High pressure chemistry of red phosphorus by
photo-activated simple molecules

M Ceppatelli$^{1,2,*}$, S Fanetti$^2$, R Bini$^{1,2,3}$, M Caporali$^1$ and M Peruzzini$^1$
$^1$ ICCOM-CNR, Institute of Chemistry of OrganoMetallic Compounds, National Research Council of Italy, Via Madonna del Piano 10, I-50019 Sesto Fiorentino (FI), Italy
$^2$ LENS, European Laboratory for Non-Linear Spectroscopy, Via N. Carrara 1, I-50019 Sesto Fiorentino (FI), Italy
$^3$ Dipartimento di Chimica “Ugo Schiff”, Università degli Studi di Firenze, Via della Lastruccia 3, I-50019 Sesto Fiorentino (FI), Italy
E-mail: *ceppa@lens.unifi.it and matteo.ceppatelli@iccom.cnr.it

Abstract. High pressure (HP) is very effective in reducing intermolecular distances and
inducing unexpected chemical reactions. In addition the photo-activation of the reactants in
HP conditions can lead to very efficient and selective processes. The chemistry of phosphorus is
currently based on the white molecular form. The red polymeric allotrope, despite more stable
and much less toxic, has not attracted much attention so far. However, switching from the
white to the red form would benefit any industrial procedure, especially from an environmental
point of view. On the other side, water and ethanol are renewable, environmental friendly and
largely available molecules, usable as reactants and photo-activators in HP conditions. Here we
report a study on the HP photo-induced reactivity of red phosphorus with water and ethanol,
showing the possibility of very efficient and selective processes, leading to molecular hydrogen
and valuable phosphorus compounds. The reactions have been studied by means of FTIR and
Raman spectroscopy and pressure has been generated using membrane Diamond (DAC) and
Sapphire (SAC) anvil cells. HP reactivity has been activated by the two-photon absorption of
near-UV wavelengths and occurred in total absence of solvents, catalysts and radical initiators,
at room T and mild pressure conditions (0.2-1.5 GPa).

1. Introduction
Phosphorus is a very important chemical element [1]. It is widely used in the industry of
detergents, fertilizers and pesticides, it is an essential element in the life cycle on the Earth and
it is also important in materials chemistry. The two most common allotropic forms of the element
are white and red phosphorus, which have significantly different chemical and physical properties.
White phosphorus is an extremely unstable and reactive molecular solid, made of tetrahedral
units, very toxic, flammable and pyrophoric, thus difficult to handle. However, due to its
reactivity, white phosphorus can be easily functionalized and is at the base of the current industry
of phosphorus, which relies on drastic reaction conditions [2], like chlorination, and of laboratory
scale research, which uses transition metal catalysts and solvents [3]. In any case, the use of
white phosphorus raises several issues related to environmental safety, particularly for aquatic
organisms, and to economic cost of handling, development, regeneration and disposal. On the
contrary red phosphorus (P$_{red}$), which is obtained from white phosphorus, is an amorphous
polymeric material, much more stable, less toxic and easy to handle. Nevertheless, due to its stability, red phosphorus is more difficult to functionalize and has not been much used so far. For this reason, it would be very convenient to exploit the advantages of red phosphorus to obtain valuable phosphorus containing compounds by using simple, largely available, economic, renewable and sustainable green chemistry molecules in absence of solvents, metal catalysts and radical initiators.

In this study new chemical reactions activated by the combined effect of pressure and photo-excitation are investigated to achieve this goal. Whereas pressure is indeed a very efficient tool for increasing the density of matter and reducing the intermolecular distances, the optical pumping of the excited electronic states can generate extremely reactive species, able to trigger chemical reactivity. In these condition it is possible to have comparable time scales for the effective intermolecular collision and for the recombination of the photo-generated excited species, thus making the reaction probability statistically significant. This method has proven to be very efficient in reducing the reaction threshold pressure [4, 5], in selecting preferential reaction paths, as in the case of the polymerization of ethylene and butadiene [6, 7], and in activating chemical reactions in otherwise stable systems, like in the case of clathrate hydrates of simple molecular systems [8, 9], where even the the extremely stable nitrogen molecules has been forced to react [10]. Within this framework, where the reacting molecules behave both as reactant and photo-activator, two other requirements must be fulfilled. The first one, is that the reacting molecules remain fluid up to the reaction pressure, in order to ensure a sufficient miscibility in the case of heterogeneous mixtures, as is the case with red phosphorus, and the second one is that they possess dissociative excited electronic states accessible by two-photon absorption of near-UV photons. Besides being a necessary conditions imposed by the diamond absorption edge, the use of two-photon excitation mechanisms using 350 nm wavelengths offers the advantage of avoiding typical UV vacuum conditions. According to these requirements, water [11, 12] and ethanol [13, 14], two molecular systems with different chemical properties, have been selected. In this study we compare the results of their high pressure photo-induced reactivity with red phosphorus.

2. Experimental

Static high pressure was generated by means of membrane DAC and SAC anvil cells. DACs were equipped with IIa type standard cut diamond anvils with 400 μm diameter culets whereas SACs, used for experiments at pressures lower than 0.1 GPa, were equipped with sapphire anvils having 5 mm culets. The sample was sideways contained by stainless steel gasket indented to a 50 μm thickness and a sample area of 150 μm diameter obtained by spark erosion drilling of the indented area. Every mixture sample was freshly prepared by depositing a few grains of red phosphorus (Sigma-Aldrich, purity > 99.99%, powder) inside the gasket and by filling the remaining volume with water (deionized and bidistilled) or ethanol (Fluka, purity >99.8%). A small ruby chip was inserted into the sample chamber for the pressure measurement through the ruby fluorescence method. Reactivity was induced by the UV multi line (UVML) emission of an Ar ion laser (Coherent Innova Sabre) centered at 350 nm. The FTIR spectra were acquired on a Bruker IFS-120 HR spectrometer with a resolution of 1 cm⁻¹. The Raman spectra were acquired using the 647.1 nm line of a Kr ion laser source (Coherent Innova). The scattered light was dispersed by a single stage monochromator (900 grooves/mm) and detected by a nitrogen-cooled CCD with a resulting instrumental resolution of 1.5 cm⁻¹.

3. Results and discussion

After the loading the purity of every sample was checked by FTIR and Raman spectroscopy. Both mixtures of red phosphorus with water and with ethanol were observed to be stable on compression up to the solidification pressure of water (1.0 GPa, 300 K) and ethanol (1.7 GPa, 300
3.1. Red phosphorus and water

At ambient pressure $P_{\text{red}}$ is stable in water and no reactivity was observed in pure $P_{\text{red}}$ and pure $H_2O$ in the same pressure and irradiation conditions, whereas, in the case of the mixture, the reactivity was observed to stop once water was completely consumed, remarking its two-fold role of photo-activator and reactant. Three areas, defined as bubbles, transparent liquid areas and solid dark areas, can be distinguished in the sample after the occurrence of the reaction. The Raman mapping of the sample indicates that these areas have characteristic spectral patterns (figure 1). Whereas the Raman spectrum measured in the dark areas corresponds to unreacted red phosphorus, the Raman spectra measured on the bubbles and on the transparent areas corresponds to reaction products. In particular the bubbles are composed by $H_2$ (rotational bands $S_0(i)$, with $i = 0, 1, 2, 3$ in figure 1) and, for pressure higher than 0.4 GPa, also by $PH_3$, whereas the transparent areas contain a mixture of three phosphorus oxyacids ($H_3PO_2$, $H_3PO_3$ and $H_3PO_4$), which have characteristic Raman signatures and whose relative amounts change with pressure. The composition of the transparent areas at different pressures can be estimated by fitting the experimental Raman spectrum with a linear combination of 1 M solutions of the three oxyacids. Within this procedure, the coefficients of the linear combination provide an estimation for the relative amounts of the three acids, which are reported in table 1 for two different pressures. The fitting results show that, whereas the amount of $H_3PO_2$ increases with pressure, that of $H_3PO_3$ and more significantly that of $H_3PO_4$ decrease with pressure.
indicating that pressure, besides enhancing the efficiency of the transformation and activating new reaction channels, as evidenced by the appearance of PH$_3$ above 0.4 GPa, also modifies the relative amounts of the three acids. Furthermore, the observation that H$_3$PO$_4$, which is the most thermodynamically stable of the three acids at least at ambient conditions, is always present in the smallest amount and decreases with pressure suggests that the reaction takes place under a kinetic rather than a thermodynamic regime, as typically occurring in high pressure phenomena. These considerations can be rationalized according to the chemical equations reported in table 2. Whereas at low pressure only H$_2$ is present in the bubbles and the ratio of water molecules per phosphorus atom (H$_2$O/P) is 2 for reaction (1), 3 for reaction (2) and 4 for reaction (3), for pressure above 0.4 GPa also PH$_3$ appears in the bubbles and the H$_2$O/P ratio reduces to 1.5 for all the reactions, indicating that pressure favors the opening of reaction channels with lower H$_2$O/P ratio leading to the formation of PH$_3$. This is also consistent with the increase in the amount of H$_3$PO$_2$ with pressure, because, among the three oxyacids, H$_3$PO$_2$ is the one containing the smallest number of O atoms. The simultaneous appearance of PH$_3$ and increase in the amount of H$_3$PO$_2$ point to reaction channel (4) as the main reaction channel activated by pressure. A key role in the reaction mechanism played by hydrogen atoms is evident not only from the formation of H$_2$, but also in the detection of PH$_3$, which can form from the direct reaction of H atoms with red phosphorus, and from the relative amounts of the phosphorus oxyacids, as indicated by the increase in the amount of H$_3$PO$_2$, which has indeed the highest number of P-H bonds. Finally this mechanism is also consistent with the observation of a few Raman bands, observed in several areas of the sample and assigned to metastable reaction intermediates identified as phosphine oxide (H$_3$PO) and phosphinous acid (H$_2$POH) [15].

3.2. Red phosphorus and ethanol
Ethanol can also be photo-dissociated at high pressure in the same irradiation conditions as water. Nevertheless, in contrast to water, where the recombination of H atoms and hydroxyl radicals takes place without the formation of no reaction products other than water itself, in the case of ethanol a complex reactivity occurs, with the formation of several reaction products, as a result of two dissociation channels involving respectively the O-H and the C-O bonds [17]. In the mixture of ethanol and red phosphorus, the observation of PH$_3$ and triethylphosphate among the reaction products, clearly indicates the participation of phosphorus to the reactive process. Moreover the role of phosphorus is evident also from the comparison of the ethanol consumption as a function of the irradiation time in pure ethanol and in the mixture with red phosphorus, which indicates a much higher transformation rate of ethanol in presence of P$_{red}$ at every investigated pressure (0.2, 0.6 and 1.5 GPa). At 0.5 GPa, whereas in the case of the mixture with P$_{red}$ ethanol is completely consumed after about 11 hours of irradiation, in pure ethanol after 30 hours of irradiation about 22.5% of ethanol is still present. Moreover, for all the studied pressures and within the investigated irradiation time scale, ethanol was always completely consumed only in presence of P$_{red}$.

| Table 1. Relative amounts the three oxyacids of phosphorus at 0.1 and 0.6 GPa obtained by Raman spectroscopy. |
|--------------------------------------------------|
| H$_2$PO$_y$ | 0.1 GPa | 0.6 GPa |
| H$_3$PO$_2$ | 28.3%  | 43.1%   |
| H$_3$PO$_3$ | 50.3%  | 45.3%   |
| H$_3$PO$_4$ | 21.4%  | 11.6%   |
Furthermore several considerations support the identification of the O-H dissociation as the main reaction channel and remark the minor importance of the C-O dissociation channel: 1) the absence of the typical reaction products observed in the reactivity of pure ethanol (2-butanol, 2,3-butanediol, and 1,1-diethoxyethane), 2) the absence of the three oxyacids of phosphorus observed in the case of water, 3) the absence of P-C bonds, 4) the detection of diethyl ether, which was expected but never detected in the reactivity of pure ethanol, 5) the formation of molecular hydrogen, never observed in the reactivity of pure ethanol at 0.5 GPa. The presence of the C-O dissociation channel is however suggested by the observation of ethane and ethylene among the reaction products, likely due respectively to the hydrogenation and dehydrogenation of ethyl radicals. These considerations are also consistent with the observed variation of the transformation rate with pressure, increasing from 0.2 to 0.6 GPa and decreasing from 0.6 to 1.5 GPa. An analogous behavior has been reported also in pure ethanol and explained by a pressure induced modification of the potential surface of the first excited electronic state along the O-H coordinate, which is responsible for a reduction of the dissociative character and a reactivity depletion [18, 19]. At all the investigated pressure (0.2, 0.6 and 1.5 GPa at room T) the reaction mechanism could be roughly described as a two-step process, where the first step is the dissociation of ethanol to form H\(_2\), PH\(_3\), triethylphosphate, diethylether, ethane, methane and the second one the decomposition of some of these products to form CH\(_4\), C\(_2\)H\(_6\), CO\(_2\) and several methyl containing species.

4. Conclusions
High pressure photo-dissociation of water and ethanol was successfully used to induce new chemical reactions leading to the quantitative transformation of red phosphorus into several reaction products and molecular hydrogen. The identified reaction mechanism involves the dissociation along the O-H bond. Whereas this is quite obvious in the case of water, it is not as straightforward in the case of ethanol, where at least two competing dissociation channels can be accessed in the investigated reaction conditions. However, the identification of the reaction products and the variation of the transformation rate with pressure, indicate the O-H splitting as the main reaction channel responsible for the reactivity. Once the excited species are generated red phosphorus is extremely efficient in capturing hydroxyl and ethoxyl radicals, and in reacting with H atoms. Pressure can be used to tune the relative amount of the reaction products in the case of water and to maximize the efficiency of the transformation in the case of ethanol. Considering that these processes occur in total absence of solvents, catalyst and radical initiators, at room temperature and pressure conditions accessible to the current

| P \(<\) 0.4 GPa (only H\(_2\) in the bubbles) | H\(_2\)O/P \(\) reaction |
|---------------|----------------|
| 2P\(_{\text{red}}\) + 4H\(_2\)O \(\rightarrow\) H\(_2\) + 2H\(_3\)PO\(_2\) | 2 (1) |
| 2P\(_{\text{red}}\) + 6H\(_2\)O \(\rightarrow\) 3H\(_2\) + 2H\(_3\)PO\(_3\) | 3 (2) |
| 2P\(_{\text{red}}\) + 8H\(_2\)O \(\rightarrow\) 5H\(_2\) + 2H\(_3\)PO\(_4\) | 4 (3) |

| P \(>\) 0.4 GPa (H\(_2\) and PH\(_3\) in the bubbles) | H\(_2\)O/P \(\) reaction |
|---------------|----------------|
| 4P\(_{\text{red}}\) + 6H\(_2\)O \(\rightarrow\) PH\(_3\) + 3H\(_3\)PO\(_2\) | 1.5 (4) |
| 2P\(_{\text{red}}\) + 3H\(_2\)O \(\rightarrow\) PH\(_3\) + H\(_3\)PO\(_3\) | 1.5 (5) |
| 8P\(_{\text{red}}\) + 12H\(_2\)O \(\rightarrow\) 5PH\(_3\) + 3H\(_3\)PO\(_4\) | 1.5 (6) |
industrial technology, using only near-UV photons to trigger the reactivity, their large-volume scaling could be appealing for green chemistry processes combining energetic interest related to the synthesis of hydrogen and environmental issues related to the chemistry of red phosphorus.

Acknowledgments
This work was supported by the European Union under Contract 284-464, by the Italian Ministero dell’Istruzione, dell’Università e della Ricerca (MIUR), by Firenze Hydrolab2 through a grant by Ente Cassa di Risparmio di Firenze and by Deep Carbon Observatory (Extreme Physics and Chemistry).

References
[1] Corbridge D E C 2000 Phosphorus 2000. Chemistry, biochemistry & technology (Amsterdam: Elsevier)
[2] Maier L 1971 Top. Curr. Chem. 19 1
[3] Peruzzini M, Gonsalvi L and Romerosa A 2005 Chem. Soc. Rev. 34 1038
[4] Bini R 2004 Acc. Chem. Res. 37 95
[5] Chelazzi D, Ceppatelli M, Santoro M, Bini R and Schettino V 2005 J. Phys. Chem. B 109 21658
[6] Citroni M, Ceppatelli M, Bini R and Schettino V 2002 Science 295, 2058
[7] Chelazzi D, Ceppatelli M, Santoro M, Bini R and Schettino V 2004 Nat. Mater. 3 470
[8] Ceppatelli M, Bini R and Schettino V 2009 J. Phys. Chem. B 113 14640
[9] Ceppatelli M, Bini R and Schettino V 2011 Phys. Chem. Chem. Phys. 13 1264
[10] Ceppatelli M, Bini R and Schettino V 2009 Proc. Natl. Acad. Sci. USA 106 11454
[11] Thomsen C L, Madsen D, Keiding S R, Thogersen J and Christiansen O 1999 J. Chem. Phys. 110 3453
[12] Andresen P and Schinke R 1987 in Molecular Photodissociation Dynamics, ed Ashfold M N and Baggott J E, (London: Royal Society of Chemistry) chapter 3
[13] Satyapal S, Park J, Bersohn R and Katz B 1989 J. Chem. Phys. 91 6873
[14] Xu K S, Amaral G and Zhang J S 1999 J. Chem. Phys. 111 6271.
[15] Ceppatelli M, Bini R, Caporali M and Peruzzini M 2013 Angew. Chem., Int. Ed. 52 2313
[16] Ceppatelli M, Fanetti S and Bini R 2013 J. Phys. Chem. C 117 13129
[17] Ceppatelli M, Fanetti S, Citroni M and Bini R 2010 J. Phys. Chem. B 114 15437
[18] Fanetti S, Ceppatelli M, Citroni M and Bini R 2011 J. Phys. Chem. B 115 15236
[19] Fanetti S, Ceppatelli M, Citroni M and Bini R 2012 J. Phys. Chem. C 116 2108