Solid-State Investigation, Storage, and Separation of Pyrophoric PH$_3$ and P$_2$H$_4$ with $\alpha$-Mg Formate

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In memory of Professor Marianne Baudler.

Abstract: Phosphine, PH$_3$—a highly pyrophoric and toxic gas—is frequently contaminated with H$_2$ and P$_2$H$_4$, which makes its handling even more dangerous. The inexpensive metal–organic framework (MOF) magnesium formate, $\alpha$-[Mg(O$_2$C$_2$H$_4$)], can adsorb up to 10 wt % of PH$_3$. The PH$_3$-loaded MOF, PH$_3$$\alpha$-[Mg(O$_2$C$_2$H$_4$)], is a non-pyrophoric, recoverable material that even allows brief handling in air, thereby minimizing the hazards associated with the handling and transport of phosphine. $\alpha$-[Mg(O$_2$C$_2$H$_4$)] further plays a critical role in purifying PH$_3$ from H$_2$ and P$_2$H$_4$: at $25^\circ$C, H$_2$ passes through the MOF channels without adsorption, whereas PH$_3$ absorbs readily and only slowly desorbs under a flow of inert gas (complete desorption time $\approx 6$ h). Diphosphane, P$_2$H$_4$, is strongly adsorbed and trapped within the MOF for at least 4 months. P$_2$H$_4$$\alpha$-[Mg(O$_2$C$_2$H$_4$)] itself is not pyrophoric and is air- and light-stable at room temperature.

Phosphine (PH$_3$), the simplest phosphorus hydride, is a colorless, pyrophoric, and highly toxic gas.[1,2] Its phosphorus weight content (91.2 %) is the highest of all stable commercial phosphorus compounds and its annual industrial production in the US exceeds a couple of thousand tons.[3] Its preparation involves either an acid- or alkali-promoted disproportionation of white phosphorus. It demands harsh reaction conditions and produces acid derivatives such as H$_3$PO$_3$ or H$_2$PO$_4$, H$_2$, and diphosphane P$_2$H$_4$ as by-products that are difficult to separate.[4–8] PH$_3$ plays an important role as a doping agent for n-type semiconductors, fumigant, polymerization initiators, and as an intermediate in the preparation of flame retardants.[9–10] Very recently, PH$_3$ has attracted further interest due to its superconductivity at high pressures and above 100 K.[11–15] PH$_3$ is also used for the synthesis of primary, secondary, and tertiary phosphanes, H$_3$PR, H$_2$PR, and PR$_2$, which involves addition of phosphorus radicals to hydrocarbons.[16–18] An even broader applicability of PH$_3$ is, however, hindered by its hazards, which are also caused by impurities from its decomposition to H$_2$, P$_2$H$_4$, and higher phosphanes.[19,20] Previously, Weston et al. investigated phosphine sorption into a series of metal–organic frameworks (MOFs) and proposed transition-metal containing MOFs, namely MOF-74-Co and MOF-74-Mn, as possible candidates for respirator and abatement applications.[10] But, a proof-of-concept study was not performed and specifically the possibility to selectively adsorb PH$_3$ from gas mixtures with MOFs has not been investigated to our knowledge. In this work, we demonstrate the adsorption/desorption and safe storage of PH$_3$ in $\alpha$-Mg formate, an inexpensive, easily produced, environmentally friendly, and commercially available material.[21,22] Our study further provides an updated crystallographic characterization of PH$_3$, which despite its ubiquity and importance had been previously mischaracterized by X-ray diffraction more than 90 years ago. Finally, we show that $\alpha$-Mg formate discriminates between PH$_3$ and its main contaminants H$_2$ and P$_2$H$_4$, and allows trapping and safe handling of pyrophoric P$_2$H$_4$ for extended periods under ambient conditions.

We started our investigation by crystallizing PH$_3$ in a glass capillary at 100 K. The obtained diffraction data obtained with a single crystal reveal a cubic face centered F-
43m space group with a lattice constant of $a = 6.3390(7)$ Å, a cell volume of 254.72(8) Å$^3$, and four PH$_3$ molecules per unit cell (Figure 1). This allows us to estimate the effective molecular volume of PH$_3$ to be 63.7 Å$^3$. Thereby we correct the only available experimental data obtained by a powder XRD measurement from G. Natta (1930), in which a cubic primitive crystal system with $a = 6.31 \pm 0.01$ Å and a cell volume of 251 Å$^3$ were assumed.[23]

In contrast to the experimental structure of NH$_3$ in which every molecule is involved in six hydrogen bonds,[24] for PH$_3$ only a very weak interaction between the molecules was found. The lack of intramolecular interactions was moreover confirmed in solution by $^1$H DOSY NMR measurements performed in THF-d$_6$ and toluene-d$_8$ (see Supporting Information for details). Solute PH$_3$ radii of $R_{\text{H}}$(PH$_3$) = 1.248 Å and $R_{\text{V}}$(PH$_3$) = 1.150 Å were found, which are only slightly larger than the reported covalent radii of the P$_\text{III}$ atom (1.10 Å).[25] From these radii PH$_3$ solute volumes of 8.1 Å$^3$ (THF) and 6.4 Å$^3$ (toluene) were calculated.

Three MOFs were chosen as promising candidates for PH$_3$ adsorption: (i) Co-MOF-74, [Co$_2$(dobdc)] (dobdc$^{2-}$ = 2,5-dioxido-1,4-benzeneedicarboxylate), (ii) [Cd$_2$(ttfb)] (ttfb$^{3-}$ = tetraethylfullulene tetrazenoate), and (iii) α-magnesium formate, α-[Mg(O$_2$CH)$_3$], which is known to reversibly adsorb/desorb ammonia.[26] Unfortunately, the H$_2$O molecules bound to the metal sites in the single crystals of Co-MOF-74 and Cd$_2$(ttfb) could not be removed upon heating in vacuum at 120 °C. In these water containing materials, no PH$_3$ could be introduced. However, the DMF molecules located in the pores of α-[Mg(O$_2$CH)$_3$] could be removed by heating to 120 °C for 12 h under dynamic vacuum. The complete loss of DMF with retention of single crystallinity was verified by a structure determination using X-ray diffraction (XRD) methods. The result is shown in Figure 2a. Activated α-[Mg(O$_2$CH)$_3$] crystallizes in a dihedral net with 4.5 × 5.5 Å wide pores[29] with a void size of 128 Å$^3$, which should be sufficient to host up to 2 molecules of PH$_3$ ($V_{\text{tr}}$(PH$_3$) = 63.7 Å$^3$). When evacuated single crystals of α-[Mg(O$_2$CH)$_3$] were pressurized under 1.2 bar of PH$_3$ gas, phosphane was readily adsorbed in the pores. The structure of the loaded MOF, PH$_3$@α-[Mg(O$_2$CH)$_3$], was determined by single crystal XRD. The solved structure is shown in Figure 2c.

The cell parameters of pristine α-[Mg(O$_2$CH)$_3$] do not change significantly after the loading with PH$_3$. The Difference Fourier Map of α-[Mg(O$_2$CH)$_3$] before loading with PH$_3$ shows no residual electron density peaks larger than 0.3 e Å$^-3$ within the channels. After loading with PH$_3$, several significant electron density peaks up to about 3.5 e Å$^-3$ appeared. The corresponding residual electron density isosurface at a 0.7 e Å$^-3$ level is shown in Figure 2b.

For the final refinement, the residual electron density was described by partially occupied P atoms, disordered over seven positions, each of them with anisotropic displacement parameters (cf. Figure 2c). The total occupancy sums up to 0.97(5) P-atoms per asymmetric unit.

Most remarkably, the PH$_3$-loaded MOF, PH$_3$@α-[Mg(O$_2$CH)$_3$], is not pyrophoric and can even be handled safely in air for short periods. At 30 °C, complete desorption of PH$_3$ occurs over 6 h, as determined by thermogravimetric analysis (TGA) of PH$_3$@α-[Mg(O$_2$CH)$_3$] under a stream of Ar (see Supporting Information, Figure S37). These findings are in agreement with the calculated preferred binding sites showing multiple possible orientations with a low binding energy of only ca. 2 kcal mol$^{-1}$ (see Supporting Information, Figure S35). The ability of PH$_3$@α-[Mg(O$_2$CH)$_3$] to only slowly release PH$_3$ allows its utilization as a convenient, safer source of PH$_3$. Indeed, after suspending PH$_3$@α-[Mg(O$_2$CH)$_3$] crystals in benzene-d$_6$, phosphane release was observed as indicated by the $^31$P and $^1$H NMR spectra of the suspension at room temperature (see Supporting Information, Figure S48–S50). The resulting empty MOF crystals can be recovered by filtration and, after drying under vacuum, they can be reused for subsequent cycles of PH$_3$ uptake.
Solid-state NMR (SS NMR) provided additional information on the nature of adsorbed phosphane in Pd@-[Mg(O₂CH₂)]. The ¹H NMR spectrum shows two well-defined peaks at δ(¹H) = 9.93 ppm (s, HCOO⁻) and 3.33 ppm (d, PH, J₂H= 184 Hz). The integral ratio of the HCOO⁻ to PH protons equals 44:3, corresponding to a ratio of one PH molecule per 22 [Mg(O₂CH₂)] units. This low PH loading is explained by the relatively long time needed for sample preparation and grinding the crystals, which leads to partial release of phosphane. The ³¹P[¹H] solid-state NMR spectrum displays a broad signal, composed of four signals with different integral ratios at δ(³¹P[¹H]) = −250.17 ppm (41 %), −250.37 ppm (7 %), −250.68 ppm (50 %) and −251.02 ppm (2 %) (Figure S29). These signals are assigned to the Phosphorus species change over time (Figure S31): After 48 h the signal at δ(³¹P[¹H]) = −250.17 ppm disappears and the signal at δ(³¹P[¹H]) = −250.72 ppm represents the major orientation (73 %) of PH molecules in the MOF, followed by the signals at δ(³¹P[¹H]) = −250.38 ppm (23 %) and δ(³¹P[¹H]) = −251.11 ppm (4 %) (Figure S31) indicating that PH molecules reorient in the MOF with time. Only 8 % of the initial PH molecules leaked from the rotor under the conditions of the ³¹P MAS NMR experiment at 25 °C (Figure S33). At low temperature (95 K), a broad asymmetric ³¹P[¹H] signal at δ = −251.00 ppm is observed (Figure S41), which—after warming to room temperature—changes shape demonstrating the dynamic behavior of PH molecules and reordering processes inside the MOF with increasing temperature. The interaction of the adsorbed PH with the formate anions in the MOF is evident as a cross peak in the ¹H-³¹P cspHETCOR NMR spectrum (Figure S39). Furthermore, a cross peak between the PH protons and a signal of an impurity at δ(³¹P) = −217.00 ppm is visible. Commercially available PHH₂ is contaminated with PH₄, and we assign this coupling to an interaction of PHH₂ with PH₄, likewise adsorbed inside the MOF [Lit: δ(³¹P-(PH₄)) = −204.97 ppm].²⁰ To investigate possible PH₄ adsorption in more detail and to ascertain whether there is a certain degree of selectivity with respect to the adsorption of PHH₂, PH₄ and PH₃—the two latter are the most important by-products in commercial phosphane production—we carried out three experiments. First, single crystals of activated α-[Mg(O₂CH₂)] were pressurized with H₂. No H₂ uptake could be observed at room temperature, in line with previous reports.²¹ Next, we attempted to load diphosphane by suspending activated MOF single crystals in freshy prepared PH₄.²²,²³ The single crystals were subsequently collected and subjected to XRD analysis. The resulting structure is shown in Figure 3a,b. Molecules of PH₄ are observed in 2 possible positions (with occupancy factors of 70 % and 19 %, respectively) inside the MOF, aligned in zigzag fashion along each channel (Figure 3b).

We could not localize the hydrogen atoms of PH₄ due to disorder. However, we were able to refine P-P distances of 2.16 Å and 2.21 Å, which are in good agreement with an expected P-P single bond length of 2.20 Å.²⁴

In contrast to free diphosphane, which is highly pyrophoric, PH₄ adsorbed into the channels of α-[Mg(O₂CH₂)] shows excellent stability. PdH₂@α-[Mg(O₂CH₂)] is a non-pyro- phoric, air-, room temperature-, and UV/Vis-light-stable substance which can be kept in open air over several weeks. This betrays tight adsorption of PH₄ molecules, which remain inside the MOF even after 4 months of storage in air, with no sign of oxidation, as verified via single crystal XRD (26 % anisotropically refined) and 4 % (isotropically refined) occupancy. Figure S51. In contrast to PH₃, PdH₃ is not released from the MOF even when suspended in an organic solvent such as benzene. Its release is only possible upon dissolving PdH₂@α-[Mg(O₂CH₂)] crystals in degassed water. During this process, PdH₃ is degraded mainly to phosphorous acid, H₃PO₄, although a significant amount of PdH₄ is still present in the solution after 6 h (Figure S52). The different PH₃ and PH₄ affinities of the MOF were confirmed by density functional theory at the PBE/DND level of theory. Whereas adsorbed PH₃ is favorable by ∆E(PH₃) = −4.69 kcal mol⁻¹ relative to free PH₃ in the gas phase, MOF-bound PdH₃ is even more stable than the free PdH₄ with ∆E(PdH₄) = −6.70 kcal mol⁻¹ (Figure S55).

To determine the discriminating ability of α-[Mg(O₂CH₂)] towards the two phosphorus species, we subjected crystals of the MOF to a PH₃:PdH₄ (5:3) mixture, obtained serendipitously by hydrolysis of CaP₄ according to a procedure published by Baudler et al.²⁴ A ³¹P SS NMR spectrum of the loaded solid showed two broad non-symmetric signals at δ(³¹P) = −215.18 ppm (PdH₄) and δ(³¹P) = −249.00 ppm (PH₃) (Figure S53). In agreement with the rather fast release of PH₃, we found a decrease of the PH₃ signal integral over time while the integrated signal intensity for PdH₄ remained constant (Figure S54). After 90 h at room temperature, the integrated signal ratio of PdH₃:PdH₄ was 0.7, corresponding to a PH₃:PdH₄ molar composition of 4:3. Treating the sample under vacuum for additional 27 h at room temperature only very slightly diminished this ratio to 0.68. These findings are at first glance surprising since the...
PH$_3$ desorption time amounts to 6 h. However, the coadsorbed larger diphosphane molecules remain encapsulated in the MOF under these conditions and likely block exit channels for the smaller PH$_3$ molecules, which are therefore entrapped, a phenomenon often observed in filters.

The initially PH$_3$·P$_2$H$_4$ (4:3) filled MOF was investigated by TGA after 10 weeks of aging under inert gas. A constant mass decay starting from 40°C to 185°C was observed (Figure S56). In the TGA-coupled mass spectrometer a m/z signal of 34 g mol$^{-1}$ was found, confirming the PH$_3$ desorption. Mass spectrometry did not reveal any evidence for free PH$_3$. most likely due to its increasing thermal instability above 40°C. Likewise, a $^3$P$_2$ SS NMR spectrum of the heated MOF did not show any signals of PH$_3$, P$_2$H$_4$ or polyphosphine (Figure S57). These results motivate further investigations of α-[Mg(O$_2$CH)$_3$] for purification and stabilization of other highly reactive gaseous molecules.

Despite its apparent ubiquity and critical role in several industries, the synthetic potential of PH$_3$ is still very much underexplored due to its toxicity and pyrophoric nature. The inexpensive and environmentally friendly magnesium formate, α-[Mg(O$_2$CH)$_3$], lowers this risk to a minimum by trapping or storage material which can be handled in air. Although hydrogen directly passes through MOFs, the MOF does not show any signals of PH$_3$. While hydrogen directly passes through the MOF channels, PH$_3$ remains temporarily adsorbed, and diphosphane is trapped inside the MOF for at least 4 months. Relatedly, the strong adsorption of diphosphane enables the use of α-[Mg(O$_2$CH)$_3$] as a safe long-term P$_2$H$_4$ trapping or storage material which can be handled in air.

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Conflict of Interest

The authors declare no competing interests.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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Solid-State Investigation, Storage, and Separation of Pyrophoric PH$_3$ and P$_2$H$_4$ with α-Mg Formate

Phosphane, PH$_3$, is a highly pyrophoric and toxic gas that is often contaminated with H$_2$ and P$_2$H$_4$. The inexpensive α-Mg formate MOF adsorbs up to 10 wt% of PH$_3$ and allows safe handling of phosphane in air. This MOF is moreover a candidate for PH$_3$ purification and long-time P$_2$H$_4$ storage in air and at room temperature.