

Monsieur de Maupassant and Phosphure de Calcium

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The other day, while idly thumbing through a rather thick volume of the collected short stories of the 19th-century French author, Guy de Maupassant (figure 1), my eye caught a paragraph designed to excite the interest of any full-blooded chemist worth his salt and, I suppose, his acids and bases as well. It read (1):

I had just finished my second term at college and had been particularly interested in chemistry and especially in a compound called phosphure de calcium which, when thrown in water, would catch fire and explode, followed by fumes of an offensive odor. I had brought a few handfuls of this compound with me, so as to have fun with it during my vacation.

“Phosphure de calcium” or tricalcium diphosphide, as it is now known to English-speaking chemists, was first made by George Pearson in 1792 by passing phosphorus vapor over quicklime heated to dull redness. The resulting product was a mixture of

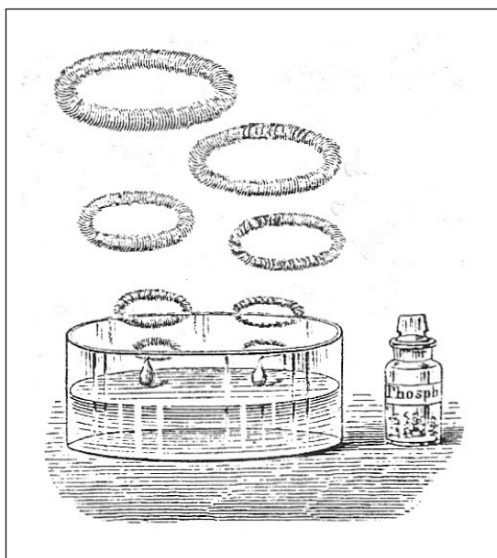


Figure 2. Characteristic smoke rings of P_4O_{10} produced by the hydrolysis of tricalcium diphosphide as depicted in R. Arendt, L. Doermer, *Grundzüge der Chemie und Mineralogie*, Voss: Leipzig, 1919, p. 288.

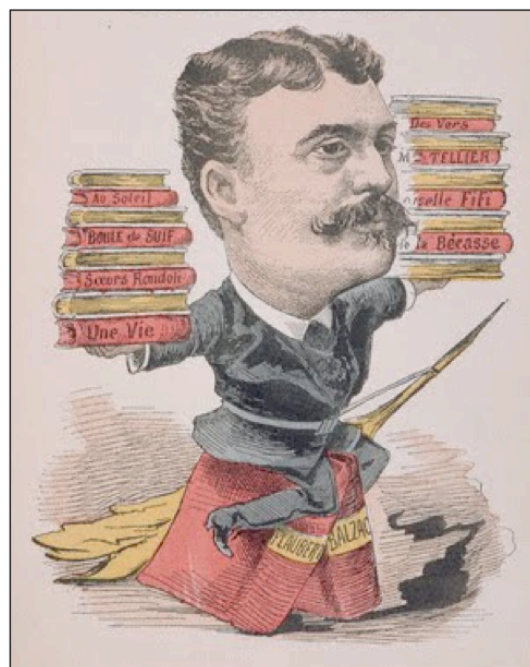
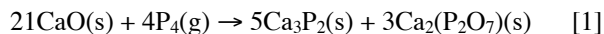
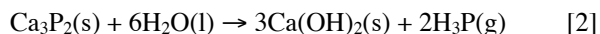


Figure 1. A period caricature of Guy de Maupassant (1850-1893).

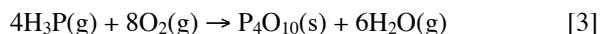
impure tricalcium diphosphide and dicalcium pyrophosphate (2):



It was later made in a much purer form by P. Vigier by melting calcium and phosphorus together under petroleum (3). When dropped in water, Ca_3P_2 hydrolyzes to give calcium dihydroxide and trihydrogen phosphide gas, otherwise known as phosphine or monophosphane:



and the latter ignites on contact with air, generating characteristic circular rings of white tetraphosphorus decaoxide (figures 2 and 3):



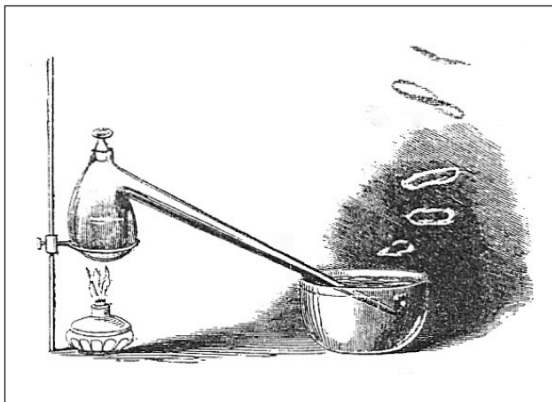
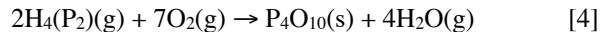


Figure 3. Characteristic smoke rings of P_4O_{10} produced by the spontaneous ignition of the hydrides of phosphorus generated by heating white tetraphosphorus in a concentrated KOH solution as depicted in J. H. Pepper, *The Boy's Playbook of Science*, Routledge: London, 1860, p. 171.

As written, these reactions are actually oversimplifications, since it turns out that pure trihydrogen phosphide is not spontaneously flammable. Rather it is the minute traces of tetrahydrogen polydiphosphide or $H_4(P_2)$ gas, generated simultaneously by the hydrolysis reaction, that in reality cause the mixture to ignite:



This, in turn, probably results from the contamination of the Ca_3P_2 with dicalcium polydiphosphide, $Ca_2(P_2)$, a compound which, when pure, gives $H_4(P_2)$ as the primary product of its hydrolysis (4):



This supposition is further supported by the fact that pure Ca_2P_3 has a blackish-violet appearance, whereas the product generated in equation 1 is reddish-brown, suggesting contamination with the brick-red polydi-

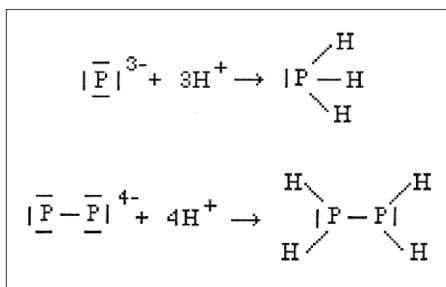


Figure 4. The structural interpretation of reactions 3 and 4 as phosphide anion protonations.

phosphide. In addition, Mg_3P_2 , which has no corresponding $Mg_2(P_2)$ analog, does not give a spontaneously flammable product upon hydrolysis (5).

The structural interpretation of these reactions is also of some interest. Both Ca_3P_2 and $Ca_2(P_2)$ are so-called Zintl phases (i.e., compounds representing the transition from ionic to metallic bonding) and both their structures and hydrolysis reactions can be rationalized in terms of the generalized 8-N rule (6). If the compounds are formally treated as having pure ionic bonding involving positive calcium ions, on the one hand, and appropriately charged phosphorus atoms, on the other, then the phosphorus atoms will homocateenate to give covalently-bonded polyphosphide anions with structures similar to those of a neutral isoelectronic element.

Thus, in Ca_3P_2 , the P atoms are formally P^{3-} anions. They are, therefore, isoelectronic with Ar atoms and should exist as isolated monoatomic phosphide anions in the solid compound. No complete crystal structure appears to have been done on Ca_3P_2 but the isoelectronic species Be_3P_2 , Mg_3P_2 , Sr_3P_2 , and Ba_3P_2

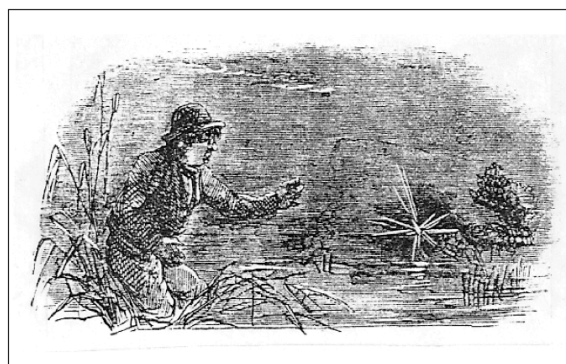


Figure 5. A 19th-century depiction of an unwary traveler being lured into a swamp by a Will-o'-the-wisp as found in J. H. Pepper, *The Boy's Playbook of Science*, Routledge: London, 1860, p. 172.

all have structures consistent with this prediction and there is no reason to suspect that the calcium compound is an exception (7). Likewise, in $Ca_2(P_2)$ the P atoms are formally P^{2-} ions and are thus isoelectronic with Cl atoms. Consequently we would expect them to dimerize into polydiphosphide P_2^{4-} anions, paralleling the formation of diatomic Cl_2 molecules, an expectation which is again confirmed by the crystal structure (8). The hydrolysis reactions of the two compounds may, therefore, be viewed as direct anion protonations, as shown in figure 4.

The spontaneous ignition of H_3P and $H_4(P_2)$ gas generated by the decomposition of dead organic matter,

particularly in peat bogs, swamps, and damp cemeteries, has been traditionally invoked to explain away the phenomenon of *ignis fatuus* (figure 5) or silly fire, also variously known as Jack-o'-lanterns, Will-o'-the-wisps, *feux follets*, corpse candles, and flying saucers (5), though the validity of this and other traditional rationales (e.g., electrical plasmas, combustion of methane, bioluminescence, etc.) has been recently challenged by Mills, who was, however, unable to suggest any satisfactory alternative explanation (9).

Given the above chemistry and the knowledge that Maupassant's short story is entitled "A Practical Joke," it is not difficult to imagine what must follow. The narrator, home from school for summer vacation, is particularly irritated by one of his father's house guests (1):

An old lady named Mme. Dufour often visited us. She was a cranky, vindictive old thing. I do not know why, but somehow she hated me. She misconstrued everything I did or said, and she never missed a chance to tattle about me ... She wore a wig of beautiful brown hair, though she was more than sixty, and the most ridiculous little caps adorned with pink ribbons. She was well thought of because she was rich, but I hated her to the bottom of my heart, and I resolved to revenge myself by playing a joke on her.

Waiting until evening, the would-be jokester sneaks up to Mme. Dufour's rooms. Carefully drying the chamber pot and filling it with a handful of calcium phosphide, he then runs to his garret bedroom to await developments (1):

Pretty soon I heard everyone coming upstairs to bed. I waited until everything was still, then I came downstairs barefooted, holding my breath, until I came to Mme. Dufour's door and looked at my enemy through the keyhole.

She was putting her things away, and having taken her dress off, she donned a white wrapper. She then filled a glass with water and putting her whole hand in her mouth as if she were trying to tear her tongue out, she pulled out something pink and white which she deposited in the glass. I was horribly frightened, but soon found it was only her false teeth she had taken out. She then took off her wig ... kneeled down to say her prayers, got up and approached my instrument of vengeance. I waited awhile, my heart beating with expectation.

Suddenly I heard a slight sound; then a series of explosions. I looked at Mme. Dufour; her face was a study. She opened her eyes wide, then shut them again and looked. The white substance was crackling, exploding at the same time, while a thick white smoke

curled up mysteriously toward the ceiling.

Perhaps the poor women thought it was some satanic fireworks, or perhaps that she had been suddenly afflicted with some horrible disease; at all events, she stood there speechless with fright, her gaze riveted on the supernatural phenomenon. Suddenly she screamed and fell swooning to the floor. I ran to my room, jumped into bed, and closed my eyes trying to convince myself that I had not left my room and had seen nothing.

"She's dead," I said to myself; "I have killed her," and I listened anxiously to the sound of footsteps. I heard voices and laughter and the next thing I knew my father was soundly boxing my ears.

Mme. Dufour was very pale when she came down the next morning and she drank glass after glass of water. Perhaps she was trying to extinguish the fire which she imagined was in her, although the doctor assured her that there was no danger. Since then, when anyone speaks of disease in front of her, she sighs and says: "Oh, if you only knew! There are such strange diseases"

Regrettably, standard biographies of Maupassant are silent on whether he ever received any formal chemical training, though they do point out that he was a realist and claim that he never wrote about anything he hadn't directly experienced for himself. Indeed, Mme. Dufour's reactions may not have been completely psychological in nature. Phosphine gas is highly toxic, causing cold sweats, weakness, extreme thirst, and, in large amounts, death by paralysis of the respiratory system. Mellor reports that one part of phosphine per 100,000 parts of air is fatal in 16-30 hours, 2.5 parts per 100,000 in 8.5-10 hours, and one part per 10,000 in 2.5-3.5 hours (5). Presumably, these data were obtained using white mice rather than summer house guests.

References and Notes

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