal of all the volatile species, that is, the solvent and PH_3, left an oily residue that, taken with H_2O and analyzed by $^{31}P\{^1H\}$ NMR spectroscopy, showed the presence of H_3PO together with a variable amount of H_3PO_2, which could not be completely eliminated.

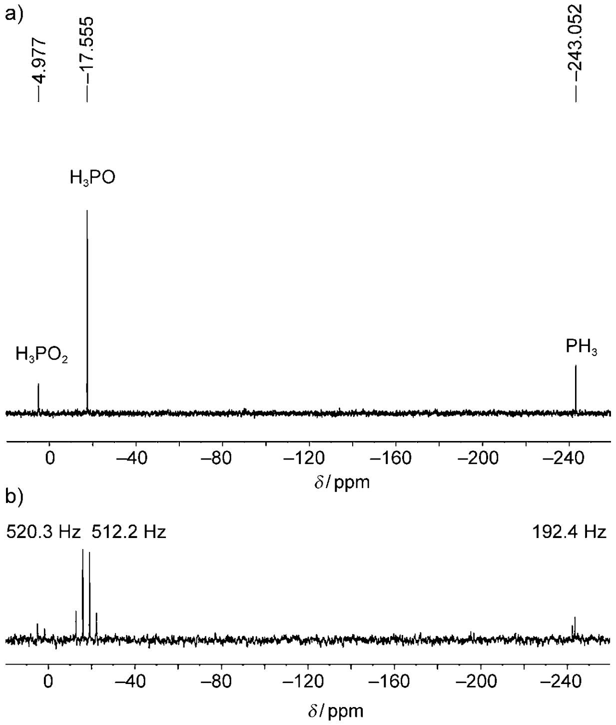


Figure 1. a) $^{31}P\{^1H\}$ NMR and b) ^{31}P NMR spectra (D_2O, RT) of an acidic H_2O/EtOH 2:1 solution of P_4 after electrolysis (30 min).

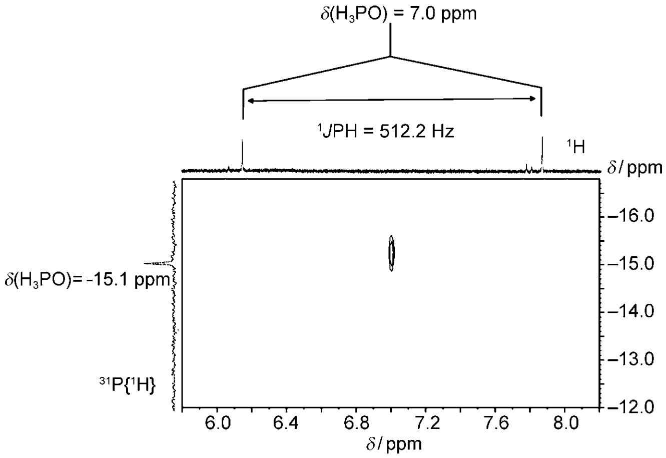
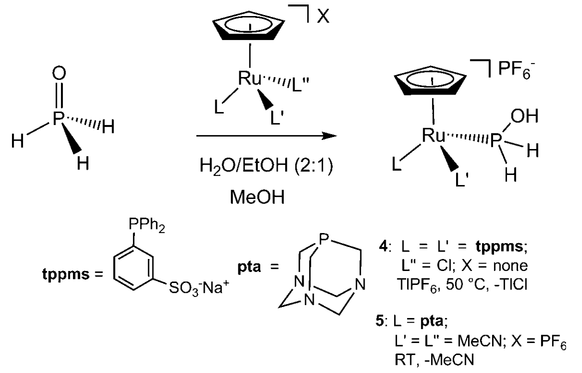


Figure 2. Section of the $^{31}P\{^1H\}$–^1H HMQC (phase-sensitive, with presaturation) 2D NMR spectrum (161.97 MHz, 25 °C) of the electrolyzed solution of P_4 in H_2O/EtOH 2:1 obtained in an Evans tube containing D_2O. The ^1H NMR spectrum was recorded using a WATERGATE (water suppression by gradient-tailored excitation) pulse sequence to suppress the H_2O peak at $\delta = 4.9$ ppm.

Confirmation for the electrochemical generation of **I** was obtained by trapping this molecule as a thermally stable derivative. A perusal of the literature available on the metal-mediated reactivity of white phosphorus[14] indicated that the ruthenium(II) complex $[CpRu(PPh_3)_2Cl]$ (**1**) is able, after chloride removal, to coordinate both white phosphorus and phosphine,[15] and also to stabilize the hydrolysis products of coordinated P_4,[16] including the lower phosphorus oxyacids H_3PO_2 and H_3PO_3.[17] These can work as ligands following ruthenium-promoted isomerization to the phosphine-like tautomers $PH(OH)_2$ and $P(OH)_3$, respectively.[17] Thus, we reasoned that a water-soluble version of complex **1** could react with a water/ethanol solution of the electrogenerated H_3PO by stabilizing the putative phosphinous acid, $H_2P(OH)$, assisting the energetically favored H_3PO tautomerization at ruthenium.

In keeping with this working hypothesis, reaction of crude **I** with the ruthenium complexes $[CpRu(tppms)_2Cl]$[18] (**2**) [Cp = cyclopentadienyl, tppms = m-$SO_3C_6H_4PPh_2^{(-)}Na^{(+)}$] and $[CpRu(pta)(CH_3CN)_2]PF_6$ (**3**)[19] (pta = 1,3,5-triaza-7-phosphaadamantane) gave as products the organometallic complexes $[CpRu(tppms)_2\{H_2P(OH)\}]PF_6$ (**4**) and $[CpRu(pta)(CH_3CN)\{H_2P(OH)\}]PF_6$ (**5**) after simple workup (Scheme 3; see the Supporting Information for details).[20]



Scheme 3. Synthesis of $[CpRu(tppms)_2\{H_2P(OH)\}]PF_6$ (**4**) and $[CpRu(pta)(CH_3CN)\{H_2P(OH)\}]PF_6$ (**5**) from H_3PO trapping.

The formation of complexes **4** and **5** confirmed that the electrogenerated phosphine oxide may be trapped before disproportionation by coordination of its tautomer, $H_2P(OH)$, to ruthenium. Both compounds were characterized by ESI-MS, IR and NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum contains a triplet centered at $\delta = 70.3$ ppm for **4** ($^2J_{PP} = 51.3$ Hz), while that of **5** has a doublet at $\delta = 74.1$ ppm ($^2J_{PP} = 63.0$ Hz) for the coordinated phosphinous acid. Switching off the proton decoupler gave triplets with identical $^1J_{PH}$ couplings (366.0 Hz), thus providing confirmation for a $H_2P(OH)$ coordinated species. Complexes **4** and **5** are the first compounds incorporating phosphinous acid and may be related to the crystallographically authenticated sulfur analogue, that is, $[CpRu(PPh_3)_2\{H_2P(SH)\}]PF_6$ (**6**), obtained by controlled hydrolysis of the P_4S_3 dinuclear sandwich complex $[\{CpRu(PPh_3)_2\}_2(\mu,\eta^{1:1}\text{-}P_{ap},P_{bas}\text{-}P_4S_3)](PF_6)_2$.[21] Both **4** and **5** are air-stable orange microcrystalline materials that share most of their chemicophysical properties with **6** and the other known $[CpRu(PPh_3)_2\{PH_{(3-x)}(OH)_x\}]^+$ derivatives ($x = 2, 3$).[17]

In conclusion, the elusive and poorly investigated phosphine oxide H_3PO (**I**) has been generated by simple electrochemical methods based on a two-step process involving first the electroreduction of white phosphorus to PH_3 in an acidic water/ethanol mixture at a lead electrode, followed by PH_3 oxidation at the zinc anode yielding H_3PO in about 70% maximum yield. Spontaneous disproportionation of **I** to PH_3 and H_3PO_2 acid takes place even at low temperature and hampers the isolation of H_3PO as a pure product. Nonetheless, H_3PO, the first defined compound of phosphorus in the −1 oxidation state, was characterized in solution by NMR spectroscopy and trapped in the coordination sphere of ruthenium(II) by tautomerization to phosphinous acid, $H_2P(OH)$, to afford stable organometallic cationic complexes. Studies are in progress to explore the reactivities of both free H_3PO and coordinated $H_2P(OH)$.

Experimental Section

CAUTION: Both white phosphorus and phosphine are very toxic, flammable, and hazardous compounds (see the Supporting Information).

H_3PO was electrogenerated in a 50 mL home-made electrochemical cell (see Supporting Information for details).[22] White phosphorus (70 mg, 0.56 mmol) was suspended in H_2O/EtOH 2:1 (30 mL) and warmed to 60 °C under nitrogen to ensure dissolution (ca. 30 min). HCl (0.5 mL, 2 M) was then added to the mixture and an electrical current with intensity $i = 150$ mA (current density 5.0 mA cm^{-2}) was applied for about 30 min while keeping the temperature constant at 60 °C. During the experiment, the mixture became cloudy and a yellowish suspension formed. Further addition of HCl (1.5 mL, 2 M) and vigorous stirring at 60 °C gave an almost colorless solution. The overall potential on the cell was −1.5–2.5 V.

A $^{31}P\{^1H\}$ NMR spectrum of an aliquot showed complete conversion of P_4 into PH_3, H_3PO, and H_3PO_2, with signals at $\delta(PH_3) = -243.05$ ppm (s); $\delta(H_3PO) = -17.55$ ppm (s); $\delta(H_3PO_2) = 4.97$ ppm (s). The relative amount depends from several factors such as reaction time, temperature, and acidity. In the experiment described above, the highest production of H_3PO was obtained with the following ratios: PH_3 (15.1%), H_3PO (68.8%), and H_3PO_2 (16.1%).

Synthesis of $[CpRu(tppms)_2\{H_2P(OH)\}]PF_6$ (**4**): $[CpRu(tppms)_2Cl]$ (**2**, 28 mg, 0.0301 mmol) was dissolved in dry MeOH (15 mL) and reacted with one equiv of solid $TlPF_6$ (10.5 mg, 0.0301 mmol) at room temperature under stirring. After 4 h, the solution was filtered by cannula to remove TlCl, giving a clear yellow solution of $[CpRu(tppms)_2(CH_3OH)]PF_6$. A H_2O/EtOH 2:1 solution (14.0 mL) of H_3PO, prepared as described above, was transferred to a Schlenk flask and evaporated under vacuum to half of the volume to remove the solvent and the volatiles (PH_3). The resulting colorless solution, containing only H_3PO (70%) and H_3PO_2 (30%), was then added dropwise to the solution of $[CpRu(tppms)_2(CH_3OH)]PF_6$, and the stirred suspension was warmed to 50 °C for 1 h, after which a clear yellow solution was obtained. Evaporation of the solvent to dryness left a yellow solid, which was washed with Et_2O (2 × 5 mL) and filtered under vacuum. Yield 19.6 mg (60%, based on complex **2**). H_3PO_2 is left unreacted, as formation of $[CpRu(tppms)_2\{PH(OH)_2\}]PF_6$ (**4c**) was not observed. See the Supporting Information for an independent synthesis of **4c** and $[CpRu(TPPMS)_2(PH_3)]PF_6$ (**4b**).

^1H NMR (400.13 MHz, CD_3OD, 20 °C): $\delta = 4.6$ (s, Cp, 5 H), 6.9–8.2 ppm (m, aromatic, 28 H). The signal for to the two $H_2P(OH)$ protons could not be directly observed as it is masked by the aromatic proton signals, but is was identified indirectly by $^1H,^{31}P$ HMQC 2D-NMR, which correlated the phosphorus resonance with a doublet at ca. 7.5 ppm ($^1J_{HP} = 366.0$ Hz; Supporting Information, Figure S6). $^{31}P\{^1H\}$ NMR (161.97 MHz, CD_3OD, 20 °C): $\delta = 70.3$ (t, $^2J_{PP} = 51.3$ Hz, $H_2P(OH)$), 46.7 (d, $^2J_{PP} = 51.3$ Hz, tppms), −145.1 ppm (sept, $^1J_{PF} = 705.9$ Hz, PF_6); ^{31}P NMR (161.97 MHz, CD_3OD, 20 °C): $\delta = 70.3$ (tt, $^1J_{HP} = 366.0$ Hz, $^2J_{PP} = 51.3$ Hz, $H_2P(OH)$), 46.7 (br d, $^2J_{PP} = 51.3$ Hz, tppms), −145.1 ppm (sept, $^1J_{PF} = 705.9$ Hz, PF_6). IR

(MeOH): ν(POH) 2488 (m), ν(PH) 2240 (w), ν(P=O) 1250 (s), ν(SO_3) 1191 (vs), ν(PF_6) 854 cm^{-1} (s). ESI-MS: $C_{41}H_{36}O_7P_3S_2Ru$, *m/z* 899, *m/z*−$H_2P(OH)$ 848.9.

Complex **5** was similarly prepared using [CpRu(pta)-$(CH_3CN)_2$]PF_6 (**3**) instead of **2** (see the Supporting Information).

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Keywords: electrochemistry · phosphine oxide · phosphinous acid · water-soluble ligands · white phosphorus

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[12] A careful calibration of the integral intensities in the ^1H NMR spectrum according to the weights of PH_3 (15.1%) and H_3PO_2 (16.1%) taken from the $^{31}P\{^1H\}$ NMR spectra also allowed the number of protons attached to phosphorus to be evaluated directly from the signal at $\delta = -17.55$ ppm, confirming the presence of three protons per phosphorus.

[13] The facile disproportionation of H_3PO and the unavoidable presence of both PH_3 and H_3PO_2 prevented us to get a more defined chemicophysical characterization of the phosphine oxide. Nonetheless, strong IR bands in the reaction mixture at about 1250 cm^{-1} were assigned to P=O stretching modes, although it was not be possible to discriminate between H_3PO and H_3PO_2 contributions. MS data for H_3PO could not be obtained owing to its quick decomposition under the working condition of the mass spectrometer.

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[20] As the electrogenerated solution of H_3PO was always contaminated by variable amounts of PH_3 and H_3PO_2, the formation of **4** and **5** was always accompanied by variable quantities of compounds [CpRu(tppms)$_2$(PH_3)]PF_6 (**4b**), [CpRu-(tppms)$_2${PH(OH)$_2$}]PF_6 (**4c**), [CpRu(pta)(CH_3CN)(PH_3)]PF_6 (**5b**), and [CpRu(pta)(CH_3CN){PH(OH)$_2$}]PF_6 (**5c**), respectively. These complexes were identified by comparison of the NMR data with those obtained from their independent syntheses from the reaction of **2** and **3** with PH_3 and H_3PO_2, respectively (Supporting Information). The presence of these contaminants has hampered the growth of crystals suitable for a crystallographic study for either **4** or **5**.

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