GEOCHEMISTRY

Origin of alkylphosphonic acids in the interstellar medium

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For decades, the source of phosphorus incorporated into Earth's first organisms has remained a fundamental, unsolved puzzle. Although contemporary biomolecules incorporate P(+V) in their phosphate moieties, the limited bioavailability of phosphates led to the proposal that more soluble P(+III) compounds served as the initial source of phosphorus. Here, we report via laboratory simulation experiments that the three simplest alkylphosphonic acids, soluble organic phosphorus P(+III) compounds, can be efficiently generated in interstellar, phosphine-doped ices through interaction with galactic cosmic rays. This discovery opens a previously overlooked avenue into the formation of key molecules of astrobiological significance and untangles basic mechanisms of a facile synthesis of phosphorus-containing organics in extraterrestrial ices, which can be incorporated into comets and asteroids before their delivery and detection on Earth such as in the Murchison meteorite.

INTRODUCTION

While phosphates (PO_4^{3-}) along with their P(+V) derivatives present the ubiquitous form of phosphorus for contemporary biochemistry due to their unique properties (*1*), the increased solubility of reduced oxidation states such as P(+III) under Earth's early, oxygen-poor atmospheric conditions has been proposed as the initial source of prebiotic phosphorus available for the first terrestrial microorganisms (*2*). Phosphorus-bearing biomolecules include RNA/DNA, adenosine diphosphate/adenosine triphosphate (ADP/ATP), and phospholipids; in each case, a phosphate group is chemically bonded to a carbon atom of a sugar, ribose (RNA and ADP/ATP) and deoxyribose (DNA), or of glycerol (phospholipids). The Murchison meteorite, a carbonaceous chondrite carrying key classes of exogenously synthesized organic molecules such as amino acids and sugars (*3*), contains phosphorus as phosphide (−III) and phosphate (+V) minerals (*4*). Schreibersite, an iron-nickel phosphide [$(Fe,Ni)_3P$] mineral found in meteorites, has been studied as a possible source of phosphite [$H_2PO_3^-$, P(+III)] minerals contained in ancient Archean carbonaceous deposits and, given the 10^3-fold greater solubility of phosphite over phosphate minerals, as the ultimate origin of soluble prebiotic phosphorus (*5*). While a purely terrestrial hypothesis might state that no "phosphorus problem" exists and that organisms could have scavenged the limited phosphorus from geologic phosphates (*2*), an extraterrestrial view advocates that meteoric minerals were delivered to Earth during the heavy bombardment period and, after aqueous processing, formed soluble phosphites that were available to the first organisms (*5*). An alternative to these hypotheses considers key chemical reactions essential to produce complex, biologically relevant organic molecules in astrophysical environments such as in interstellar ices in deep space before their delivery to Earth (*6*, *7*).

A notable class of molecules that has these characteristics of an impending abiotic synthesis in extraterrestrial ices are alkylphosphonic acids [$R{-}P(O)(OH)_2$], with "R" signifying an alkyl group (C_nH_{2n+1}). These molecules represent the only phosphorus-containing organic compounds of extraterrestrial origin identified thus far (*8*). Alkylphosphonic acids—which carry methyl (CH_3), ethyl (C_2H_5), isopropyl/*n*-propyl (C_3H_7), and *n*-butyl (C_4H_9) chains—were identified in the Murchison meteorite and exhibit the carbon-phosphorus bond that Cooper *et al.* (*8*) noted would be critical to survive aqueous alteration on the parent body. Thus, alkylphosphonic acids represent both a soluble and bioavailable source of phosphorus that could persist on an aqueously altered body before their delivery to Earth as well as the potential for the formation of phosphate esters in extraterrestrial bodies without aqueous alteration. While phosphorus-bearing minerals such as schreibersite have been investigated as a source of alkylphosphonic acids (*5*, *9*–*11*), the unique potential of an alternative formation scenario, the synthesis of alkylphosphonic acids in phosphorus-doped ices condensed on interstellar grains in cold molecular clouds through interaction with ionizing radiation, has not been fully explored yet. Functional groups, which might be linked to alkylphosphonic acids, have been proposed in processed phosphine (PH_3)–rich ices by infrared spectroscopy (*7*). However, any discrete alkylphosphonic acids were not identified in this study (*7*) because the overlapping absorption bands of these complex organic molecules prevent their unambiguous detection (*12*). The organic chemistry of carbonaceous chondrites such as Murchison is consistent with icy bodies having at least partially interstellar organic matter (*3*). In addition, interstellar analog ices have shown the potential to yield complex organic molecules of biochemical relevance from fundamental biomolecules such as amino acids (*13*) to simple sugars (*14*). These interstellar compounds can be incorporated eventually into planetesimals, comets, and asteroids (*8*). Phosphine (PH_3) presents a promising phosphorus source for these interstellar ices, as phosphine has been observed in the circumstellar envelope of the carbon star IRC+10216 (*15*), from which it can be ejected to the interstellar medium and may eventually become incorporated into cold molecular clouds and, hence, icy grains. In addition, phosphine might be formed on interstellar grain surfaces from atomic phosphorus and atomic hydrogen in a manner

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analogous to the formation of water from atomic oxygen and atomic hydrogen (*16*). These phosphine molecules would immediately become a component of icy grain mantles. Note that in molecular clouds, gas phase routes to phosphine are closed. Furthermore, phosphine has been assigned as the carrier of the phosphorus signal detected in comet 67P/Churyumov-Gerasimenko in the framework of the Rosetta mission (*17*). Likewise, interstellar analog ices of phosphine-water exposed to ionizing radiation generate a homolog series of phosphorus oxoacids including phosphonic acid (H_3PO_3), phosphoric acid (H_3PO_4), and pyrophosphoric acid ($H_4P_2O_7$) (*18*). Therefore, the addition of organic carbon to these interstellar ice analogs could provide the critical reactant necessary to establish the plausible formation of alkylphosphonic acids in extraterrestrial ices.

Here, we present compelling evidence on the synthesis of the three simplest alkyl phosphorus oxoacids—methyl (CH_3), ethyl (C_2H_5), and propyl (C_3H_7) phosphonic acid—formed in interstellar ice analogs containing phosphine (PH_3), water (H_2O), and methane (CH_4) exposed to energetic electrons as a proxy for secondary electrons generated during the interaction of galactic cosmic rays with interstellar ices at temperatures of 5 K (*19*). These secondary electrons initiate much of the interstellar chemistry within ices (*20*); our energy doses are equivalent to those received by ices during the lifetime of molecular clouds of typically 10^6 to 10^7 years (*21*). Previous studies demonstrated that irradiated ices of phosphine and carbon dioxide (CO_2) produced phosphorus oxoacids (*18*) and phosphino formic acid (*22*) but no alkylphosphonic acids. The inability of carbon dioxide and carbon monoxide to generate reduced carbon in phosphine ices, although they are more abundant than methane on typical interstellar ices, suggests that methane (CH_4), which is a known component of interstellar ices at levels of up to 5%, represents a realistic source of organic carbon for these experiments. By exploiting reflectron time-of-flight mass spectrometry (ReTOF-MS) coupled with tunable photoionization (PI) and isotopic experiments of mixtures with $H_2{}^{18}O$ and $^{13}CH_4$, the present study represents the very first discovery of individual alkylphosphonic acids in processed interstellar ice analogs in cold molecular clouds synthesized abiotically upon interaction with ionizing radiation. Since molecular clouds represent nurseries of stars and planetary systems, the detection of these alkylphosphonic acids suggests that these molecules could have been at least partially delivered to our solar system from their interstellar nurseries via circumstellar disks, thus defining where in deep space phosphorus-bearing molecular precursors relevant to the origins of life might be synthesized.

The experiments were carried out in an ultrahigh-vacuum vessel at base pressures of typically 8×10^{-11} torr by exposing ice mixtures of phosphine (PH_3), water ($H_2O/H_2{}^{18}O$), and methane ($CH_4/{}^{13}CH_4$) to energetic electrons at interstellar temperatures of 5 K. These studies replicate the processing of polar interstellar ices by galactic cosmic ray–initiated electron cascades for a few 10^6 years covering a representative lifetime of cold molecular clouds (*21*). Taking advantage of interstellar model ices, sometimes referred to as analog ices, signifies an endorsed methodology in the astrophysics community to reveal the underlying reaction mechanisms and products such as alkylphosphonic acids in interstellar ices. The chemical modification of the ices was probed online and in situ via Fourier transform infrared spectroscopy. After the irradiation, the ices were annealed to 320 K to sublime the molecules via temperature-programmed desorption (TPD). During the TPD process, individual molecules were ionized at distinct photoionization energies in the gas phase via single-photon vacuum ultraviolet photoionization and mass resolved by PI-ReTOF-MS to identify the synthesized alkyl phosphorus oxoacids and their structural isomers selectively. The solid residues that remained at room temperature were analyzed after derivatization exploiting two-dimensional gas chromatography coupled with ReTOF-MS (GC×GC-TOF-MS).

RESULTS

Infrared spectroscopy of irradiated ices represents a valuable tool for identifying small, individual molecules and functional groups of phosphorus-bearing molecules (*23*). The exploitation of water-rich ices (PH_3:H_2O:CH_4, 1:10:2) in our experiments is appropriate for analog ices, since water serves as a major constituent of interstellar ices (*24*). However, as a strong infrared absorber, the water-rich ice obscures several newly emerging infrared absorptions, and the only products observed were diphosphine (P_2H_4) [ν_1 (2274 cm^{-1}) and ν_3 (1067 cm^{-1})] and the ν(P—O) (1014 cm^{-1}) and ν(P═O) (1153 cm^{-1}) fundamentals; both latter assignments were verified via the shift of the peak positions using $H_2{}^{18}O$ (table S1). Previous infrared studies on irradiated ices of phosphine (PH_3); water (H_2O); and a hydrocarbon mixture of methane, ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}) in water-depleted ices (*7*) indicated that functional groups of alkyl phosphorus oxoacids result from the exposure of ices to ionizing radiation at 5 K. Because the infrared absorptions of individual alkyl phosphorus oxoacids fall in a similar range, and hence, overlap, infrared spectroscopy alone does not allow an identification of discrete and unique organic molecules such as alkyl phosphorus oxoacids (*25*).

Photoionization reflectron time-of-flight mass spectrometry

To probe individual alkyl phosphorus oxoacid isomers selectively, we used PI-ReTOF-MS. Here, the subliming alkyl phosphorus oxoacids were photoionized at discrete photon energies and identified according to their mass-to-charge (*m*/*z*) ratios. This requires the knowledge of the ionization energies for the alkyl phosphorus oxoacids along with their structural isomers (Fig. 1 and fig. S1). Isomers for each molecular formula can be divided into two groups: isomers carrying the P═O functional group with ionization energies larger than 10 eV and isomers without the P═O moiety holding ionization energies less than 9 eV. Therefore, we first selected a photoionization energy of 10.49 eV to photoionize all isomers; thereafter, a photoionization energy of 9.93 eV was chosen to photoionize only the isomers without the P═O moiety. The mass spectra of the subliming molecules were recorded as a function of temperature and are compiled in Fig. 2; the sublimation temperatures, ion count intensities, and mass-to-charge ratios of the $H_2{}^{16}O/H_2{}^{18}O$- and $^{12}CH_4/{}^{13}CH_4$-bearing samples were analyzed to determinate the number of oxygen and carbon atoms based on their mass shifts (table S2).

Considering the main focus of our work, the search for individual alkylphosphonic acids, we are focusing first on ions linked to the molecular formula H_5CPO_3, which includes the methylphosphonic acid isomer [$CH_3P(O)(OH)_2$]. In the $PH_3/H_2O/CH_4$ ices, this should lead to the observation of ion counts at m/z = 96 ($H_5CPO_3{}^+$) upon photoionization of the subliming molecules; using ^{18}O labeling ($PH_3/H_2{}^{18}O/CH_4$), the signal should shift by 6 u to m/z = 102 ($H_5CP^{18}O_3{}^+$). On the other hand, ^{13}C labeling ($PH_3/H_2O/{}^{13}CH_4$) is anticipated to increase the ion counts by 1 u to m/z = 97 ($H_5{}^{13}CPO_3{}^+$). The TPD profiles recorded at a photoionization energy of 10.49 eV

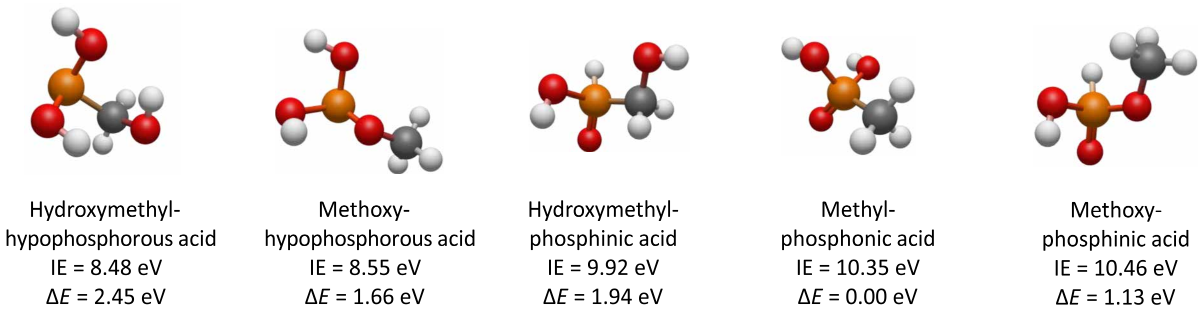

Fig. 1. Adiabatic ionization energies (IE) and relative energies (Δ*E*) for methylphosphonic acid along with structural isomers calculated at the B3LYP/cc-pVTZ//CCSD(T)/CBS level of theory (CCSD(T)/CBS energy on B3LYP/cc-pVTZ optimized geometry).

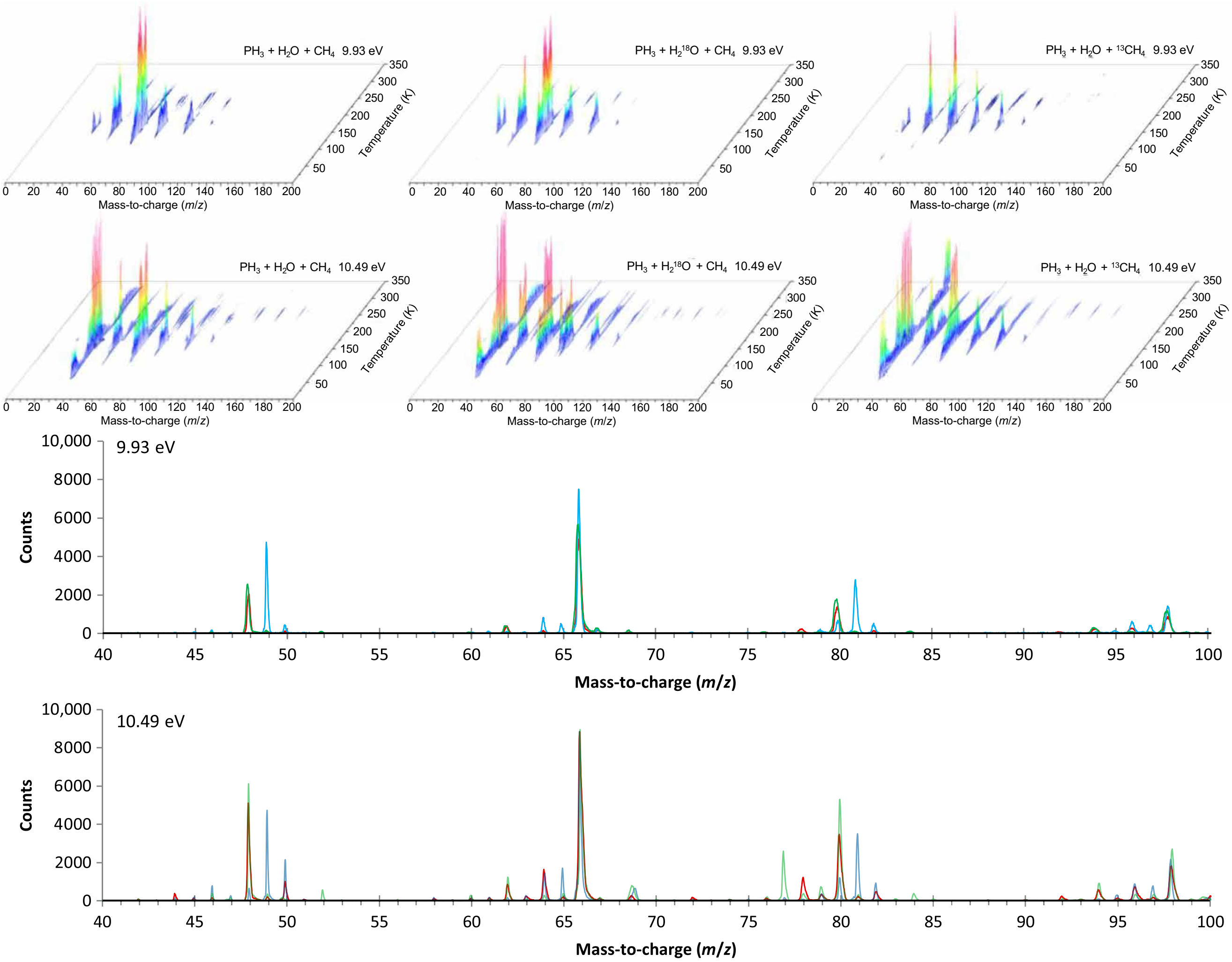

Fig. 2. TPD profiles and integrated mass spectra at 9.93 and 10.49 eV depicting isotopically-labeled $PH_3/H_2O/CH_4$. PI-ReTOF-MS data recorded at photon energies of 9.93 eV (**top row**) and 10.49 eV (**second row**) as a function of temperature of the newly formed products subliming into the gas phase from the irradiated $PH_3/H_2O/CH_4$ (**left**), $PH_3/H_2{}^{18}O/CH_4$ (**center**), and $PH_3/H_2O/{}^{13}CH_4$ (**right**) ices. The integrated mass spectra at 9.93 eV (**third row**) and 10.49 eV (**bottom row**) are also shown, with the $PH_3/H_2O/CH_4$ mixture shown in red, $PH_3/H_2{}^{18}O/CH_4$ in green, and $PH_3/H_2O/{}^{13}CH_4$ in blue.

reveal clear signals at m/z = 96, 102, and 97, demonstrating that molecules with the molecular formulas H_5CPO_3, $H_5CP^{18}O_3$, and $H_5{}^{13}CPO_3$ are subliming from the irradiated $PH_3/H_2O/CH_4$, $PH_3/H_2{}^{18}O/CH_4$, and $PH_3/H_2O/{}^{13}CH_4$ ices, respectively (Fig. 3). Note that blank studies, experiments conducted under identical conditions but without irradiating the ices, do not show any ion counts at these mass-to-charge ratios, demonstrating that any signal at m/z = 96, 102, and 97 is linked to the processing of the ice samples by ionizing radiation.

For the nonisotopically labeled ices ($PH_3/H_2O/CH_4$), at a photon energy of 10.49 eV, the signal at m/z = 96 appears as a single peak (Fig. 3, red line). Ions at this mass-to-charge ratio can be linked to

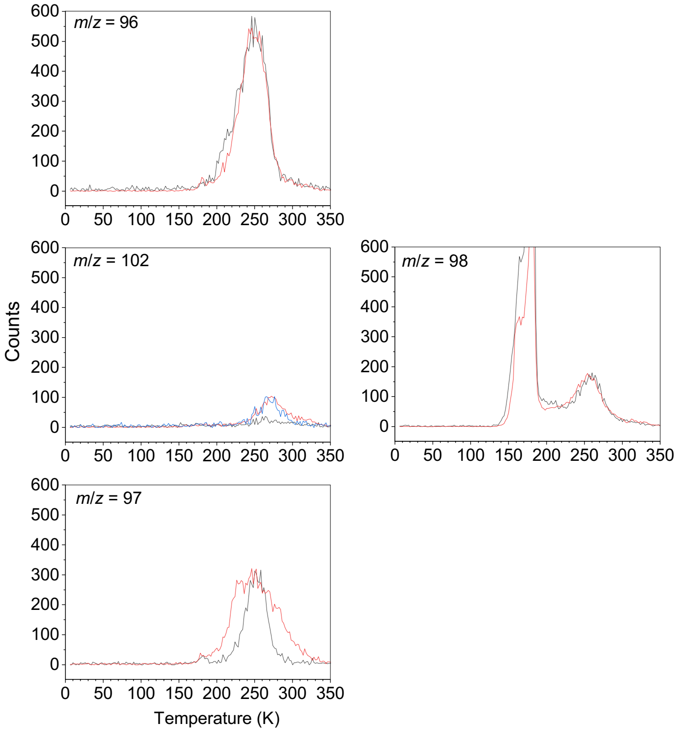

Fig. 3. TPD profiles of photoionized H_5CPO_3 isomers along with their ^{18}O and ^{13}C substituted counterparts ($H_5CP^{18}O_3$ and $H_5{}^{13}CPO_3$) recorded at $m/z = 96$, 102, and 97 subliming from the processed $PH_3 + H_2O + CH_4$ (**top**), $PH_3 + H_2{}^{18}O + CH_4$ (**center**), and $PH_3 + H_2O + {}^{13}CH_4$ (**bottom**) ices. The TPD profiles are shown for photon energies of 9.93 eV (black), 10.35 eV (blue), and 10.49 eV (red). The middle right graph shows $m/z = 98$ for the $PH_3 + H_2{}^{18}O + CH_4$ systems to demonstrate the presence of the H_6CP_2O compounds, which would also be present in the $m/z = 96$ ($PH_3 + H_2O + CH_4$) and $m/z = 97$ ($PH_3 + H_2O + {}^{13}CH_4$) signals.

parent ions of the H_5CPO_3 isomers, potentially the desired methylphosphonic acid [$CH_3P(O)(OH)_2$], as well as to parent ions associated with H_6CP_2O isomers. The carrier(s) can be distinguished on the basis of ^{18}O labeling. Here, H_5CPO_3 isomers ($m/z = 96$) would shift the signal by 6 u to $m/z = 102$ ($H_5CP^{18}O_3$), whereas the presence of H_6CP_2O isomers would only result in a shift by 2 u to $m/z = 98$ ($H_6CP_2{}^{18}O$) because of the presence of three versus one oxygen atoms, respectively. A comparison of the TPD profile at $m/z = 96$ in the $PH_3/H_2O/CH_4$ ices with those recorded at $m/z = 102$ and 98 in the $PH_3/H_2{}^{18}O/CH_4$ ices reveals that most of the signal at $m/z = 96$ can be explained by H_6CP_2O isomers (70%) ($m/z = 98$; red line), whereas close to 30% of the ions originate from H_5CPO_3 isomers ($m/z = 102$; red line). A closer look at the TPD profile of $m/z = 97$ recorded for the $PH_3/H_2O/{}^{13}CH_4$ system at 10.49 eV reveals the presence of a single carbon atom. Furthermore, as indicated in Fig. 3, three sublimation events can be inferred from the TPD profile of $m/z = 97$. The sublimation event peaking at 250 K agrees well with the sublimation event of the H_6CP_2O isomers ($m/z = 96$), whereas the sublimation peaking at 280 K correlates with the $H_5CP^{18}O_3$ isomers ($m/z = 102$); the sublimation starting at 180 K at $m/z = 97$ suggests hitherto unidentified less polar molecule(s). Therefore, the data recorded at a photon energy of 10.49 eV propose that the sublimation event peaking at 280 K can be associated with the formation of H_5CPO_3 isomers. To assign the H_5CPO_3 isomer(s), we conducted additional experiments at photon energies of 9.93 and 10.35 eV (Fig. 3). This is best visualized for the TPD trace at $m/z = 102$ for the $PH_3/H_2{}^{18}O/CH_4$ ices. Here, the TPD profiles for $H_5CP^{18}O_3{}^+$ overlap for 10.49 eV (red line) and 10.35 eV (blue line); no signal at $m/z = 102$ was observed at 9.93 eV (black line), indicating that the hydroxymethylhypophosphorous acid [$HOCH_2P(OH)_2$], methoxyhypophosphorous acid [$CH_3OP(OH)_2$], and hydroxymethylphosphinic acid [$HOCH_2PH(O)OH$] isomers can be eliminated as products: Their ionization energies are below 9.93 eV; hence, a signal should be present at 9.93 eV upon photoionization. The 10.35 eV experiment can discriminate between the two remaining $H_5CP^{18}O_3$ isomers, methylphosphonic acid [$CH_3P(O)(OH)_2$] and methoxyphosphinic acid [$CH_3OPH(O)OH$], since the latter cannot be photoionized at this energy (IE = 10.46 eV). Consequently, the signal at $m/z = 102$ recorded at 10.35 eV (blue line) confirms the synthesis of the methylphosphonic acid isomer via its molecular parent at $m/z = 102$ [$CH_3P(^{18}O)(^{18}OH)_2$]. Note that besides methylphosphonic acid, the main target of this study, additional molecules were detected (fig. S2). For the phosphorus oxoacids, hydroxyphosphine (H_2POH) and phosphinic acid [$H_2P(O)OH$] were probed, revealing consistent results with previously investigated ices of phosphine and water (*18*). In addition to methylphosphonic acid, both methylphosphine oxide (CH_3PH_2O) and methoxyphosphine oxide [$CH_3OP(O)H_2$] were detected as well, thus exposing the synthesis of a homologous series of three methyl-substituted phosphorus oxoacids: methylphosphine oxide (CH_3PH_2O), methoxyphosphine oxide [$CH_3OP(O)H_2$], and methylphosphonic acid [$CH_3P(O)(OH)_2$].

Two-dimensional gas chromatography coupled with ReTOF-MS

Besides subliming into the gas phase, phosphorus-bearing molecules may persist within the solid residues remaining after the ice sublimation in the course of the TPD phase to 320 K. These residues were solvated and analyzed using GC×GC-TOF-MS (Fig. 4 and tables S3 and S4). Phosphorus oxoacids and alkylphosphonic acids were detected through a comparison of the dual retention times ($R_{t1} \times R_{t2}$) on both columns along with the mass spectra of the trimethylsilyl derivatives based on the molecular ion (M^+) and the methyl loss channel ($M{-}15^+$) with known standards. Data were recorded for the residues formed from the $PH_3/H_2{}^{18}O/CH_4$ ices along with those remaining in the $PH_3/H_2O/{}^{13}CH_4$ ices (Supplementary Materials).

Three alkylphosphonic acids were detected in the solvated residues. Methylphosphonic acid [$^{13}CH_3P(O)(OH)_2$] was observed via $m/z = 241$ (M^+) and 226 ($M{-}15^+$) in the solvated $PH_3/H_2O/{}^{13}CH_4$ residues. The mass shift by 1 u compared to the methylphosphonic acid [$CH_3P(O)(OH)_2$] standard indicates the presence of only one carbon atom. In the solvated $PH_3/H_2{}^{18}O/CH_4$ residues, this signal shifts by 6 u to $m/z = 246$ and 231, demonstrating that three oxygen atoms are present in this molecule. Ethylphosphonic acid [$C_2H_5P(O)(OH)_2$] and *n*-propylphosphonic acid [$C_3H_7P(O)(OH)_2$] were also detected in both solvated residues via their methyl loss fragments at $m/z = 241$ and 256 ($PH_3/H_2O/{}^{13}CH_4$) and 245 and 259 ($PH_3/H_2{}^{18}O/CH_4$), respectively. Mass shifts compared to the standards by 6 u indicate the presence of three oxygen atoms ($PH_3/H_2{}^{18}O/CH_4$), whereas a mass increase by 2 and 3 u ($PH_3/H_2O/{}^{13}CH_4$) verify two and three carbon atoms, as predicted for the ethyl- and *n*-propylphosphonic acids, respectively. Therefore, on the basis of a cross correlation of the retention times and the mass shifts in the ^{13}C- and ^{18}O-labeled ices, the formation of methyl-, ethyl-, and *n*-propylphosphonic acid could be established. The quantities of the synthesized phosphorus

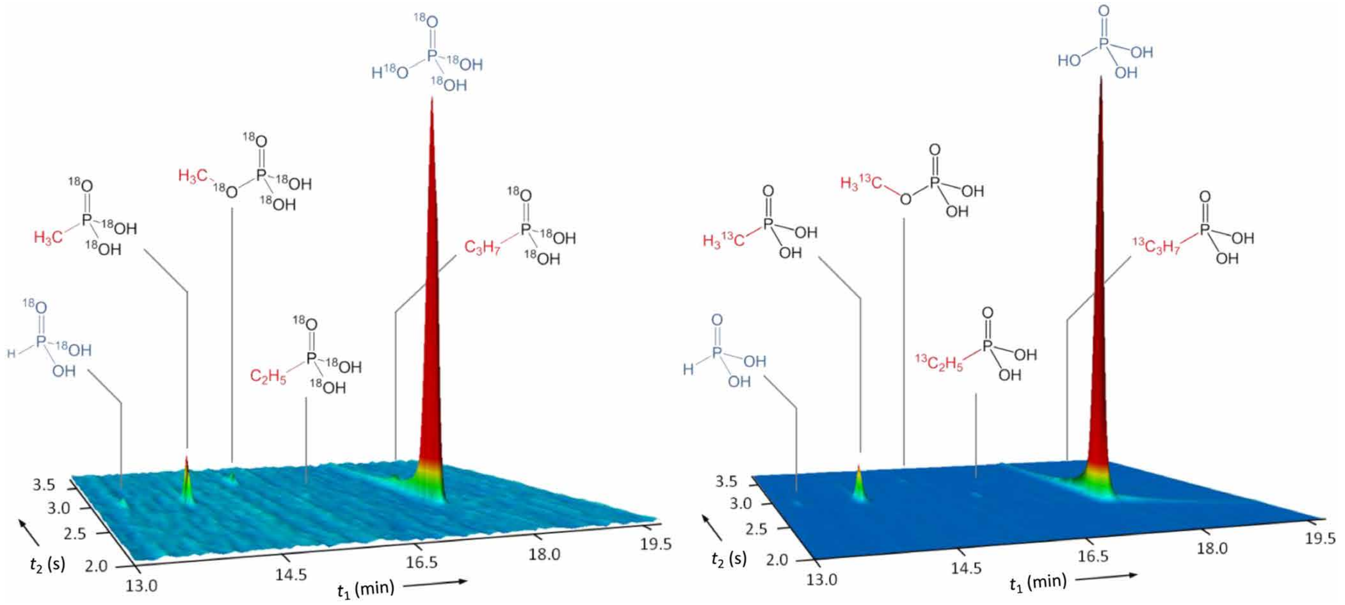

Fig. 4. Organophosphorus compounds detected in the room temperature residues irradiated ices by multidimensional gas chromatography. The residues from $PH_3/H_2{}^{18}O/CH_4$ (**left**) and $PH_3/H_2O/{}^{13}CH_4$ (**right**) ices are shown. Further details and scaled chromatograms are provided in the Supplementary Materials (figs. S3 and S4). In Murchison, 1 g of the meteorite contained 9 nmol of methylphosphonic acid and 6 nmol of ethylphosphonic acids.

oxoacids and of the alkylphosphonic acids are presented here for the $PH_3/H_2O/{}^{13}CH_4$ system considering the partial ${}^{16}O/{}^{18}O$ exchange, as discussed above. For methyl-, ethyl-, and *n*-propylphosphonic acid, 280 ± 13, 10 ± 2, and 2.5 ± 0.6 ng were determined, which results in an alkylphosphonic acid molar ratio of 150 ± 6:5 ± 1:1. This enhanced formation of methylphosphonic acid compared to ethylphosphonic acid is consistent with the analysis of the Murchison meteorite. Note that propyl- and *n*-butyl phosphonic acids were detected in Murchison, but these derivatives were not quantified. In our experiments, conversion yields to methyl-, ethyl-, and *n*-propylphosphonic acid were determined to be 1.7 ± 0.3, 0.05 ± 0.01, and 0.012 ± 0.002%, respectively.

DISCUSSION

The present study provides compelling evidence on the facile synthesis of the three simplest alkylphosphonic acids—methylphosphonic acid [$CH_3P(O)(OH)_2$], ethylphosphonic acid [$C_2H_5P(O)(OH)_2$], and propylphosphonic acid [$C_3H_7P(O)(OH)_2$]—upon interaction of ionizing radiation with phosphine-bearing interstellar analog ices. The detection of these P(+III) compounds endorses the hypothesis that alkylphosphonic acids—the only known organic phosphorus-containing molecules of extraterrestrial origin, as detected in the Murchison meteorite, and potential source of bioavailable phosphorus to Earth's first organisms—can be synthesized abiotically within mantles of interstellar icy grains as present in molecular clouds. The identification of methylphosphonic acid [$CH_3P(O)(OH)_2$] further signifies the presence of P(+V) and the P—O—C backbone found in contemporary biomolecules. If confirmed, given the capacity for P(+V)—O—C bond formation in interstellar ice analogs of phosphine, water, and methane, the replacement of methane in these ice mixtures with glycerol would feasibly produce fundamental building blocks of biomolecules such as of RNA and DNA. Recent studies demonstrated the favorable phosphorylation of sugars in microdroplets of aqueous phosphoric acid (*26*), and the linkage of sugars with phosphoric acid in ices exposed to ionizing radiation would reasonably provide alternative phosphorylation routes in deep space. Alkylphosphonic acids serve as a soluble reduced-oxidation state phosphorus-containing compound that Gulick (*2*) proposed as a prebiotic source of phosphorus, while methylphosphate demonstrates the ability of P(+V)—O—C linkages to form in interstellar ices and acts as a prototype for larger biomolecules carrying this moiety. The suite of extraterrestrial phosphorus-containing compounds continues to expand with the recent discovery of PO (phosphorus monoxide) among the shells of several oxygen-rich stars (*27*), thus demonstrating the need to understand the once-marginalized phosphorus chemistry in astrophysical environments. Our results demonstrate that additional products, such as methylphosphine (PH_2CH_3) and hydroxyphosphine (H_2POH), are formed in these ices and can be released into the gas phase, where they may be detected by microwave spectroscopy. The key objective of all laboratory astrophysics research is to improve the understanding of astrophysical systems, and our results provide fundamental knowledge toward the phosphorus chemistry in extraterrestrial environments beyond just interstellar ices, including meteorites, comets, and even planets. Considering that molecular clouds are nurseries of stars and planetary systems, the detection of alkylphosphonic acids suggests that these molecules could have been at least partially delivered to our solar system from their interstellar nurseries via circumstellar disks. These compounds subsequently become incorporated in asteroids and comets before their delivery to Earth, thus defining where in deep space phosphorus-bearing molecular precursors relevant to the origins of life might be synthesized.

MATERIALS AND METHODS

Experiments were performed in a stainless steel chamber at pressures of 8×10^{-11} torr using magnetically suspended turbomolecular pumps backed by oil-free scroll pumps (*28*). A polished silver mirror was mounted to a rotatable cold head that reached temperatures of

5 K using a two-stage closed-cycle helium refrigerator. A gaseous mixture of phosphine (PH_3; 99.9995%), methane (CH_4; 99.999%), and water (H_2O; high-performance liquid chromatography grade) was deposited onto the cold silver target with an ice composition ratio of 10:2:1 for H_2O:CH_4:PH_3. Isotopically labeled water [$H_2{}^{18}O$; 99 atomic % (at %)^{18}O] and methane ($^{13}CH_4$; 99 at % ^{13}C) were used in duplicate experiments, thus accessing three distinct ices: $PH_3/H_2O/CH_4$, $PH_3/H_2{}^{18}O/CH_4$, and $PH_3/H_2O/{}^{13}CH_4$. Using laser interferometry, the thickness of the ice was determined to be 750 ± 50 nm (*29*), while the composition ratio used the integrated absorption coefficients of the infrared vibrational bands taken from a Nicolet 6700 Fourier transform infrared spectrometer (see "Infrared and conversion yields" in the Supplementary Materials) (*7*). The ices were irradiated with 5-keV electrons for 1 hour at 2.0×10^{12} electrons cm^{-1} s^{-1}; the CASINO simulation (*30*) calculated the average penetration depth to be 270 nm with a maximum penetration depth of 630 nm and resulted in an average dose of 27 ± 6 eV molecule^{-1}. Therefore, the ice thickness is larger than the maximum penetration of the electrons; hence, the electrons only interact with the ices. After irradiation, the ices were annealed at 1 K min^{-1} to 320 K and then held constant for 1 hour. The subliming molecules were detected using PI-ReTOF-MS at two photoionization energies: 9.93 and 10.49 eV (see "Photoionization energy generation" in the Supplementary Materials) (*28*). An additional experiment at 10.35 eV was performed for the $PH_3/H_2{}^{18}O/CH_4$ mixture, while the $PH_3/H_2O/CH_4$ mixture was also subjected to a nonirradiation "blank" experiment at 10.49 eV photoionization energy. The blank experiment found no products at all, which confirms that irradiation is necessary for reactions. The solid residues that remained after sublimation were aqueously extracted and derivatized with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide with 1% trimethylsilyl chloride and analyzed using two-dimensional gas chromatography time-of-flight mass spectrometry (see "GC×GC-TOF-MS analysis" in the Supplementary Materials). Using DB-5ms Ultra Inert for the first column, DB Wax for the second column, and helium as a carrier gas (1 ml min^{-1}), compounds were identified by comparing the retention time ($R_{t1} \times R_{t2}$) and mass spectra of the samples to standards (tables S3 and S4 and figs. S3 to S7).

For the calculations, the geometries of neutral molecules and cations were optimized by the hybrid density functional B3LYP/cc-pVTZ, and CCSD(T)/cc-pVQZ energies (*31*–*34*) were then calculated and extrapolated to completed basis set limits (*35*), CCSD(T)/CBS, with B3LYP/cc-pVTZ zero-point energy corrections. The adiabatic ionization energies were computed by taking the difference between the ionic and the neutral states corresponding to similar conformation. At this level of theory, the accuracy of adiabatic ionization energies is expected to be within 0.05 eV. The Gaussian 09 program (*36*) was used in the electronic structure calculations.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/8/eaaw4307/DC1

Supplementary Text

Table S1. Infrared absorption peaks before and after irradiation for $PH_3 + H_2O/H_2{}^{18}O + CH_4/{}^{13}CH_4$.

Table S2. PI-ReTOF-MS ion counts detected from irradiation of the $PH_3 + H_2O + CH_4$ ice mixture and confirmed using $H_2{}^{18}O$ and $^{13}CH_4$.

Table S3. Identified alkylphosphonic acids and phosphorus oxoacids as trimethylsilyl derivatives by GC×GC-TOF-MS.

Table S4. Quantities of identified alkylphosphonic acids and phosphorus oxoacids in the $PH_3/H_2O/{}^{13}CH_4$ ice mixture and the irradiation yield (molecules eV^{-1}).

Fig. S1. Temperature programmed desorption profiles associated with mass-to-charge ratios (m/z) of H_5CPO, H_5CPO_2, H_5CPO_3, and H_5CPO_4.

Fig. S2. Calculated ionization energies (IE) and relative isomeric energies (Δ*E*) for the isomers of H_5CPO, H_5CPO_2, H_5CPO_3, and H_5CPO_4.

Fig. S3. Organophosphorus compounds detected in the room temperature residues irradiated ices composed of $PH_3/H_2{}^{18}O/CH_4$ by multidimensional gas chromatography.

Fig. S4. Organophosphorus compounds detected in the room temperature residues irradiated ices composed of $PH_3/H_2O/{}^{13}CH_4$ by multidimensional gas chromatography.

Fig. S5. Time-of-flight mass spectra of silylated phosphorus compounds identified in the residue from irradiated ices of $PH_3/H_2O/{}^{13}CH_4$.

Fig. S6. Time-of-flight mass spectra of silylated phosphorus compounds in the residue from irradiated ices of $PH_3/H_2{}^{18}O/CH_4$.

Fig. S7. Time-of-flight mass spectra of silylated methylphosphonic acid identified in residues of ices $PH_3/H_2{}^{18}O/CH_4$ and $PH_3/H_2O/{}^{13}CH_4$.

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