The two faces of phosphorus

Jonathan R. Nitschke considers how the story of phosphorus, an element that glows without fire, nicely illustrates the pursuit of scientific knowledge — including how such knowledge goes on to serve many purposes, for better or for worse.

Among the rainbow of other phosphorus allotropes — red, purple and black — the white allotrope, P_4, was the first discovered and has the most interesting story. Its cold glow generated awe and wonder among the seventeenth-century audience that first beheld it, and served as a beacon to the curiosity of the first modern scientists, who carried out experiments into its properties and uses. Their narrative is our own — the struggle to shine the light of reason on the dark myths of our ancestors, using the empirical method to draw deep and predictively useful knowledge out of shadows. Yet the pale fire of phosphorus also serves as a warning light to us across the centuries, for much of this knowledge was not used to benefit humanity.

The discoverer of P_4 is believed to have been Hennig Brandt of Hamburg, whose quest for the philosopher's stone led him, in around 1669, to pyrolyse in a furnace the solid residue of human urine[1]. The yellow-white sublimate he obtained displayed the remarkable property of luminescence, emitting light without the flames, heat and smoke associated with combustion. Only in 1974 were the glowing species revealed to be transient oxidation products (HPO and P_2O_2) that form on the surface of P_4 by reaction with atmospheric oxygen[2]. These species form in electronically excited states, and their decay back to the ground state occurs with spontaneous emission of visible light.

The slow, luminescent oxidation of white phosphorus can readily gain speed — in the bulk, P_4 is known to be pyrophoric, catching fire spontaneously in air. This easy flammability, moderated by combining P_4 with inert materials, served to make the first cheap and reliable matches, known as 'Lucifers', the name of the best-selling brand. Lucifers were outlawed worldwide during the first years of the twentieth century because they were dangerous to property — a fire

could be started by carelessly jostling a box of matches — and also to health. White phosphorus is nearly as toxic as cyanide, and chronic exposure led to an awful form of bone necrosis among match workers known as 'phossy jaw'.

The toxicity and spontaneous flammability of P_4 make it a terrible weapon. During the Second World War, both sides dropped many tons of P_4 on each others' cities in incendiary bombs that released an incandescent rain of burning liquid phosphorus. Phosphorus burns are grievous — P_4 continues to burn on skin and 'burrows' into flesh. In addition, the phosphoric anhydride (P_4O_{10}) produced by burning readily hydrolyses into phosphoric acid (H_3PO_4), dehydrating and causing acid burns.

Research carried out before and during the Second World War revealed an even more terrible use for phosphorus: a few organophosphate esters with P-linked substituents, such as fluoride and cyanide, were shown to act as highly potent acetylcholine esterase inhibitors. These nerve agents, as they came to be called, are among the most toxic human poisons known, killing through the disruption of essential nerve activity.

In contrast to these nefarious uses, phosphate (PO_4^{3-}) is an essential nutrient for all living organisms. It can be found, for instance, in the backbone of DNA; in adenosine triphosphate, which shuttles energy between biomolecules; and in hydroxyapatite, which is a form of basic calcium phosphate that makes up bones. Other organophosphates, although similar in structure to nerve agents, proved much more toxic to pests than human beings. Those had a role in the 'green revolution' of the 1960s, which saw agricultural yields improve in many parts of the world. Examples include glyphosate (also known as Roundup), which acts as a potent weed killer, and malathion, which inhibits arthropod versions of acetylcholine esterase more effectively than mammalian versions, thus killing insects.

Recently, phosphorus has found a variety of new uses, in particular in the context of new phosphine ligands (R_3P, where R is an alkyl or aryl group) for metal-catalysed transformations. The Nobel Committee have honoured the discoverers of both ruthenium-catalysed alkene metathesis and palladium-catalysed C–C bond-forming reactions, both of which depend on organophosphine ligands. Black phosphorus, which has a graphite-like sheet structure, is an electrical conductor of interest in rechargeable batteries. Elemental P_4 has even recently been rendered insensitive to oxygen through encapsulation in a host molecule, allowing its reactivity to be modulated[3].

New applications of phosphorus chemistry are assured by the element's utility and ubiquity. We hope that our better angels will guide us in these enquiries, rather than the demons that saw phosphorus forged into weapons of war. ❐

References

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