

On the origin of the Murchison meteorite phosphonates. Implications for pre-biotic chemistry†

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Ab initio calculations, combined with experimental studies on the anaerobic hydrolysis of phosphalkynes under thermal and photochemical conditions suggest a potential, exogenous source of reduced oxidation state phosphorus for the early Earth.

Whilst it is clear that derivatives of orthophosphoric acid ($\text{H}_x\text{PO}_4^{3-x}$; $x = 1-3$) are the key phosphorus moieties in contemporary biochemistry¹ there is growing opinion that Nature may have exploited lower oxidation state phosphorus species during the early development of life on Earth.² Gulick pointed out as long ago as 1955, that both H-phosphonic (P(III); H_3PO_3) and H-phosphinic (P(I); H_3PO_2) acids could have been accessible on the early Earth if the redox potential of that environment was appropriately reducing.³ More recently Schink and Friedrich have identified sulfate-reducing bacteria which exploit the reverse process, oxidation of H-phosphonic to orthophosphoric acid, as a key step in microbial energy metabolism; $4\text{HPO}_3^{2-} + \text{SO}_4^{2-} + \text{H}^+ = 4\text{HPO}_4^{2-} + \text{HS}^-$ for which $\Delta G^\circ = -87 \text{ kcal mol}^{-1}$, based on sulfate, or $-22 \text{ kcal mol}^{-1}$ based on phosphate.⁴ These authors point out that this type of microbial energy metabolism may have operated on the anoxic early Earth should a source of reduced oxidation state phosphorus have been readily available. Herein lies the problem. Within the oxygen-rich environment of the Earth today, essentially all phosphorus sources are based on the fully oxidised orthophosphate. However, the pre-biotic Earth was almost certainly oxygen-poor and probably reducing in potential,⁵ an environment in which lower oxidation state phosphorus species such as phosphonic (H_3PO_3) and phosphinic (H_3PO_2) acids and their derivatives would certainly have been more stable. The question then is how could reduced oxidation state phosphorus have been produced on and/or delivered to the early Earth?

The redox couples $\text{H}_3\text{PO}_4/\text{H}_3\text{PO}_3$ (-276 mV) and $\text{HPO}_4^{2-}/\text{HPO}_3^{2-}$ (-690 mV) suggest that *ca.* 13 and 32 kcal mol^{-1} are required to reduce orthophosphate to H-phosphonate depending upon pH.⁶ Whilst such energy input is accessible from electrical discharges associated with early Earth volcanic activity⁷ interest has turned towards an exogenous delivery mechanism of reduced

oxidation state phosphorus species as components of extraterrestrial ice-grains, meteorites or cometary fragments.⁸ A key observation in support of this hypothesis was the extraction of methyl and ethylphosphonic acids at nmol g^{-1} concentrations (Fig. 1d; R = Me, Et) in addition to orthophosphate (at $\mu\text{mol g}^{-1}$ levels) from the Murchison meteorite.⁹ As found for other molecules of interstellar origin, these phosphonic acids were observed to have enhanced isotopic D/H ratios (δD) of *ca.* 219 suggesting that they are unlikely to be terrestrial contaminants.¹⁰ We report here the first experimental evidence that hydrolytic modification of interstellar phosphorus molecules may have acted as a source of Murchison-type phosphonates.

Very few phosphorus molecules have been identified within the interstellar medium. The principal ones include PH_3 ,¹¹ metal rich phosphides such as schreibersite $(\text{Fe,Ni})_3\text{P}$,¹² $\text{P}\equiv\text{N}$ ¹³ and $[\text{P}\equiv\text{C}]^-$.¹⁴ We are currently exploring the anoxic hydrolytic modification of

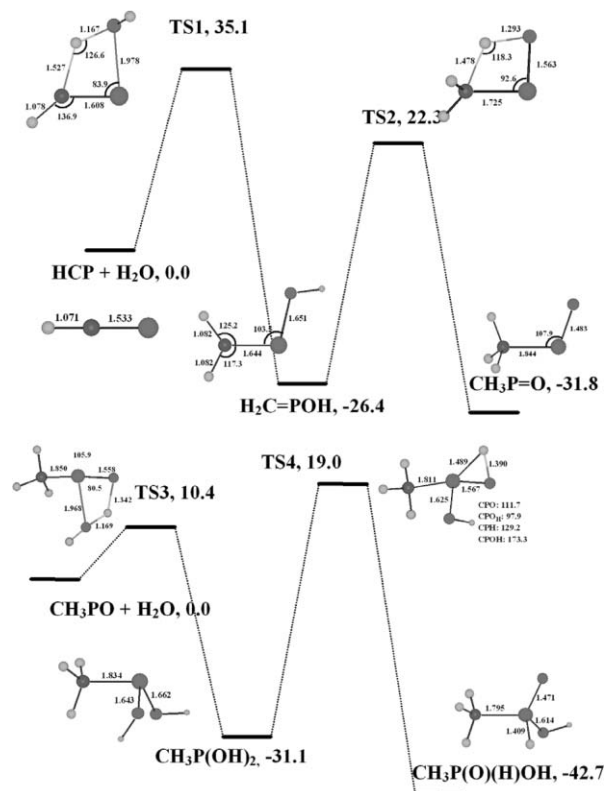


Fig. 1 *Ab initio* G3X level studies on the reaction of $\text{P}\equiv\text{CH}$ with H_2O showing both intermediates (lower species) and transition states (upper species; indicated TS1–4). Energy values in kcal mol^{-1} .

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each of these species and here report our preliminary work on the molecular radical $[P=C]^\cdot$. This radical has been detected in cool carbon-rich interstellar gas clouds,¹⁴ such as that surrounding the ageing star IRC+10216, and is presumed to have been formed from interactions between interstellar P^+ and CH_4 .¹⁵ It is a member of the class of unsaturated molecules well-known in interstellar chemistry¹⁶ and is proposed to be a daughter fragment of molecular $P=CH$ which has been hypothesised to be absent from the gas phase due to condensation on interstellar ice grain surfaces.¹⁴ Moreover, as this radical is the only such interstellar phosphorus species containing the P–C bond, we were especially interested to explore whether this molecule, or more specifically the parent $P=CH$, could act as a precursor to the Murchison phosphonic acids.

Our *ab initio* calculations at the G3X level[‡] reveal that hydrolytic modification of $P=CH$ to methylphosphonic acid *via* the equation $P=CH + 3H_2O = CH_3P(O)(OH)_2 + H_2$ is thermodynamically favourable by *ca.* 96 kcal mol⁻¹. A more detailed theoretical analysis of the $P=CH/H_2O$ system reveals that sequential nucleophilic attack of water takes place preferentially at phosphorus *via* several intermediates. Thermodynamic analysis suggests that H_2O attack at phosphorus should lead to either the *P*-hydroxyphosphaalkene, $CH_2=POH$ or the more stable (by 5.4 kcal mol⁻¹) methylphosphoroso tautomer $CH_3P=O$ (Fig. 1). Subsequent addition of a second equivalent of H_2O to $CH_3P=O$ affords methyl-dihydroxyphosphine $CH_3P(OH)_2$ which would be expected to re-arrange to the more stable (by 11.6 kcal mol⁻¹) tautomer methyl-H-phosphinic acid $CH_3P(O)H(OH)$. However, whilst phosphoalkyne hydrolysis is undoubtedly favourable thermodynamically, significant energy barriers exist along the reaction coordinate. Four of the key transition states have been identified and modelled (Fig. 1). The energy barrier for addition of H_2O to $P=CH$ is 35.1 kcal mol⁻¹, the gas-phase transition state TS1 possessing significant simultaneous H–C and O–P bond forming interactions as well as both deforming the $\angle P-C-H$ angle from 180° to 136.8° yet elongating the C–P distance by only 0.075 Å (*ca.* 5%). Clearly an energy barrier of this magnitude would preclude chemical reactions within the interstellar medium unless: (a) alternative gas-phase reagents are involved (*e.g.*, reaction between H_2O^+ and $P=CH$ to afford $[CH_2=POH]^+$ has zero energy barrier), (b) alternative energy sources (*e.g.*; photochemical, cosmic ray *etc.*) and/or (c) some form of surface catalysis on interstellar ice grains were available. We believe that each of these possibilities may be feasible and our ongoing theoretical studies are examining these systems.§

Building upon the above theoretical studies, we reasoned it should be possible to simulate hydrolytic modification of $[P=C]^\cdot$ by exploring a model compound of parent $P=CH$, since the latter is the simplest member of the well-known phosphoalkyne family of molecules $P=CR$, R = organic fragment.¹⁷ We have compared the hydrolytic behaviour of one such model compound, (2,2-dimethylpropylidene)phosphine¹⁸ $P=CCMe_3$ under both thermal and photochemical conditions. Thus, ³¹P{¹H}-NMR analysis of an anaerobic two-phase system comprising $P=CCMe_3$ and D_2O (1 : 1000 mole ratio) reveals the gradual evolution of a single major new species after several days (*ca.* 70% conversion after 6 days) exhibiting a strong 1 : 1 : 1 triplet coupling pattern with δ_P 36.2 ppm and a ¹J_{PD} of 83 Hz. In addition, ¹³C{¹H}-NMR analysis reveals the expected doublet resonances for CMe_3

quaternary and methyl carbons at δ_C 29.12 (²J_{PC} 7.5 Hz) and 30.08 ppm (³J_{PC} 2.7 Hz) respectively. Of most significance however, is the presence of an apparent doublet of quintets of triplets (dq²) coupling pattern at δ_C 41.61 ppm which is consistent with, and simulated by,¶ the suite of coupling constants ¹J_{PC} 89.0 Hz; ¹J_{CD} 19.1 Hz and ²J_{CD} 2.3 Hz, expected for a $[DPCD_2]$ methylene moiety (Fig. 2). These collected data are clearly supportive of this species being ¹BuCD₂P(O)D(OD), resulting from the addition of two equivalents of D_2O to $P=CCMe_3$. In addition to ¹BuCD₂P(O)D(OD), as the major product we observe three new species appearing within the $P=CCMe_3/D_2O$ system over time (<10% after 11 days) displaying respectively a 1 : 1 : 1 triplet ³¹P-NMR resonance at δ_P 36.0 ppm (¹J_{PD} 84 Hz), a doublet resonance at δ_P 36.6 ppm (¹J_{PH} 545 Hz) and a singlet resonance at δ_P 30.9 ppm which we assign as ¹BuCD₂P(O)D(OH), ¹BuCD₂P(O)H(OH) and ¹BuCD₂P(O)(OX)₂ (X = H or D) respectively. Negative ion mass spectrometry|| located both [¹BuCD₂P(O)D(O)]⁻ and [¹BuCD₂P(O)H(O)]⁻ at 138.08 (theor: 138.08) and 137.07 respectively whilst also providing further evidence for the presence of the phosphonate [¹BuCD₂P(O)(OH)(O)]⁻ at 153.07 (theor: 153.06). The latter product, neopentylphosphonic acid ¹BuCD₂P(O)(OX)₂ is the direct model for the Murchison phosphonates and we presumed that it formed by either the scavenging of di-oxygen by neopentylphosphonic acid within the sealed tube or by photo-induced reaction with di-oxygen or water. Indeed, we have independently prepared and characterised neopentylphosphonic acid and have confirmed (by ³¹P-NMR) that photochemical irradiation of an oxygen-free aqueous solution of ¹BuCH₂P(O)H(OH) (3 mM; 298 K; 4 h) with a low pressure mercury vapour arc tube (emissions at 254 nm; *ca.* 500 mW and 185 nm; *ca.* 40 mW) affords cleanly a 63% conversion to a mixture composed solely of neopentylphosphonic acid ¹BuCH₂P(O)(OH)₂ (δ 29.0, t, ²J_{PH} 17.5 Hz) and H-phosphonic acid in a 1 : 0.7 molar ratio. Subsequent introduction of air and re-irradiation for 4 h affords complete conversion of the system to neopentylphosphonic acid and phosphoric acid in a 1 : 1.2 molar ratio respectively.

Thus, we believe our model studies suggest that condensed interstellar $P=CH$ is capable of undergoing thermally-induced, anaerobic hydrolysis to alkyl H-phosphinic acids and that phosphonic acids may result from a subsequent photo-induced

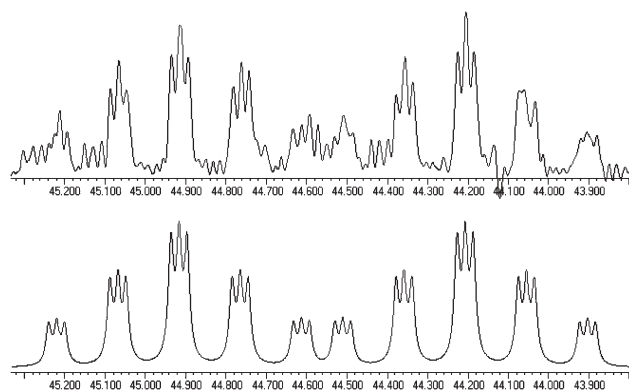


Fig. 2 Partial ¹³C{¹H}-NMR spectrum of ¹BuCD₂P(O)D(OD) emphasising coupling to the $[CD_2P(O)D]$ carbon. Experimental (top; 125.7 MHz; 300 K) and simulated (bottom; gNMR version 4.1.2; Adept Scientific, UK) using ¹J_{PC} 89.0 Hz; ¹J_{CD} 19.1 Hz and ²J_{CD} 2.3 Hz.

redox process in aqueous solution. This latter process is effective under anaerobic conditions but leads to more efficient conversions to fully oxidised phosphorus in the presence of di-oxygen. Moreover, our experiments support the conclusion that an interstellar phosphalkyne hydrolysis mechanism is capable of producing D-enrichment in the resulting phosphonic acids *via* formation of kinetically non-labile [C–D] linkages. Deuterium incorporated within the hydroxyl or [P–D] groups of either phosphonic or phosphinic acids is envisaged to undergo rapid and complete H/D exchange with terrestrial water sources following Earth-impact of the parent meteorite body thus leading to attenuation of deuterium enrichment at these sites.

This thermal behaviour contrasts significantly however with the behaviour of the P=CCMe₃/H₂O system under photochemical conditions. Thus, irradiation with a low pressure mercury vapour arc tube of an anoxic mixture of P=CCMe₃ and oxygen-free water (1 : 25 molar ratio) at a combined vapour pressure of 1 mTorr at 298 K, in a purpose-built photochemical reactor, for a period of one hour affords a white, water-soluble component and a yellow organic-miscible component. The water-soluble material comprises H-phosphonic HP(O)(OH)₂ and orthophosphoric acids P(O)(OH)₃ as the sole phosphorus-containing products in a 15 : 1 molar ratio respectively by ³¹P-NMR spectroscopy. We envisage that the orthophosphoric acid is produced *via* photolysis of H-phosphonic acid in water, a process we have observed in parallel experiments on the hydrolytic processing of metal phosphides.¹⁹ The organic material contains no phosphorus and returns a C : H ratio of 5.93 : 1 consistent with a C₄H₈ fragment ratio (theor: 6 : 1). However, at least 17% w/w consists of a black, non-volatile ash upon combustion, whose composition is still under investigation. Electrospray mass spectrometric analysis (H₂O : CH₃CN) of this organic material reveals a broad range of fragments from *m/z* 165–835, with a base peak at *m/z* 399 suggestive of oligomers. We are currently exploring this photochemical transformation, especially the organic component, in more detail.

Our four key conclusions may be summarised as follows. (1) Formation of the Murchison phosphonic acids, and potentially phosphonates on interstellar icy bodies in general, could have occurred *via* anaerobic hydrolytic modification of condensed molecular species derived from [P=C]. (2) These hydrolyses also allow us to explain the enhanced D : H isotope ratios of interstellar phosphonates. (3) Divergent behaviour in the P=CR/H₂O system may result from thermal and photochemical stimulation, dependent upon the nature of the group R. (4) The observation of H-phosphonic acid as the chief product from the P=CR/H₂O system under photolytic conditions is most intriguing given the earlier hypotheses of Schwartz *et al.*,² Gulick³ and Friedrich and Schink⁴ along with the observation that this species is also the chief product from the anaerobic hydrolysis of meteoritic phosphide minerals.^{19,20} It is conceivable that H-phosphonic acid may be a key hydrolytic by-product of more than one interstellar phosphorus molecule and this is something we are actively investigating.²¹

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Notes and references

‡ All calculations were carried out using the Gaussian 03 suite of programs.²² Geometry optimisations and vibrational frequency calculations were performed at B3LYP/6-311+G(3 df, 2 p) level. Scale factor of 0.9854 was used for zero-point energy corrections. The accurate energetic parameters were evaluated using G3X model chemistry, which approximates the electron correlation level of QCISD(T,Full)/G3XLarge.²³

§ We are focusing especially upon the possibility of surface transition metal catalysis since preliminary DFT and coupled cluster calculations suggest that P=CH binds to the known interstellar ions Fe⁺ and Mg⁺ with binding energies of the order of 24 kcal mol⁻¹. In both cases, strong Fe–P and Fe–C binding is involved such that the ∠P–C–M angles lie within the 85–90° range. This bonding obviously leads to structural distortions which should activate the phosphalkyne towards hydrolytic modification and may suggest a reason for the non-detection of un-modified P=CH in IRC+10216. More detailed studies on metal-binding and possible activation of P=CH towards hydrolysis are in progress.

¶ The [CD₂P(O)D] portion of the spectrum has been simulated using gNMR version 4.1.2 (Adept Scientific, UK), see ESI for details.

|| Samples were analysed by injection of 0.1 ml of a *ca.* mM aqueous solution into a Bruker microTOF instrument operating under electrospray conditions with a 1 : 1 v/v acetonitrile : water mobile phase at 0.6 ml min⁻¹. The instrument was calibrated externally using sodium formate.

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