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Red Phosphorus

High-Pressure Chemistry of Red Phosphorus and Water under Near-UV Irradiation[**]

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Phosphorus is a key element in chemistry, physics, and biology, as well as in Earth and planetary sciences. Among the allotropes of phosphorus, the white molecular form (P_4), despite its extreme reactivity and toxicity, is currently preferred in industrial and research chemistry over the more-stable and less-toxic red polymeric one (P_{red}), because it is easily obtained and functionalized.[1–5] The less-reactive red phosphorus has had much less importance so far and has been employed in the industry of matches and, to a lesser extent, to produce flame retardants in plastics and aluminum phosphide. In view of the intrinsic reduced toxicity, particularly for aquatic organisms, switching from the extremely toxic white to red phosphorus would benefit any industrial procedure for organophosphorus compounds, from an environmental viewpoint, and could attract a large interest from organophosphorus manufactories.

High-pressure conditions are often used in chemistry to control the equilibrium constant and the reaction rate of a chemical reaction. Pressure is indeed the most effective tool for modifying intermolecular interactions to induce unexpected and amazing chemical transformations in condensed molecular systems, typically occurring in the GPa range.[6–15] Despite the very attractive possibility of synthesizing new materials in the absence of solvents and catalysts, according to the principles of green chemistry,[16] at the moment the application of these reactions is strongly limited by the high pressures required, which can not be achieved by large volume apparatuses. However, the combination of high pressure and electronic photoexcitation has been demonstrated to be very efficient in selecting preferential reaction paths and in reducing the threshold pressure for the reaction, even to a few tenths of a GPa, where applications can be envisaged.[17] Recently, the two-photon dissociation of water molecules by near-UV radiation at moderate pressures has been used to generate H atoms and $^{\bullet}OH$ radicals and to induce chemical reactions in fluid mixtures and in clathrate hydrates.[18–20] This approach is employed herein to trigger a very efficient reactivity between red phosphorus and water at room temperature and a few tenths of a GPa, leading to the formation of a large amount of H_2 and to a pressure-tuned quantitative oxidation and/or disproportionation of phosphorus to different phosphorus oxyacids and PH_3. The reaction occurs in the total absence of solvents, catalysts, and radical initiators.

Beyond the fundamental and applicative interest related to the chemistry of phosphorus under non-conventional conditions, obtaining H_2 from water is also relevant to the current goal of environmentally friendly synthetic methods based on renewable sources to produce the energy vector of the future. Finally, being that phosphorus is an essential element in the life cycle and in minerals, abiotic formation of phosphorus-containing compounds in terrestrial and space environments could also be relevant.[21,22]

The stability of the mixture of P_{red} and water was checked on compression up to 0.6 GPa using a diamond anvil cell (DAC; Supporting Information Sections 1.1 and 2). Irradiation of the sample at this pressure for five hours, using the UV multi-line (UVML) emission of an Ar ion laser centered at appoximately 350 nm, resulted in the occurrence of a chemical reaction, as evidenced by the formation of bubbles and by the almost complete consumption of the red phosphorus (Figure 1). Three different areas were roughly identified by visual inspection of the sample as bubbles, transparent, and dark areas. For the three areas, the two most informative frequency regions of the Raman spectrum at 200–1200 cm^{-1} and 2100–2500 cm^{-1} are separately presented and discussed herein.

The Raman spectra of the bubbles in the 200–1200 cm^{-1} frequency region (Figure 2A) are dominated by four sharp bands, identified as the $S_0(0)$ (355 cm^{-1}), $S_0(1)$ (589 cm^{-1}), $S_0(2)$ (816 cm^{-1}), and $S_0(3)$ (1033.5 cm^{-1}) rotational bands of H_2.[23] Other product bands, broader and weaker, which are the only signals observed in the transparent areas, also appears in some bubbles (traces e, h, and l). The Raman spectra of the transparent areas in the 200–1200 cm^{-1} frequency region show product bands with peak frequencies measured at 428, 526, 805, 898, 941, 1005 (shoulder), 1022, and 1135 cm^{-1} (Figure 2B, traces d, x, y, and z). Finally, the Raman spectra measured in the dark areas of the sample (Figure 2C, traces u, v, and w) only show the bands of amorphous red phosphorus.[24] Excluding the rotational bands of H_2, all the product bands observed in the 200–1200 cm^{-1} spectral region

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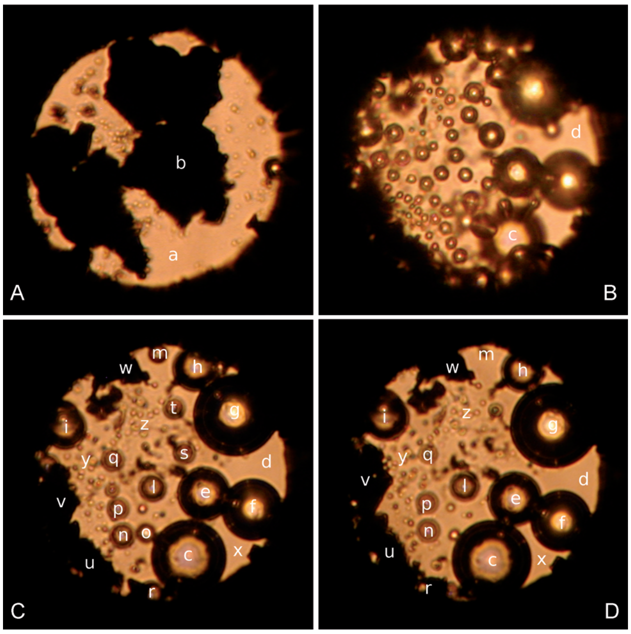

Figure 1. Microphotographs illustrating the evolution of a mixture of red phosphorus and water (respectively dark and transparent areas in photo A) in a DAC at 0.6 GPa and 298 K before and after the photoinduced reaction: A) before irradiation, the ruby chip for pressure measurement is visible on the right side of the gasket edge; B) after laser irradiation (350 nm, 500 mW, 5 h); C) 24 h after irradiation, D) 48 h after irradiation. The lower case letters indicate the different regions of the sample mapped by Raman spectroscopy in Figure 2.

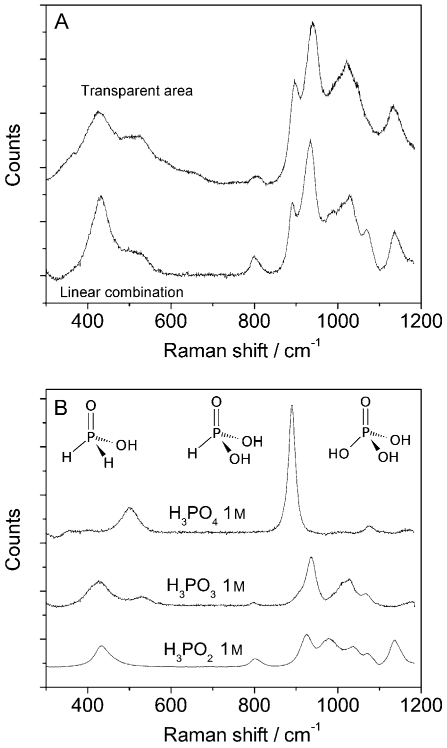

Figure 3. A) Comparison between the experimental Raman spectrum measured in a transparent zone at 0.6 GPa (upper trace) and the spectrum obtained by a linear combination of the spectra measured on 1 M solutions of H_3PO_2, H_3PO_3, and H_3PO_4 at ambient pressure, suitably weighted to reproduce the experimental profile (lower trace). B) Raman spectra of 1 M solutions of H_3PO_2, H_3PO_3, and H_3PO_4 in the 200–1200 cm^{-1} frequency range.

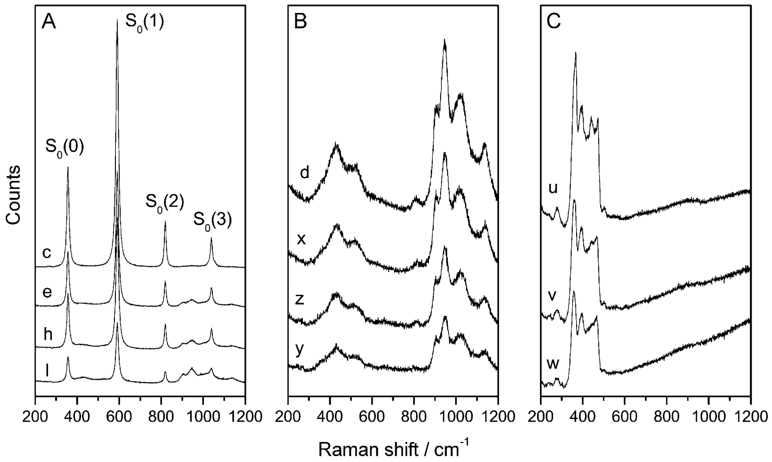

Figure 2. Raman spectra collected in the low frequency region (see Figure 1 for the labels): A) spectra measured in four different bubbles (traces c, e, h, and l); B) spectra measured in four different transparent areas (traces d, x, y, and z); C) spectra measured in three dark areas (traces u, v, and w).

may be attributed to phosphorus oxidation products generated by chemical reaction with H atoms and ·OH radicals formed during the photodissociation of water.

For comparative purposes, we measured the Raman spectra of 1 M aqueous solutions of the H_3PO_2, H_3PO_3, and H_3PO_4 acids (Figure 3B). Each acid presents characteristic spectral signatures identified in the Raman spectra measured in the transparent areas: at 802 and 1138 cm^{-1} for H_3PO_2, at 529 and 942 cm^{-1} for H_3PO_3, and at 892 cm^{-1} for H_3PO_4. The experimental spectrum measured in a transparent area could be reproduced by a linear combination of the spectra of the three phosphorus acids. The coefficients of the linear combination provided an estimation of the relative amounts of the three acids and the excellent agreement between the two spectra (Figure 3A), except for a small residual intensity owing to unreacted red phosphorus in the spectrum of the reacted mixture, allowed us to conclude that the Raman spectrum of the products in the 200–1200 cm^{-1} frequency region is entirely attributed to molecular hydrogen and the three acids, whose relative concentrations were estimated as 43.1 % of H_3PO_2, 45.3 % of H_3PO_3, and 11.6 % of H_3PO_4 (Supporting Information Section 1.2).

Also in the 2100–2800 cm^{-1} frequency range, characteristic Raman spectra could be measured both in the bubbles and in the transparent areas (Figure 4). A sharp peak at 2330 cm^{-1} (Figure 4B, traces c, l, and g), assigned to the P–H stretching mode of gaseous phosphine (PH_3)[25] (2314 cm^{-1} in the liquid at 300 K, $P < 3$ MPa[25,26]), characterizes the spectra

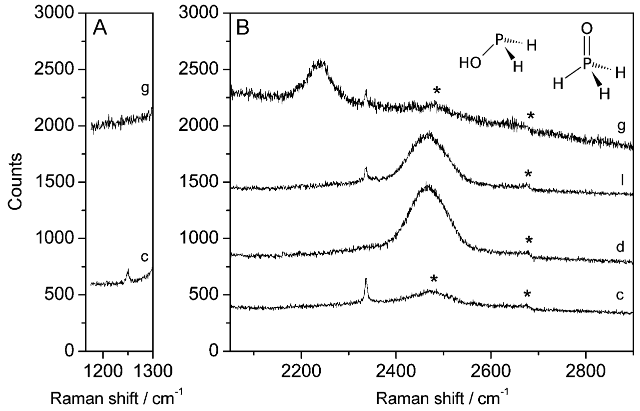

Figure 4. Raman spectra measured in the 1150–1300 cm^{-1} (A) and in the 2100–2800 cm^{-1} (B) frequency ranges on a transparent area (trace d) and on several bubbles (traces c, l, and g). See Figure 1 B for the label matching with the sample zones. The sharp band at 2330 cm^{-1} is due to the P–H stretching vibration of PH_3. The bands at 1250 and 2470 cm^{-1} have been assigned to the P=O and P–H stretching of H_3PO, whereas the band at 2236 cm^{-1} has been assigned to the P–H stretching of PH_2OH). The asterisks indicate Raman signals from the diamond anvils.

of the bubbles. The full Raman spectrum measured on a bubble is reported in Figure 5. The spectra measured in the transparent areas of the sample show a strong band centered at 2465 cm^{-1}, superimposed on the two-phonon band of diamond (Figure 4B, trace d). The spectrum obtained after the deconvolution of the diamond band could be reproduced by two bands centered at 2411 and 2456 cm^{-1} and assigned to the P–H stretching mode of H_3PO_2 and H_3PO_3, respectively. No other bands but those of diamond were detected in the dark areas. The assignment of all the Raman bands of the products is reported in the Supporting Information, Table S1.

We studied several samples under analogous reaction conditions and the results were consistent. On the contrary, for pressures below 0.1 GPa the reactivity was much slower and the products, as well as their relative amounts, were significantly different. Only H_2 was identified in the bubbles, without any evidence of PH_3, whereas in the liquid transparent areas the relative amounts of the three oxyacids were estimated as: H_3PO_2 28.3%, H_3PO_3 50.3%, and H_3PO_4 21.4%.

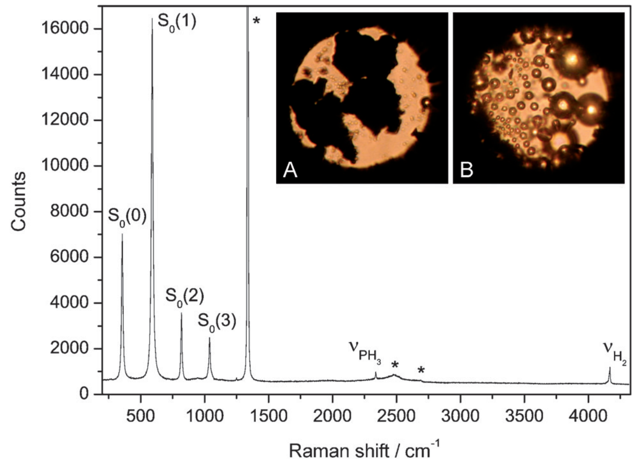

Figure 5. Images of a sample at 0.6 GPa and 298 K taken before (A) and after (B) irradiation (350 nm, 500 mW, 5 h) and Raman spectrum measured on a bubble from (B). The rotational bands of H_2 ($S_0(i)$ with $i=0,1,2,3$) and the vibrations of H_2 and PH_3 are the only observed bands. The asterisks indicate Raman signals from the diamond anvils of the DAC.

Under ambient conditions and in absence of irradiation, red phosphorus is practically insoluble and stable in water. However, a very slow spontaneous oxidation to H_3PO_4 is reported in Ref. [27], where the initial oxidation of P_{red} to H_3PO_2, identified as the rate-limiting step, and further oxidation to H_3PO_4, by way of H_3PO_3, was proposed. PH_3 is also reported to form as an intermediate in trace amounts. However, after 24 hours only 0.2–0.7% of the starting P_{red} reacted with water, increasing to about 3% after four months. The product composition was reported as about 40% of both H_3PO_4 and H_3PO_3 and 19% of H_3PO_2. Recently, irradiation of water in the presence of crystalline P_{red}, using visible wavelengths above the band gap of red phosphorus (1.7 eV), has been performed[28] to explore the possibility of using crystalline red phosphorus as a semiconducting photocatalyst for the synthesis of hydrogen from water. Red phosphorus remained stable even after several days irradiation, only acting as an electron-hole generator, as indicated by its extremely low consumption to form H_3PO_4 and PO_4^{3-} in ppm amounts.

Our findings indicate that in the absence of irradiation red phosphorus and water are stable up to 0.6 GPa for a few days and that only extremely low reactivity is induced by irradiation of the sample (UVML 350 nm, 500 mW, 5 h) for pressures lower than 0.1 GPa. In contrast, our experimental data unambiguously show a fast and quantitative reaction driven by the photodissociation of water for pressures higher than 0.1 GPa. At this pressure, the identified reaction products are H_2 in the bubbles and H_3PO_2 (28.3%), H_3PO_3 (50.3%), and H_3PO_4 (21.4%) in the liquid transparent areas. We propose the following gross chemical equations, shown in Equations (1–3):

$$2\,P_{red} + 4\,H_2O \rightarrow H_2 + 2\,H_3PO_2 \qquad (1)$$

$$2\,P_{red} + 6\,H_2O \rightarrow 3\,H_2 + 2\,H_3PO_3 \qquad (2)$$

$$2\,P_{red} + 8\,H_2O \rightarrow 5\,H_2 + 2\,H_3PO_4 \qquad (3)$$

At higher pressure, the chemical reaction between red phosphorus and water became extremely efficient, leading to the complete consumption of red phosphorus under the same irradiation conditions as at 0.1 GPa. Moreover, the increase of pressure modified the relative amount of the reaction products. At 0.6 GPa, not only H_2, but also PH_3, were detected in the bubbles, and the composition of the liquid areas changed with an increase in the amount of H_3PO_2 (43.1%) and a corresponding decrease in those of H_3PO_3 (45%) and H_3PO_4 (11.6%) with respect to lower pressure. The formation of PH_3 observed at 0.6 GPa can be accounted for by the gross chemical equations shown in Equations (4–6):

$$4\,P_{red} + 6\,H_2O \rightarrow PH_3 + 3\,H_3PO_2 \quad (4)$$

$$2\,P_{red} + 3\,H_2O \rightarrow PH_3 + H_3PO_3 \quad (5)$$

$$8\,P_{red} + 12\,H_2O \rightarrow 5\,PH_3 + 3\,H_3PO_4 \quad (6)$$

Notably, at each pressure investigated, H_3PO_4 (more stable than H_3PO_2 and H_3PO_3 according to ambient pressure thermodynamics) was always observed in the smallest amount, in contrast to what was reported in Ref. [27]. Moreover, the relative amount of H_3PO_4 decreased with the increase in pressure. The reactivity appears therefore to be ruled by kinetics, a quite common occurrence in high-pressure reactions.[7] These results show the role of pressure, not only in the activation of the reaction, but also in the availability of different reaction mechanisms, thus suggesting the possibility of tuning the composition of the reaction products using different pressures.

According to the proposed chemical equations, the number of water molecules per phosphorus atom is two for Equation (1), three for Equation (2) and four for Equation (3), which account for the formation of H_2 and are the processes that occur at low pressure; whereas the ratio is reduced to 1.5 for Equations (4–6), which account for the formation of PH_3 and are active only at higher pressures (above 0.6 GPa). With increasing density, the mean free path of the water molecules is indeed reduced, thus favoring reactions that involve a lower number of molecules.

Also, the changes in the relative composition of the three oxyacids in the liquid transparent areas can be explained considering the lower number of O atoms, and hence of water molecules, required to form H_3PO_2 with respect to H_3PO_3 and H_3PO_4. Only the water molecules in the proximity of the red phosphorus surface, where the generation of $^{\bullet}OH$ and H fragments occurs by the two-photon dissociation of an electronically excited water molecule, are expected to be involved in the reaction mechanism. Within this context, reactive processes involving a lower number of water molecules are statistically favored.

The bubbles appear to be entirely composed of H_2 and PH_3. However, in our experiments, H_2 is by far the main reaction product present in the bubbles at every investigated pressure and PH_3 is detected only above 0.4 GPa. This observation indicates that, whereas the H_2 forming reactions (1–3) are always open, the PH_3 forming ones (4–6) become active only with increasing pressure. Furthermore, the relative amounts of H_3PO_2 and H_3PO_3 suggest that, whereas at low pressure (H_3PO_2 28.3 %, H_3PO_3 50.3 %, H_3PO_4 21.4 %) the reaction (2) is favored with respect to (1) and (3), at higher pressure (H_3PO_2 43.1 %, H_3PO_3 45.3 %, H_3PO_3 11.6 %) the efficiency of reactions (4) and (1) increase, leading to the formation of H_3PO_2. Moreover, the simultaneous appearance of PH_3 and an increase in H_3PO_2 with pressure suggest that reaction (4) is the main PH_3 forming mechanism.

The formation of PH_3 is favored by pressure and likely originates from the reaction of red phosphorus with the excited species generated by the photodissociation of water, as recently shown by experimental data consistent with our results.[29] Other PH_3 forming mechanisms from the high-pressure photoinduced reactivity of H_3PO_2, H_3PO_3, or H_3PO_4 with water can be excluded, as indicated by the stability of the 1M phosphorus acid solutions under the same pressure and irradiation conditions (Supporting Information, Section 1.3).

H_2 can be synthesized from the excited hydrogen atoms generated by the two-photon dissociation of water under high density conditions.[20] The key role of excited hydrogen atoms in the activation of the reaction is also explained by the relative amount of the three oxyacids. The formation of PH_3 (containing three P–H bonds) at higher pressure and the increase with pressure in the relative amount of H_3PO_2 (containing two P–H bonds) with respect to H_3PO_3 (containing one P–H bond) suggest a higher efficiency for the reactivity of the photogenerated H atoms at higher density. H_3PO_4, which does not contain a P–H bond, is present in the smallest amount at every pressure and its amount decreases with increasing compression.

Finally, the three Raman bands observed in a few bubbles at 1250, 2236, and 2470 cm^{-1} (Figure 4) may be interpreted on the basis of metastable intermediates. In particular, the bands at 1250 (P=O stretching) and 2470 cm^{-1} (P–H stretching of $-PH_3$ groups) appear together, whereas the band at 2236 cm^{-1} (P–H stretching of $-PH_2$ group) appears as a single band in different bubbles. These bands can be tentatively explained with the presence of H_3PO (phosphine oxide) and PH_2OH (phosphinous acid) species, which may form as metastable intermediates along the stepwise hydrolytic disproportionation of phosphorus.[30] Despite the lack of Raman spectra of such species in the literature, the frequencies of these modes fairly agree with computed and IR values.[31] The formation of such species as reaction intermediates strengthens the proposed reaction mechanism based on the successive addition of H atoms and $^{\bullet}OH$ radicals.

In conclusion, we reported an extremely efficient reaction between red phosphorus and water. The reaction is activated by the two-photon dissociation of water at high pressure using near-UV photons and occurs with the complete consumption of red phosphorus to form H_2, PH_3, H_3PO_2, H_3PO_3, and H_3PO_4 in the complete absence of solvents, catalysts, and radical initiators. These results represent an advance in the fundamental knowledge of innovative phosphorus chemistry and can be of interest for clean energy and environmental issues, related to the synthesis of hydrogen and to the reduced toxicity of red versus white phosphorus. The synthesis of remarkable amounts of H_2 and of other P-oxyacids of commercial value from abundant and safe reactants are indeed relevant issues, considering the great demand for alternative synthetic methods and hydrogen-renewable sources. The possibility of controlling the product composition by tuning the pressure of the reaction is also relevant for its applications. In addition, the pressure and temperature conditions required for the reaction to occur, do not impose any technological limit on the possibility to scale the process up to large volume apparatuses.

Experimental Section

The high pressure experiments were performed using a membrane diamond anvil cell (DAC), equipped with IIa type bevel cut diamonds having 400 μm culet tips, whereas the low pressure experiments were performed using a sapphire anvil cell (SAC) equipped with 5 mm culet tips. The sample dimensions were typically those of a cylinder with 150 μm diameter and approximately 45 μm height. The cells were loaded with red phosphorus purchased from Aldrich (99.99 + %, powder) and deionized and bidistilled water. Reproducible and consistent results were obtained under the same experimental conditions during more than twelve experiments. Each experiment was performed on a freshly prepared sample and checked by FTIR and Raman spectroscopy after loading the cell. The samples were irradiated using the UVML emission of an Ar ion laser peaked at approximately 350 nm. The Raman spectra were measured using the 647.1 nm emission from a Kr ion laser source. The scattered light was dispersed by a single stage monochromator and analyzed by a nitrogen-cooled CCD detector with a resulting instrumental resolution of 1.5 cm^{-1}. The FTIR spectra were measured on a Bruker IFS-120 HR spectrometer with a resolution of 1 cm^{-1}. See the Supporting Information for further experimental details.

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