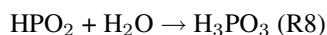
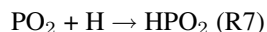
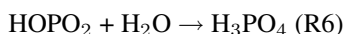
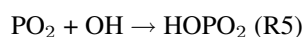
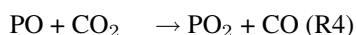
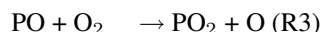
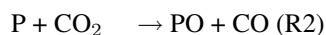
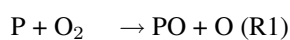


## Atmospheric Oxidation Chemistry of Meteor Ablated Phosphorus

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Phosphorus, P, is a key biological element with major roles in replication, information transfer, and metabolism. Interplanetary dust particles contain  $\sim 0.1\%$  P by weight, and meteoric ablation in the  $1\ \mu\text{bar}$  region of a planetary upper atmosphere can generate significant amounts of atomic P, which will then undergo atmospheric processing before deposition at the surface. Orthophosphate (oxidation state +5) is the dominant form of inorganic P at the Earth's surface; however, due to the low water solubility and reactivity of such P(V) salts, they have a poor bio-availability. In contrast, less oxidised forms of P (oxidation state  $\leq +3$ ) are far more bio-available. It has been suggested that these reduced forms of P may have originated from extra-terrestrial material that fell to Earth during the heavy bombardment period. Previous studies have focused on the direct delivery of P to the surface in meteorites, to undergo processing through aqueous phase chemistry. In contrast, the atmospheric chemistry of P has so far been ignored.

The vaporized P atoms entering the upper atmospheres of the terrestrial planets will undergo chemical processing to form a variety of compounds in which P may exist in different oxidation states due to the presence of both oxidizing and reducing agents. Initial oxidation of P is likely to proceed *via* reactions 1-4 to produce  $\text{PO}_2$ . From  $\text{PO}_2$ , an exothermic route to phosphoric acid exists *via* the formation of  $\text{HOPO}_2$  (R5-6); however, the bio-available compound phosphonic acid ( $\text{H}_3\text{PO}_3$ ) should also form *via*  $\text{HPO}_2$  (R7-8):



Using a pulsed laser photolysis (PLP)-laser induced fluorescence (LIF) technique, reactions R1-4 have been studied as a function of temperature for the first time. P atoms were generated in the presence of  $\text{O}_2$  and  $\text{CO}_2$  by PLP of  $\text{PCl}_3$ , and the subsequent growth and decay of the PO radical monitored by LIF. Initial investigations into the reaction of  $\text{P} + \text{O}_2$  (R1) indicated an inverse pressure dependence, with the rate decreasing with increasing pressure. We attribute this pressure dependence to the interference of two reactive low-lying metastable states of P (the  $^2\text{D}$  and  $^2\text{P}$  states), which are quenched at higher bath gas pressures. Thus by conducting experiments at high bath gas pressures ( $\sim 20$  torr) rate coefficients for the reaction of ground state  $\text{P}(^4\text{S})$  could be measured. The removal rates of both excited states of P with  $\text{O}_2$  and  $\text{CO}_2$  have also been investigated, and studies of the reactions of  $\text{PO}_2$  (R5 and R7) are currently underway.

In addition to understanding the reaction kinetics, the ablation process is also under investigation. Using a meteoric ablation simulator, the temperature at which P and PO ablate from apatite, a phosphorus rich mineral, has been measured, and compared with a computer model of the process.