Reactions of Diatomic PH in Low-temperature Matrices: New Molecules and Mechanisms

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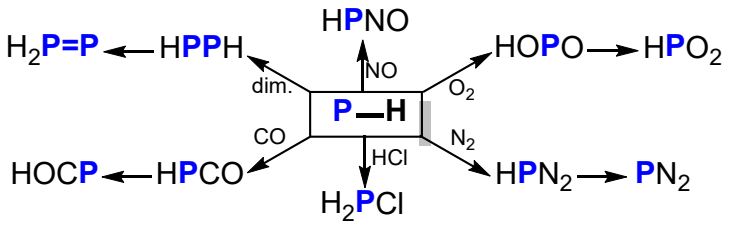

Diatomic PH is the simplest phosphorus-containing molecule that is highly reactive due to its triplet spin multiplicity in the ground state, and it serves as a transient intermediate in the decomposition reactions of phosphine (PH_3). In contrast to the broad applications of PH in synthetic phosphorus chemistry, its fundamental reactivity remains scarcely explored due to the instability at ambient conditions. By using matrix-isolation IR and UV-vis spectroscopy, the reactions of PH with small molecules including CO, NO, O_2, N_2, and HCl have been studied. A number of exotic phosphorus-containing small molecules have been synthesized and characterization.[1-6] Furthermore, the novel structures and reactivity of these molecules have been disclosed from both aspects of experiment and theory. For instance, the oxidation of PH by O_2 yields monomeric metaphosphorous acid HOPO, an important intermediate in the atmospheric degradation of organic phosphorus compounds (OPCs). In stark contrast to the properties of the famous HONO analogue, spontaneous conformational conversion in HOPO through quantum mechanical tunneling (QMT) can be observed in solid N_2-matrix at 2.8 K. Furthermore, the photolysis of HOPO yields the parent dioxophosphorane HPO_2 and a novel hydroxyl radical complex OH-OP. This hydrogen-bonded complex is extremely unstable, since it can convert to HOPO by overcoming a rather low activation barrier of 0.28 ± 0.02 kcal mol^{-1} as derived from the experimental kinetics in the Ar-matrix at temperatures above 12.0 K.

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