Surface reactions of phosphine (PH_3) with H or D atoms on icy surfaces at low temperatures

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Phosphine (PH_3) is one of the phosphorus (P)-bearing molecules identified in the interstellar medium (ISM) whose fractional abundance is 10^{-8} relative to H_2 in IRC +10216.[1] Since the interstellar PH_3 is considered to primarily form by grain surface reactions, it may have experienced several processes after its formation on grains. In the present study, we performed experimental and computational studies on the surface reactions of PH_3 with H or D atoms under the conditions in the ISM.

All experiments were performed using the Apparatus for Surface Reaction in Astrophysics (ASURA) system, which mainly consists of a stainless-steel vacuum chamber, multiple turbo molecular pumps, an aluminum (Al) substrate attached to a closed-cycle helium cryostat, a quadrupole mass spectrometer, and an FTIR spectrometer. Gaseous PH_3 was produced by the reaction of calcium phosphide (Ca_3P_2) with water in a vacuum vessel and was deposited onto the reaction substrate covered with water ice (porous amorphous, compact amorphous, or crystalline) with a thickness of 30 monolayers at 10 K. Atomic H or D was produced by the dissociation of H_2 or D_2 in the microwave-induced plasma and cooled to 100 K before collisions with the substrate. The reaction was monitored in-situ by FTIR, and the desorbed products were detected by the QMS. Details of the computational method for the calculation of the binding energy of P-bearing species on ice and the reaction dynamics were shown elsewhere.[2]

When solid PH_3 was exposed to H atoms on ices at 10 K, the peak intensity of the P-H stretching band at 2320 cm^{-1} decreased with atom exposure times, and ~80% of the initial PH_3 was lost from the substrate after 20 min. Any other P-bearing products were not confirmed in the FTIR analysis. We expect that the initial process for the reaction of solid PH_3 with an H atom is the H-abstraction from PH_3 ($PH_3 + H \rightarrow PH_2 + H_2$), followed by the H addition to the formed PH_2, resulting in the formation of PH_3 again ($PH_2 + H \rightarrow PH_3$). In that case, the net abundance of solid PH_3 should not change even after the H-abstraction and addition reactions. The observed phenomena may be explained by the loss of PH_3 from the icy surface by chemical desorption, which utilizes the heat of reaction for the desorption of a molecule from a substrate.[3]

When solid PH_3 was exposed to D atoms, a new peak appeared at 1686 cm^{-1}, which can be assigned to the P-D stretching band for deuterated phosphines such as PH_2D, PHD_2, and PD_3. Of note, with increasing D-exposure time, the peak intensity of the P-D stretching band decreased. This is reasonably explained by the preferential H-D substitution of PH_3 followed by the chemical desorption of its deuterated species. In the presentation, more detailed quantitative experimental and computational results will be presented.

[1] Agundez, M. et al. *Astrophys. J. Lett.* 2014, *790*, L27.
[2] Nguyen, T. et al. *Astrophys. J.* 2021, 918, 73.
[3] Oba, Y. et al. *Nat. Astron.* 2018, 2, 228.