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Synthesis of the hitherto elusive formylphosphine (HCOPH₂) in the interstellar medium – a molecule with an exotic phosphorus peptide bond†

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The formylphosphine (HCOPH₂) molecule was detected in the gas phase via isomer selective photoionization reflectron time-of-flight mass spectrometry (PI-ReTOF-MS). Synthesized in carbon monoxide (CO)–phosphine ices (PH₃) exposed to ionizing radiation, the formation mechanism involves an initial phosphorus–hydrogen bond rupture in phosphine yielding the phosphino radical (PH₂) along with atomic hydrogen, addition of the suprathreshold hydrogen atom to carbon monoxide leading to the formyl radical (HCO), and recombination of both radicals to formylphosphine (HCOPH₂). This molecule represents the isovalent counterpart of the ubiquitous interstellar formamide (HCONH₂). This study provides a fundamental framework to explore the synthesis and stability of the simplest isovalent counterpart of interstellar formamide (HCONH₂) and suggests that formylphosphine (HCOPH₂) should be detectable in the interstellar medium eventually providing a missing link between phosphorus-bearing complex organic molecules detected in the interstellar medium and on comet 67P/Churyumov–Gerasimenko.

The peptide bond (–CO–NH–) represents a vital functional group in biochemistry linking two amino acid monomers and signifies an essential building block of peptides and protein chains.^{1,2} Molecules containing a peptide bond are of considerable interest in the astrochemistry and astrobiology communities as key tracers to probe the formation of biorelevant, complex organic molecules on the molecular level with formamide (HCONH₂)³ being detected toward Sagittarius B2 in the interstellar medium (ISM) and also in meteorites such as Murchison.⁴ Dedicated laboratory simulation studies mimicking the processing of interstellar ice analog samples containing, for instance, ammonia (NH₃), carbon dioxide (CO₂), and carbon

monoxide (CO) verified peptide bond formation upon exposure of these ices to ionizing radiation.^{1,5,6} Surprisingly, the phosphorus peptide moiety (–CO–PH–) as an isovalent counterpart to the peptide bond has received only minor attention although phosphorus containing molecules are ubiquitous in the ISM.^{7–10} Of relevance to the phosphorus peptide linkage, simple molecules carrying a carbon–phosphorus bond^{8,10,11} along with phosphine (PH₃) have been detected in the circumstellar envelope of the carbon rich Asymptotic Giant Branch (AGB) star IRC +10216.^{7,10} Very recently, singly ionized phosphorus atoms – likely formed from the phosphine (PH₃) parent molecule – were also assigned in the coma of the comet 67P/Churyumov–Gerasimenko.⁹

A close inspection of the inventory of the nearly 200 molecules detected so far in interstellar and circumstellar environments¹² reveals that for nearly each phosphorus containing molecule observed in the interstellar medium, an isovalent nitrogen-containing counterpart exists. Therefore, given the presence of phosphine (PH₃) along with the observation of interstellar formamide (HCONH₂) and the finding that an interaction of ionizing radiation with ices of carbon monoxide (CO)–ammonia (NH₃) leads to formamide (HCONH₂),^{13,14} formylphosphine (HCOPH₂, **III** Fig. 1) – the simplest molecule carrying the phosphorus peptide moiety – should be synthesized in interstellar ices containing carbon monoxide (CO) and phosphine (PH₃). However, to our best knowledge, HCOPH₂ (**III**) has neither been identified in ‘earthly’ nor extraterrestrial environments. Computational studies on the CH₃PO surface suggest that HCOPH₂ (**III**) along with methyloxophosphine (CH₃PO, **IV** Fig. 1), methylene phosphinous acid (HOPCH₂, **II** and **II'**) represent energy minima with CH₃PO (**IV**) embodying the global energy minimum.^{13,15,16} Consequently, despite widespread interest in the isovalent HCOPH₂ (**III**) molecule from the astrochemical community to constrain the largely unknown interstellar phosphorus chemistry and from the preparative inorganic and physical chemical viewpoint as isovalent systems of the nitrogen analogous formamide (HCONH₂) molecule, the synthesis of HCOPH₂ (**III**) has remained elusive.

Here, we report on the very first experimental detection of the hitherto elusive HCOPH₂ (**III**) molecule in the gas phase.

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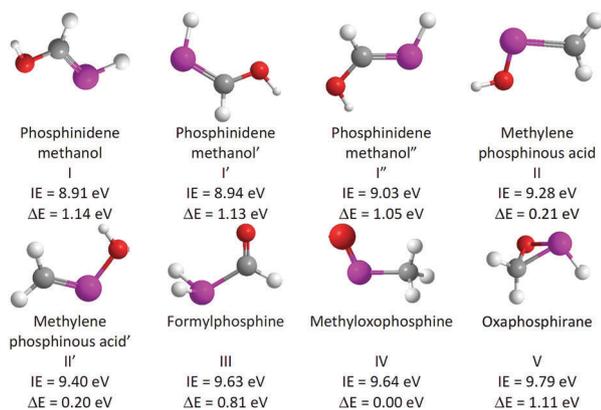


Fig. 1 The adiabatic ionization energies (IE) and relative energies (ΔE) of formyl-phosphine along with its isomers obtained with B3LYP/cc-VTZ/CCSD(T)/CBS calculations. More details see Table S1 (ESI[†]).

Our experiments are combined with density functional theory and *ab initio* electronic structure calculations (Table S1, ESI[†]) to validate the stability of gas phase HCOPH₂ (III). The experiments were carried out in an ultrahigh vacuum (UHV) surface science machine operated at a base pressure of a few 10⁻¹¹ Torr.¹⁹ Binary ices of phosphine (PH₃) with carbon monoxide (CO), ¹⁸O-carbon monoxide (C¹⁸O), or ¹³C-carbon monoxide (¹³CO) as well as ternary mixtures of phosphine (PH₃) with ¹⁸O-carbon monoxide (C¹⁸O) and ¹³C-carbon monoxide (¹³CO) were prepared in separate experiments with thicknesses of 700 ± 100 nm at 5.5 ± 0.2 K at ratios of 1 : 2 ± 0.5 and 1 : 1 : 1 ± 0.2 for the binary and ternary mixtures, respectively. The non-equilibrium chemistry and bond-cleavage processes were initiated by exposing these ices to energetic electrons as proxies for secondary electrons originating from galactic cosmic radiation (GCR) penetrating interstellar ices^{5,17,18} at average doses of 0.8 ± 0.2 eV molecule⁻¹ and 0.6 ± 0.1 eV molecule⁻¹ for phosphine and carbon monoxide, respectively (Table S2, ESI[†]). This low dose along with overlapping absorptions of functional groups of phosphorus-oxygen bearing molecules prohibits an identification of HCOPH₂ (III) *via* Fourier transform infrared (FTIR) spectroscopy.¹⁷ Only carbon dioxide (CO₂), dicarbon monoxide (C₂O), and diphosphine (P₂H₄) along with their ¹³C and ¹⁸O labelled counterparts could be clearly assigned (Table S3 and Fig. S1a–c, ESI[†]). After the irradiation, the ices were heated at a rate of 1 K min⁻¹ to 320 K

(temperature programmed desorption; TPD). During the TPD phase, the subliming neutral molecules were ionized *via* tunable vacuum ultraviolet (VUV) photoionization (PI), mass resolved in a reflectron time-of-flight mass spectrometer (PI-ReTOF-MS), and then detected by their arrival times through a multichannel plate *via* their mass-to-charge ratios. By systematically tuning the photoionization energies from 10.49 eV *via* 9.67 eV and 9.45 eV (Table S4, ESI[†]), specific structural isomers can be selectively ionized based on their ionization energies (IE) as obtained from accompanying electronic structure calculations to eventually determine which isomer(s) is(are) formed. This strategy leads ultimately to the identification of HCOPH₂ (III).

The mass spectra of the subliming molecules released from the irradiated phosphine–carbon monoxide ices are compiled in Fig. 2 and Fig. S2 (ESI[†]) as a function of temperature recorded at photon energies between 10.49 eV and 9.45 eV. The comparison of the data of the non-irradiated ice mixture and the processed ices reveals several newly formed molecules. In addition to the precursor phosphine (PH₃) ($m/z = 34$; IE = 9.87 eV), phosphanes like diphosphine (P₂H₄) ($m/z = 66$; IE = 8.8 eV) and triphosphane (P₃H₅) ($m/z = 98$; IE = 7.80 eV) along with its fragment P₂H₂ ($m/z = 64$),¹⁹ the data recorded for the PH₃–CO system at 10.49 eV reveal a clear trace at mass-to-charge (m/z) of 62 (Fig. 2b and 3a, b). Accounting for the molecular weight of phosphine (34 amu) and carbon monoxide (28 amu), the molecular weight of 62 amu is consistent with the formation of a molecule of the formula PH₃CO. The TPD profile at $m/z = 62$ exhibits an onset of the ion counts at 100 K and a maximum close to 125 K (Fig. 3a). To substantiate that the species monitored at $m/z = 62$ (Fig. 3a and b; black trace) are connected to a molecule with the formula PH₃CO, two additional isotopic experiments were carried out by replacing carbon monoxide with ¹³C and ¹⁸O in separate experiments (Fig. 3b). The TPD profiles recorded at $m/z = 63$ and 64 are shifted by 1 amu and 2 amu in the ¹³C and ¹⁸O carbon monoxide experiments, respectively. The early sublimation event starting at 100 K and peaking close to 125 K match nicely the early sublimation event in the PH₃–CO system observed at $m/z = 62$. These findings propose that the product molecules contain one carbon atom and one oxygen atom, a finding which is consistent with the molecular formula PH₃CO. Note that the late sublimation event in the PH₃–C¹⁸O system observed at $m/z = 64$, which peaks at 150 K, is associated with

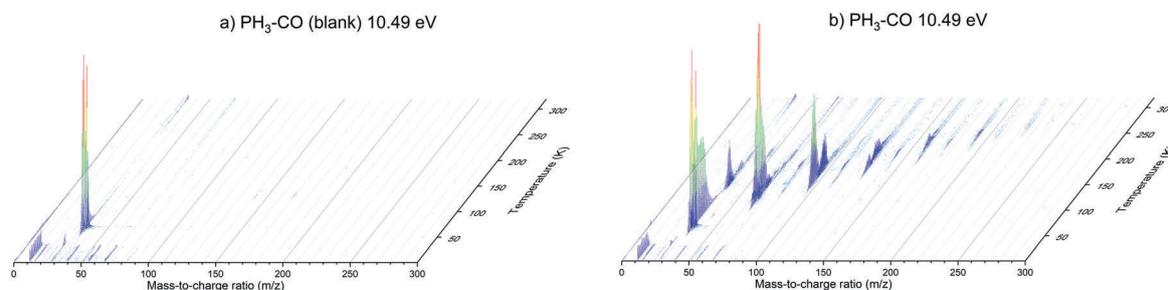


Fig. 2 PI-ReTOF-MS spectra of the subliming molecules recorded at distinct ionization energies for the irradiated ice mixtures containing phosphine (PH₃) and carbon monoxide (CO) and its isotopic counterparts (C¹⁸O, ¹³CO). Panel (a and b) show the non-irradiated and irradiated ice mixture (PH₃/CO) at the highest photon energy of 10.49 eV. See full set of experiments in Fig. S2 (ESI[†]).

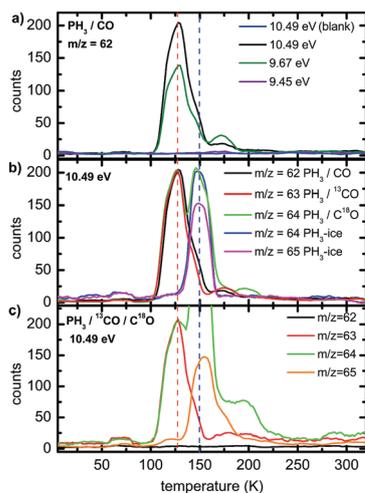


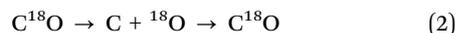
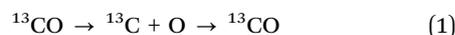
Fig. 3 TPD profiles recorded at various mass-to-charge ratios and photon energies required for the detection of formylphosphine (HCOPH₂). The *m/z* ratios and photon energy of each trace are defined in the legend. For *m/z* 64, the trace of the P₂H₂⁺ fragment is extracted from Turner *et al.*¹⁹

the fragment P₂H₂⁺ of triphosphane (P₃H₅), which can also be observed in neat phosphine ices exposed to ionizing radiation.¹⁹

We also carried out a control experiment at identical conditions with phosphine (PH₃) and carbon monoxide (CO), but without exposing the ice to energetic electrons. In this control study, no signal was observed at *m/z* = 62 (Fig. 2a and 3a), which validates that the PH₃CO product results from the radiolysis of the ices, but not from the photoionization laser and/or gas phase ion–molecule reactions of the subliming molecules.

Having proven the formation of a new molecule with the molecular formula PH₃CO (62 amu) along with its ¹³C and ¹⁸O substituted counterparts, we are focusing our attention now on the assignment of the PH₃CO product isomer(s). This goal is accomplished by selectively photoionizing specific structural isomers based on their distinct ionization energies. The electronic structure calculations reveal the existence of five closed shell structural isomers (I–V) along with three *cis–trans* isomers (I', I'', II'), whose adiabatic ionization energies and relative energies are presented in Fig. 1. At a photon energy of 10.49 eV, all isomers can be ionized, whereas at 9.67 eV all isomers except V can be ionized. Finally, at 9.45 eV, only isomers I–II are accessible to ionization. It is important to note that the TPD profile recorded at *m/z* = 62 at a photon energy of 9.45 eV does not reveal any ion counts (Fig. 3a, blue curve). Therefore, we can conclude that isomers I and II are not formed in the present experiments. Likewise, a comparison of the TPD traces of *m/z* = 62 recorded at 10.49 eV and 9.67 eV reveals that the ion counts at 9.67 eV can only originate from photoionization of isomers III and/or IV, but not from isomer V, whose ionization energy is above 9.67 eV. Consequently, based on the photoionization studies within the phosphine (PH₃)–carbon monoxide (CO) ices, we can conclude that the HCOPH₂ (III) and/or the CH₃PO (IV) isomer are/is formed. The difference of the adiabatic ionization energies of 0.01 eV between both isomers falls within the error limits of the computations; therefore, isomer III and IV cannot be discriminated.

A detailed analysis of the molecular structures of both isomers III and IV underlines a critical difference in their possible formation pathways. While in HCOPH₂ (III), the carbonyl moiety as derived from the carbon monoxide reactant stays intact, the carbon and oxygen atoms of the carbon monoxide reactant have to undergo homolytic bond rupture in order to synthesize CH₃PO (IV). In principle, a homolytic bond rupture in carbon monoxide is energetically feasible as it requires only 11 eV and can be induced by the energetic electrons. Therefore, ¹³C and ¹⁸O carbon monoxide can be radiolyzed *via* eqn (1) and (2), respectively; term symbols are omitted for clarity. The carbon and oxygen atoms can then also recombine back to recycle ¹³C and ¹⁸O carbon monoxide *via* eqn (1) and (2), but then can also recombine leading to ¹³C¹⁸O and CO *via* eqn (3) and (4). This process has been only observed at elevated doses in excess of about 3 eV per carbon monoxide molecule.²⁰



Therefore, we carried out an additional experiment utilizing a ternary ice mixture containing phosphine (PH₃) with ¹⁸O-carbon monoxide (C¹⁸O) and ¹³C-carbon monoxide (¹³CO). Recall that based on the molecular structure, the homolytic bond rupture of carbon monoxide represents a critical prerequisite to synthesize CH₃PO (IV) and should lead to signal not only at *m/z* = 63 (¹³CH₃PO⁺) and 64 (CH₃P¹⁸O⁺), but also at *m/z* = 65 (¹³CH₃P¹⁸O⁺) (Fig. 3c). Whereas the early sublimation event in the TPD profiles of *m/z* = 63 and 64 peaking at 125 K verify the formation of ¹³CH₃PO and CH₃P¹⁸O in the electron irradiated ternary ices, signal at *m/z* = 65 at a level of close to 10 counts does not match the onset of the sublimation at 100 K for the early sublimation event; these ion counts can be matched nicely with signal of *m/z* = 65 observed in experiments with neat phosphine ices exposed to ionizing irradiation originating from the P₂H₂⁺ fragment (Fig. 3b, dashed purple line). Likewise, no ion counts were detected at *m/z* = 62 verifying that carbon monoxide cannot be formed *via* eqn (4). Therefore, we can conclude that CH₃PO (IV) is not formed in our experiments and that HCOPH₂ (III) along with its ¹³C and ¹⁸O substituted counterparts represents the exclusive isomer synthesized in our studies. The carbon monoxide reactant stays intact thus resulting in the formation of the carbonyl moiety in HCOPH₂ (III).

It is stimulating to explain the underlying mechanism of the synthesis of HCOPH₂ (III). Experiments with neat phosphine ices revealed that upon interaction of energetic electrons, a phosphine molecule (PH₃) can undergo unimolecular decomposition to form the phosphino (PH₂) radical along with a suprathermal atomic hydrogen (H) (reaction (5)). This suprathermal hydrogen atom has excess kinetic energies of up to a few eV and can add to the carbon atom of the carbon monoxide molecule forming the formyl radical (HCO; eqn (6)). Recent experiments in carbon monoxide–methane,²¹ carbon monoxide–ammonia,⁶

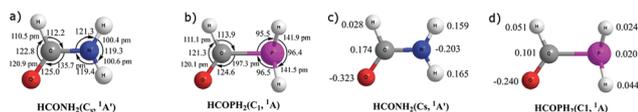
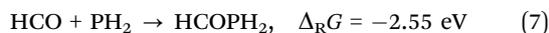


Fig. 4 Bond lengths and bond angles (in degree) (a and b) along with partial charges (c and d) of formamide and formylphosphine, optimized at the B3LYP/cc-pVTZ level of theory.

and carbon monoxide–methanol ices²² also demonstrate that suprathreshold hydrogen atoms react with carbon monoxide forming the formyl radical (HCO). If the formyl radical (HCO) has a favorable recombination geometry with the phosphino radical (PH₂), both radicals can recombine without barrier leading to the formation of HCOPH₂ (**III**) reaction (7) as confirmed by calculations (Table S5 and Fig. S2, S3, ESI[†]). Considering the average velocity of 138 m s⁻¹ of HCOPH₂ (**III**) subliming at 125 K and the distance between the ice and the photoionization laser of 2 mm, the lifetime of the subliming HCOPH₂ (**III**) must be at least 10 μs to endure the time between the sublimation and the photoionization event.



A comparison of the molecular structure of the isovalent formamide (HCONH₂) with HCOPH₂ (**III**) reveals an elongated carbon–phosphorus single bond of 197.3 pm compared to a carbon–nitrogen bond length of 135.7 pm suggesting partial double bond character due to resonance stabilization of the peptide moiety (Fig. 4). This significant resonance stabilization is also evident from the enhanced negative charge on the oxygen atom (−0.323 *e*) in formamide compared to only −0.240 *e* in formylphosphine. The existence of a partial C=N double bond character is also reflected in a planar structure (C_s point group) of formamide (HCONH₂) in contrast to HCOPH₂ (**III**), which has no symmetry at all due to the freely rotatable carbon–phosphorus single bond. Consequently, the replacement of single nitrogen atom by a phosphorus atom elongates the C–P bond length compared to the C–N bond.

To summarize, the conducted experiments provide clear evidence that the HCOPH₂ (**III**) molecule can be synthesized easily in astrophysical ices containing phosphine and carbon monoxide upon exposure to energetic electrons released by galactic cosmic rays at ultralow temperatures once penetrating ice coated interstellar nanoparticles. With upper yields of 0.02 molecules eV⁻¹ as synthesized on interstellar icy grains in cold molecular clouds (ESI[†]), HCOPH₂ (**III**) can sublime once the molecular clouds transits to star forming regions into the gas phase, where it can be detected *via* microwave spectroscopy. With the commission of the Atacama Large Millimeter/Submillimeter Array (ALMA), the prospective detection of heavier

molecular weight organics such as HCOPH₂ (**III**) will continue to grow, and an understanding of these data will rely on advances in experimental laboratory astrophysics such as PI-ReTOF-MS as proposed here eliminating the gap between observational and laboratory data that existed for decades.

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Conflicts of interest

There are no conflicts to declare.

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