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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 ~0.1% P by weight, and meteoric ablation in the 1 μbar 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 PO_2. From PO_2, an exothermic route to phosphoric acid exists *via* the formation of $HOPO_2$ (R5-6); however, the bio-available compound phosphonic acid (H_3PO_3) should also form *via* HPO_2 (R7-8):

$$P + O_2 \rightarrow PO + O \text{ (R1)}$$

$$P + CO_2 \rightarrow PO + CO \text{ (R2)}$$

$$PO + O_2 \rightarrow PO_2 + O \text{ (R3)}$$

$$PO + CO_2 \rightarrow PO_2 + CO \text{ (R4)}$$

$$PO_2 + OH \rightarrow HOPO_2 \text{ (R5)}$$

$$HOPO_2 + H_2O \rightarrow H_3PO_4 \text{ (R6)}$$

$$PO_2 + H \rightarrow HPO_2 \text{ (R7)}$$

$$HPO_2 + H_2O \rightarrow H_3PO_3 \text{ (R8)}$$

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 O_2 and CO_2 by PLP of PCl_3, and the subsequent growth and decay of the PO radical monitored by LIF. Initial investigations into the reaction of P + 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}D and ^{2}P states), which are quenched at higher bath gas pressures. Thus by conducting experiments at high bath gas pressures (~20 torr) rate coefficients for the reaction of ground state P(^{4}S) could be measured. The removal rates of both excited states of P with O_2 and CO_2 have also been investigated, and studies of the reactions of 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.