

Special Materials in Pyrotechnics:

IV.^[1] The Chemistry of Phosphorus and its Compounds

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ABSTRACT

The combustion chemistry of phosphorus and its compounds in pyrotechnic applications is discussed. Whereas red phosphorus (RP) and phosphorus sulfides can be used as fuels, the phosphates can be used as oxidizers in metal-containing pyrolants. Phosphorus combustion mainly occurs in the gas phase after volatilization of the parent phosphorus source, be it P_4 or P_{red} . The enormous sensitivity of RP and its mixtures is mainly due to high strain in red phosphorus building blocks and trace amounts of phosphoric acids formed in non-stabilized RP. The inherent danger of RP/chlorate mixtures is believed to result for the most part from acid-base reactions in non-stabilized RP mixtures leading to the highly reactive species ClO_2 , which will trigger ignition.

Keywords: red phosphorus, phosphate, phosphide, white phosphorus, chlorate, smoke, Armstrong's mixture

Introduction

Aside from group one of the periodic system of elements (Li–Cs), only the 15th group (N–Bi) finds full application in pyrotechnics. Whereas nitrogen is nearly ubiquitous as nitrate (NO_3^-), dinitramide ($N(NO_2)_2^-$) or nitroformate ($C(NO_2)_3^-$) in oxidizers, arsenic (As) has found application as realgar (As_4S_4) in white fire Bengal applications. Likewise antimony (Sb) is used as metalloid or sulfide (Sb_2S_5) in white fire and glitter applications. Finally bismuth (Bi) is applied as the oxide, Bi_2O_3 , as an oxidizer in both delay elements and micro-crackling star applications^[2,3] and most recently the sulfide (Bi_2S_3) has found

introduction as non-toxic fuel in delay compositions.^[4]

Phosphorus (P), the element from the second row of group 15, is very well known as a potent fuel in pyrotechnics. Nevertheless phosphorus is not an everyday fuel, although applied in everyday products such as safety match strikers. This striking situation arises from the special properties of phosphorus, which are high flammability at room temperature and inherent sensitivity to electrostatic discharge, mechanical impact and heat.

Among the fuels applied in pyrotechnics, phosphorus plays a prominent role. The proverbial polymorphy of the element and the application of the element in everyday articles like safety matches, in countermeasure ammunition, and finally in such inhumane devices as incendiary bombs require a detailed look at the element and its compounds in pyrotechnic applications.

It is the purpose of the present paper to give an overview of the chemistry of phosphorus and its combustion in pyrotechnics. An exhaustive review on red phosphorus and its application in screening smoke compositions has been written by Davies.^[5] The discussion of general military applications of phosphorus is the subject of an upcoming paper.

Modifications of Phosphorus

When discussing phosphorus, one has to look at the modifications of the element (allotropes) in general. Virtually no other element occurs in such a large number of modifications. Nevertheless within the scope of this paper only two modifications will be addressed, the white tetrahedral (P_4) and the red amorphous (P_x).

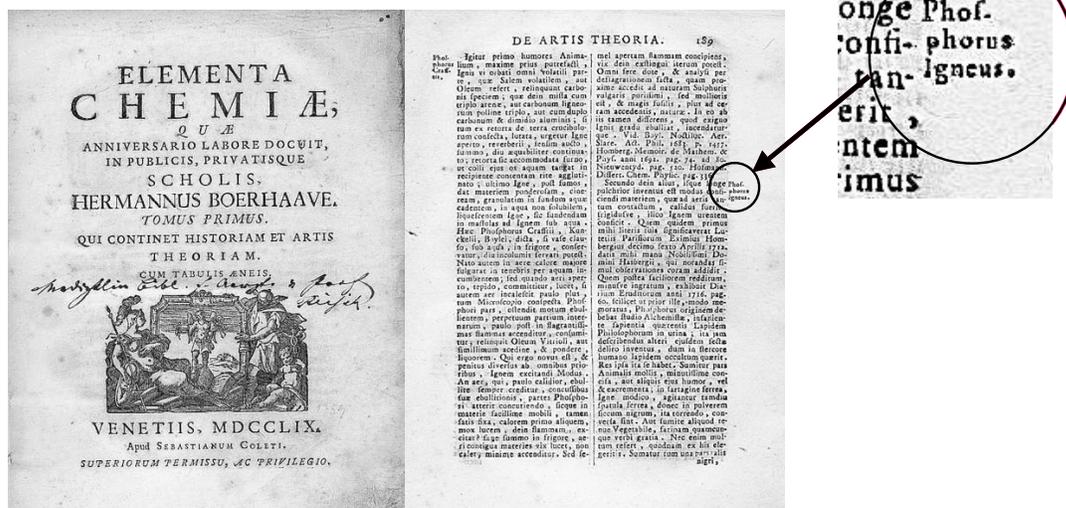


Figure 1. *Elementa Chemiae* of Hermannus Boerhaave, Vol. 1 from 1759, page 178 refers to white phosphorus probably for the first time in chemical literature.^[7]

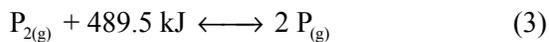
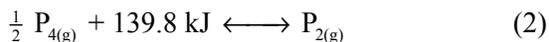
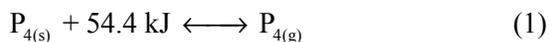
Phosphorus was originally discovered by the German pharmacist Hennig Brand in the year 1669 while fusing a mixture of urine, limestone and coal in a porcelain retort. After several hours of heat treatment Brand observed a green glowing substance, which was condensed white phosphorus. A fascinating-to-read book about the discovery, application and history of this element has been written by J. Emsley.^[6] Figure 1 shows one of the first monographs on chemistry mentioning igniting phosphorus^[7] written by Hermannus Boerhaave, who was born just one year before the element's discovery in 1668. Although phosphorus was discovered in the 17th century, Lavoisier in the 18th century was the first to recognize it as an element.

Table 1 displays the most important modifications of phosphorus.

White Phosphorus (WP)

White phosphorus (P₄) is the modification that originally gave the element its name (Greek: fosforos = light carrier) due to its white-green chemiluminescence in the air,^[8] most impressively observed in a dark room. White phosphorus is the starting material for the synthesis of any other phosphorus allotrope as can be seen from Figure 2.

In the cold, white phosphorus (WP) is a brittle substance showing conchoidal fracture and becoming waxy at ambient temperature. Under an inert atmosphere—otherwise it would enflame—WP fuses at 44.1 °C to give a clear and highly refractive liquid. The melt vaporizes at 280 °C. In both the condensed and gas phases, phosphorus is composed of P₄ molecules. Above 800 °C, in the gas phase, the P₂ units start to form which dissociate again at T > 2000 °C to give monatomic P_(g).



Due to the tetrahedral geometry of the P₄ molecule, it is highly reactive as can be seen from its low ignition temperature of 35 °C. Finely dispersed white phosphorus ignites spontaneously at ambient temperature. WP is soluble in many organic solvents and also in PCl₃ and PBr₃. At T > 200 °C white phosphorus slowly transforms into modifications having higher thermodynamic stability such as red, violet and black phosphorus as can be seen in Figure 2.

Table 1. Properties of Phosphorus Modifications.

Parameter	Unit					
Designation		P	White	Red	Hittorf	Metallic
CAS-No.			[12185-10-3]	[7723-14-0]	[7723-14-0]	[7723-14-0]
Constitution	—		$P_{4(s)}$	P_x	$(-P_8P_2P_9-)_x$	$(-P_6-)_n$
Atomic mass	A.U.	30.9738				
Color			White-yellow	Orange-violet red	Violet-brown	Silvery, graphite like
Density	$g \cdot cm^{-3}$		1.82	~ 2.3	2.36	2.69
Melting point	$^{\circ}C$		44.25	~590 subl.	~ 620 subl.	>620 subl.
Boiling point	$^{\circ}C$		281	n.a.	n.a.	n.a.
Structure			P_4	amorphous	$((P_8)(P_2)(P_9))_n$	$(P_6)_n$
Resistivity	$\Omega \cdot cm$		none	$>10^9$	none	>1000
Solubility			in organic solvents	no	no	no
Toxicity			yes	no	no	no
Odor			fishy	fishy	fishy	mild fishy
Ignition Temperature	$^{\circ}C$		ambient temperature	~ 300	~ 400	~ 500

Due to both its high reactivity and solubility in organic media, white phosphorus is highly toxic. MAW (*Maximum Allowable Workplace concentration*) according to German regulations is 0.15 mg m^{-3} .

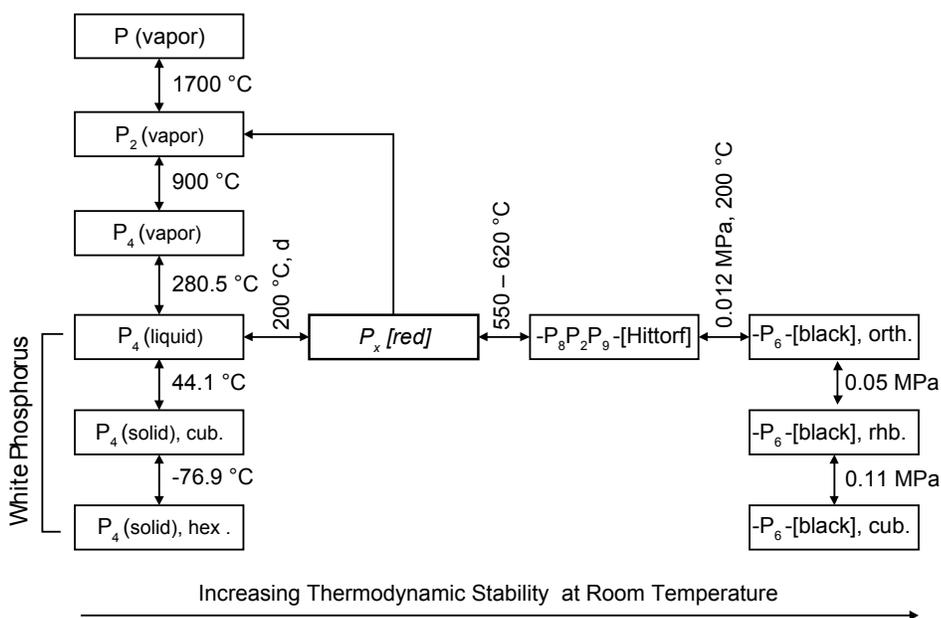


Figure 2. Simplified phase diagram of phosphorus.

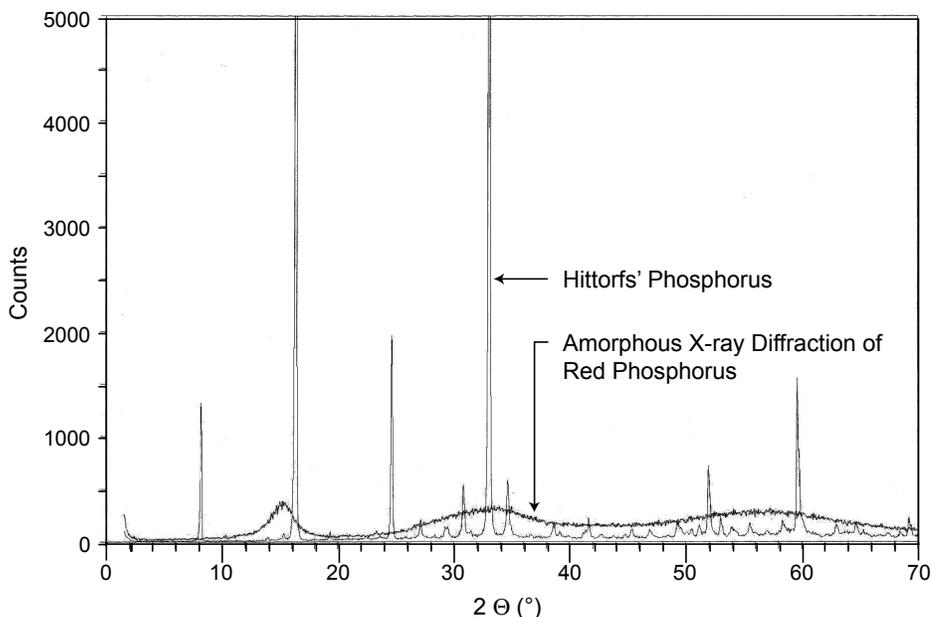


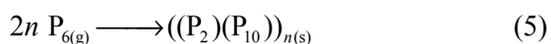
Figure 3. X-ray diffraction of red phosphorus overlaid with crystalline Hittorf's phosphorus

Red Phosphorus (RP)

Whereas defined structures can be assigned to white, violet and the black modification, red phosphorus is an amorphous material whose microscopic structure properties and appearance are strongly dependent on the type of synthesis. Hence red phosphorus cannot be designated as an allotrope but rather as an undefined mixture of phosphorus allotropes. Since the type of production strongly influences the properties of the red phosphorus, it is not possible to give exact physical values for any of the properties of the material but only broad ranges.

With decreasing grain size RP will appear as a violet-brown to orange-red powder.^[9]

Although amorphous with respect to X-ray diffraction (Figure 3) several molecular building units of the red phosphorus have been resolved in the last years. According to Pfitzner^[10] and Hartl^[11] the main constituents of RP are chains made from alternating (P₂)(P₁₀)-units. Those have been assumed to form upon dimerisation of bullvalene-type P₆ units as has been found by Schröder.^[12]



The structural building blocks of the (P₂)(P₁₀) strongly resemble the known pentagonal tube units found in the violet allotrope that is the "Hittorf's phosphorus", which is composed of cross-layers of ((P₈)(P₂)(P₉))_n units. This explains the ease of formation of the latter modification upon slow heating of red phosphorus, which can be interpreted in terms of a rearrangement of bonds into the more stable and less strained pentagonal tube conformation.

In addition red phosphorus is said to comprise units made from condensed butterfly units. These units are formally built by opening an edge of the P₄-tetrahedron and fusing the free valences to give a new σ-bond between the still highly strained butterfly units.

At present a minimum of two identified different structural building units are responsible for the entire macroscopic structure and behavior of RP. It is also clear that the ratio of both units will strongly depend on the formation mechanism and thus properties vary dependent on the manufacturing process.

Recently Pfitzner and co-workers succeeded in isolating two new allotropes of phosphorus, **1** and **2** by treating both (CuI)₈P₁₂ and (CuI)₃P₁₂ with aqueous KCN solution. Phosphorus **1** consists of nano-rods made from P₈-cages con-

nected by P_4 rings $((P_8)(P_4))_n$, and phosphorus 2 consists of P_{10} cages that are linked by P_2 units $((P_{10})(P_2))_n$.^[13]

Whereas the latter $((P_8)(P_4))_n$ and $((P_{10})(P_2))_n$ units are thermodynamically stable and relatively unstrained, the above mentioned butterfly units impart high strain into the red phosphorus. It is hence that the strain may be released upon energy input such as impact, friction, heat or electrostatic discharge to give free valences which in turn cause self ignition of the material. In addition slow phase transition processes yielding free valences have to be considered when focusing at the long-term stability of red phosphorus.

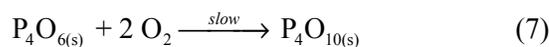
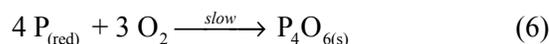
The “crystallization” of red phosphorus was the object of a diploma thesis by Rudolf.^[14]

Reactions of Phosphorus

Long-Term Reactions

Red phosphorus is prone to reactions that pose some difficulties when considering long term storage of pyrotechnic compositions. Oxidative and hydrolytic degradation of red phosphorus is especially pronounced with small particles sizes ($<10 \mu\text{m}$). Shechkov and coworkers^[9] have found that oxidation of small fraction RP

($<10 \mu\text{m}$) occurs much faster than could be solely explained on the basis of greater surface area. This is explained on the basis of differing chemical constitution of the different fractions, as was demonstrated by different absorption band edge. The primary degradation reaction either in the presence or absence of water is the oxidation of red phosphorus to give phosphorus trioxide.



These products in turn react with atmospheric moisture to give

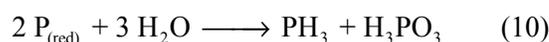


Figure 4 shows the FTIR spectrum of non-stabilized red phosphorus. The labeled peaks on the spectrum clearly display the signatures of P_4O_6 , H_3PO_3 and H_3PO_4 . These byproducts would lead to severe degradation of any pyrotechnic composition if included. Thus red phosphorus has to be treated in order to impede the formation of these byproducts. Norris^[15] has investi-

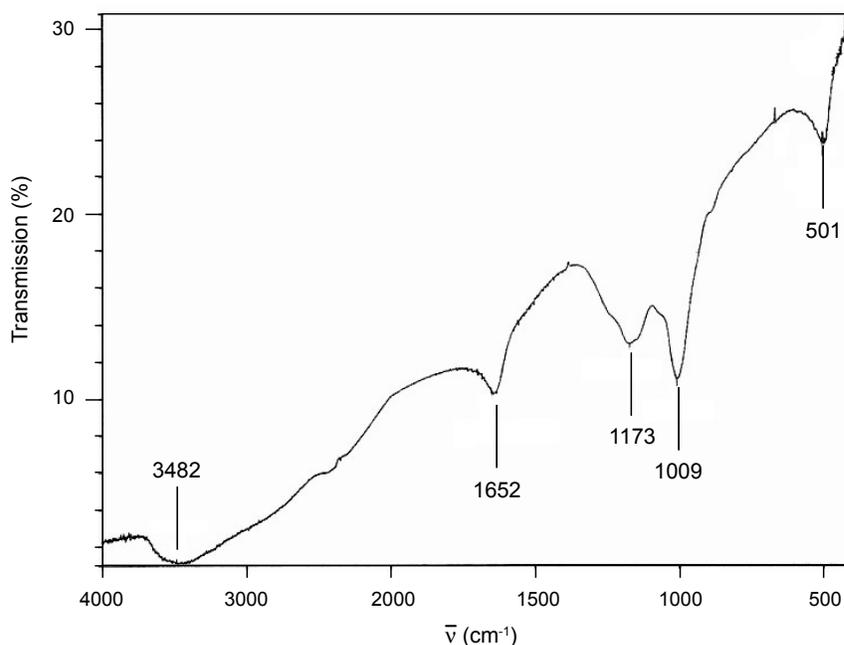


Figure 4. FTIR-spectrum (KBr) of non-stabilized red phosphorus.

gated the degradation of red phosphorus under the influence of air and moisture. Walz and Beard have investigated the action of water on RP.^[36]

Stabilisation of Red Phosphorus

To avoid problems with long term stability of red phosphorus, manufacturers treat the raw material in several ways. These treatments include:

- oiling with low melting paraffins, as dust suppressants,
- microencapsulation, as a protective measure against impact, friction and action of chemical agents,
- basic and amphoteric substances to buffer traces of phosphorus acids that themselves have been found as to catalyze the above side reactions and
- stabilizers to impede the phosphane (PH_3) formation.

Epoxy resins are employed as microencapsulation agents, which cover the pure RP grain. In addition the encapsulation process reduces the free surface by scavenging the dust that would be otherwise very prone to ignition due to, for example, adiabatic compression. These encapsu-

lating agents are additionally treated with phthalic acid esters to render the protective coat more flexible in order to reduce the mechanical sensitivity. In the past the hydroxides of both magnesium and aluminum have found application as buffer substances. Today tin-oxide hydrates ($\text{SnO}\cdot(\text{H}_2\text{O})_n$) are applied as state-of-the-art inhibitors against phosphane formation.

Figure 5 displays the FTIR spectrum of HB 700 red phosphorus manufactured by Clariant, the world's leading manufacturer of red phosphorus. Only trace signatures of the above discussed byproducts are discernible. The development of stabilized red phosphorus has been described by Hoerold, Ratcliff^[16] and Eisen-träger.^[17] Lissel^[18] from German WIWEB has conducted a comparative investigation on the stability of several commercially available red phosphorus types.

Incompatibilities of Red Phosphorus

Many severe accidents are reported in the literature from the handling of red phosphorus especially when inexperienced persons such as children are involved. These accidents are due to some chemical incompatibilities of the red phosphorus.

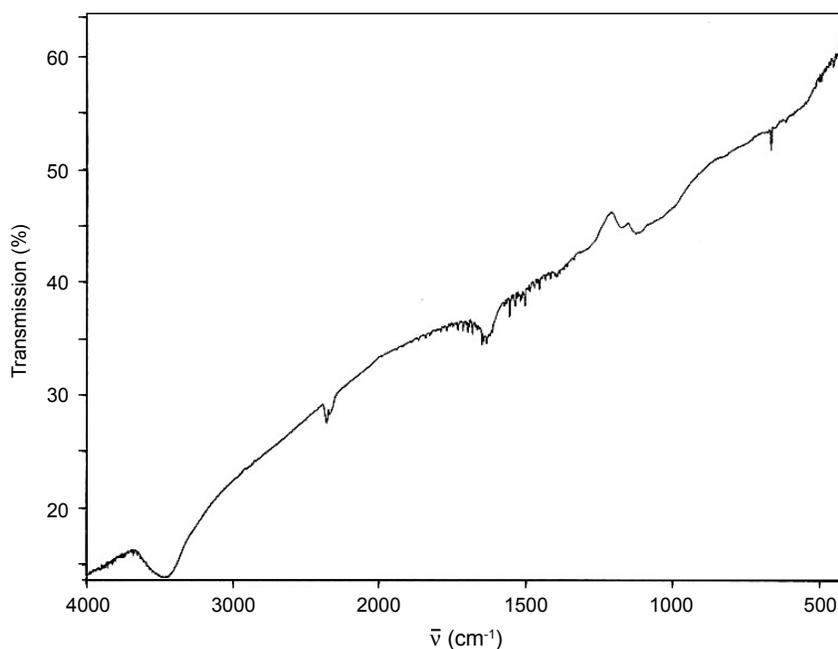
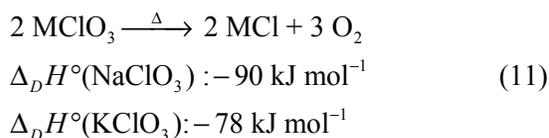


Figure 5. FTIR-spectrum (KBr) of stabilized red phosphorus.

Mixtures with Chlorates

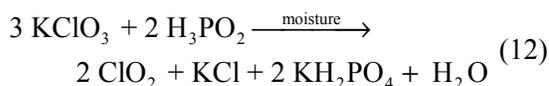
The most “prominent” reported combinations are mixtures of red phosphorus with the chlorates of either sodium or potassium. Potassium chlorate/RP is reported as Armstrong’s mixture in the literature. The extreme sensitivity of these mixtures and the unpredictable behavior with respect to ignition is still somewhat obscure. Nevertheless several plausible causes will be discussed in the following.

The chlorates of both sodium and potassium possess exothermic enthalpies of decomposition according to the general dissociation process:



In addition the thermal decomposition of chlorates occurs at relatively low activation energies of $\sim 200 \text{ kJ mol}^{-1}$ ^[19] calling again for low ignition stimulus and fast reaction rates with suitable fuels.

Given the amount of acid present in untreated RP (as indicated by its FTIR spectrum), it is not very surprising that upon contact of this material with chlorates the respective chlorine oxides may be formed, which are known as to decompose fiercely. In 1971 Rollins^[20] investigated the chemistry of Armstrong’s mixture and found experimental confirmation of the following exothermic reaction taking place in RP/KClO₃ mixtures with non-stabilized or UV sensitized (that is, sun light!) RP.



In addition, trace amounts of white phosphorus in RP may trigger accidental reactions.

Mixtures with Miscellaneous Partners

A series of other contact pairs have also been recognized to be highly dangerous due to very high mechanical and thermal sensitivity. These materials are

- perchlorates,
- nitrates of the transition metals (e.g., AgNO₃),
- permanganates, chromates, dichromates,

- inorganic peroxides and
- coruscative^{a)} partners having low enthalpy of fusion (e.g., Mg and Zn).

Despite the incompatibility with Mg and Zn, the above pairs suffer from the described acid-base reaction when working with non-stabilized RP. The coruscative partners owe their danger to the low ignition stimulus needed to initiate these mixtures.

Although incompatible, in view of the above compilation, Shimizu^[22] reported on the combustion behavior of ternary systems made from gallic acid, potassium perchlorate and RP as well as phthalic acid anhydride/potassium perchlorate/RP mixtures. He observed three stoichiometric ranges showing (1) linear combustion, (2) sizzling combustion and (3) explosion phenomenon. In addition mixtures of barium chlorate (*sic!*) and red phosphorus have been disclosed as incendiary payload constituent for military application.^[23] In view of the above, stabilized RP may be indeed stable enough not to undergo spontaneous explosion in these mixtures.

Combustion Properties of Red Phosphorus

When heated to $T > 300 \text{ }^\circ\text{C}$, RP ignites in ambient air showing a brilliant yellow flame with evolution of a dense white smoke.

Figure 6 displays the DTA/TG plot of red phosphorus (type SF/Clariant). At $T \sim 260 \text{ }^\circ\text{C}$ both the start of an exothermic reaction as well as a mass increase are discernible. The peak temperature for the oxidation process is $405 \text{ }^\circ\text{C}$. This coincides with the maximum in the TG plot, which calls for $\sim 25 \%$ increase in mass. At higher temperatures a series of consecutive oxidation processes are resolved all accompanied with a decrease in weight to -99% at $600 \text{ }^\circ\text{C}$.

The combustion process of phosphorus occurs in the gas phase and thus has to be understood as a successive process involving phase changes according to the following equations:

^{a)} The term coruscative, originally coined by F. Zwicky,^[21] refers to mixtures that upon combustion only yield (a) solid product(s). According to the general equations $X + Y \rightarrow XY$ and $AB + CD \rightarrow AD + CB$; the latter describing metathetical reactions thus including also thermic systems.

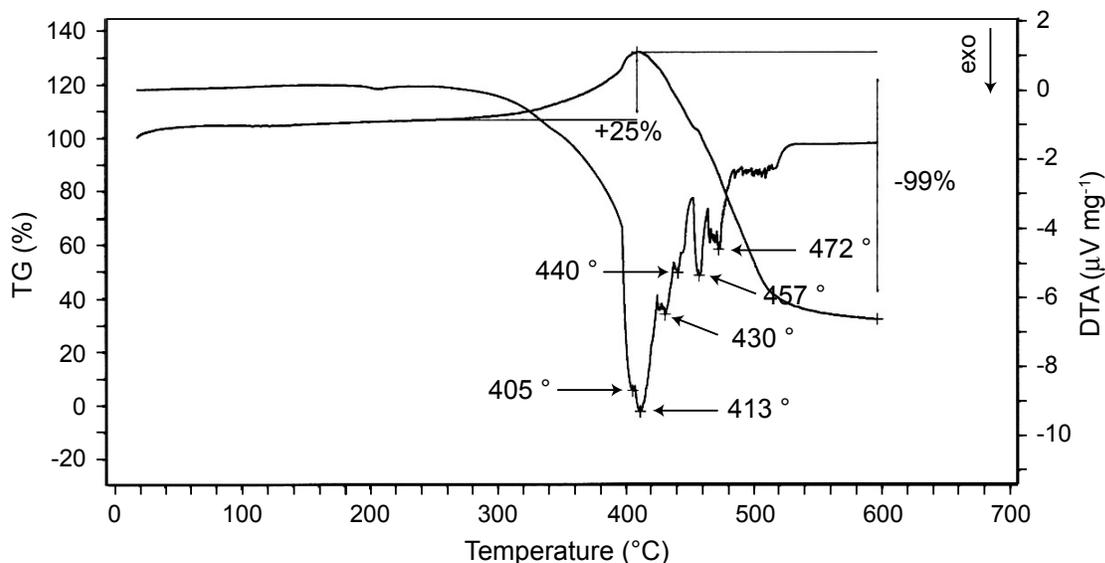
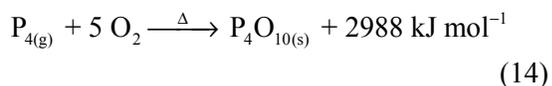
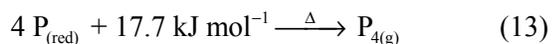
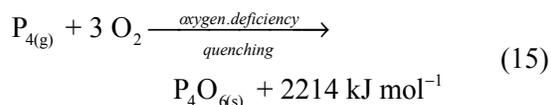


Figure 6. DTA/TG plot of stabilized red phosphorus.



Under oxygen deficient conditions or under quenched conditions, when much heat is carried away by the environment, the following process also occurs:



The P_4O_6 suboxide often yields white to yellowish stains that can be found on flat surfaces around burning RP pellets.

At $T > 70^\circ\text{C}$ this oxide again ignites to combust with atmospheric oxygen to give the pentoxide according to the following equation:

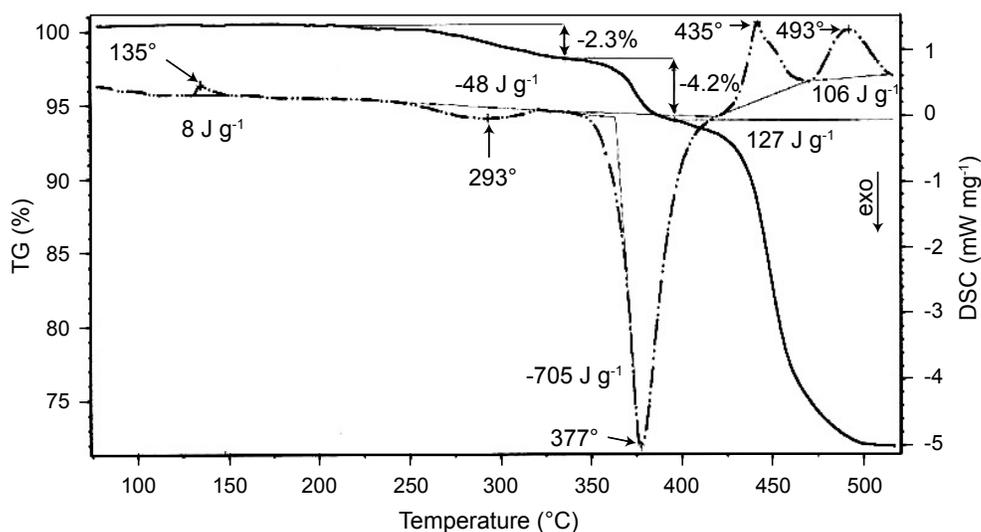


Figure 7. DSC/TG plot of smoke composition under helium.

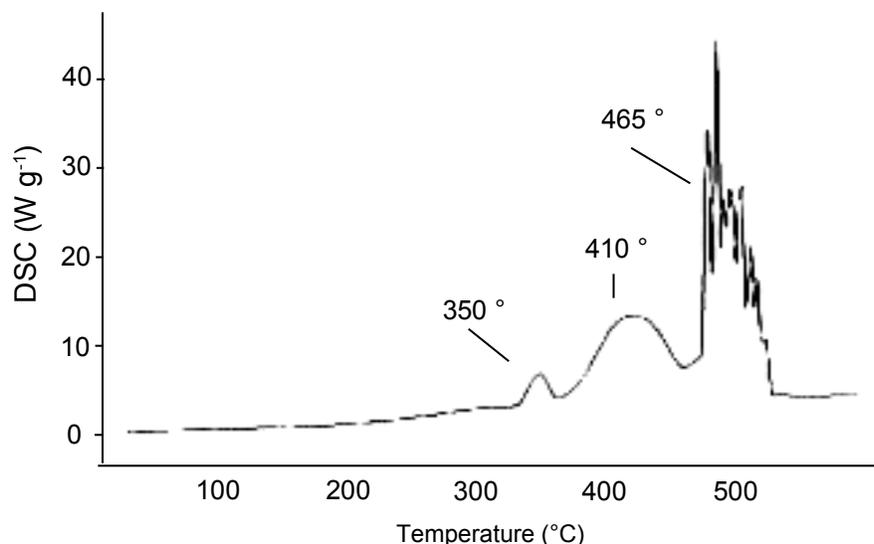
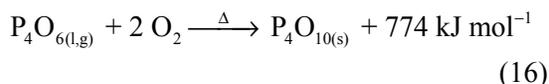


Figure 8. DSC plot of smoke composition under air.



In mixtures with oxidizers such as alkali nitrates the combustion behavior differs from pure red phosphorus in that the ignition occurs at lower temperatures.

Figure 7 displays the DSC and TG plots for the investigation of a smoke composition based on RP, potassium nitrate, zirconium and polychloroprene binder (60, 25, 10, 5 wt-%) under a helium atmosphere at heating rate of 10 K min^{-1} .

The (*rhombic* \rightarrow *trigonal*) crystal transition for KNO_3 is observed at $135 \text{ }^\circ\text{C}$. A shallow exothermal process has its maximum at $\sim 300 \text{ }^\circ\text{C}$; the nature of which is unclear at present. A strong exotherm at $377 \text{ }^\circ\text{C}$ is due to reaction of molten potassium nitrate (mp: $341 \text{ }^\circ\text{C}$) with zirconium, which nicely matches with values found by Kubota.^[24] The strong mass loss from 400 to $500 \text{ }^\circ\text{C}$ is due to the vaporization of phosphorus.

Figure 8 displays a DSC plot for the same smoke composition but under a constant stream of air (50 ml min^{-1}). The crystal transition of potassium nitrate has now vanished. Three exotherms are observed at 350 , 410 and $465 \text{ }^\circ\text{C}$, respectively, which are due to the oxidation of both zirconium and phosphorus.

The absence of atmospheric oxygen in the first experiment allows for distinction between

single exothermic reactions in the PIR (Pre-Ignition-Reaction) temperature range. In addition the phosphidation reaction such as $\text{Zr} + \text{P} \rightarrow \text{ZrP}$ is likewise possible, but it has only been observed to start at $T > 500 \text{ }^\circ\text{C}$ having activation energy of $21 \pm 12.5 \text{ kJ mol}^{-1}$.^[25]

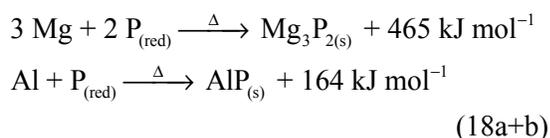
Combustion of the above mentioned consolidated composition in air occurs at $T \sim 295 \text{ }^\circ\text{C}$. Thus the unexplained PIR reaction—detected in both the anaerobic and aerobic experiment at $T \sim 295 \text{ }^\circ\text{C}$ —triggers the actual ignition of the composition.

The high heat of combustion of phosphorus is a prominent feature of the element. In addition there is a large negative neutralization enthalpy available for the pentoxide to react with basic metal oxides according to the general Eq. 17:

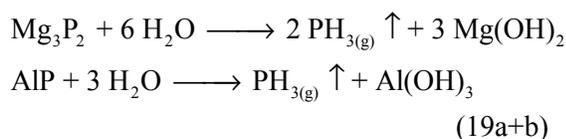


Since most phosphorus containing compositions are oxygen deficient with respect to the amount of red phosphorus included, other ingredients can react with the red phosphorus. Such ingredients can be metallic fuels, such as Mg, Al, Ti, Zr.

In the case of group 2 elements and aluminum phosphorus yields ionic phosphides according to Eqs. 18a and b^[26]



The phosphides of both aluminum and magnesium react with water and dilute acids to produce phosphane (PH₃) and the corresponding hydroxide. Since phosphane is highly toxic (MAW < 0.1 mg m⁻³) and highly flammable, it is no longer acceptable to manufacture pyrotechnic compositions based on red phosphorus that use either of these fuels. Likewise other materials using magnalium (Mg₃Al₄) or calcium silicides CaSi_x (x = 1, 2) that would yield calcium phosphide (Ca₃P₂), are now obsolete (note that Ca₃P₂ is the main product formed upon reaction of Al/Ca₃PO₄ mixtures in rodenticide type matches against moles).



Since this chemical incompatibility has led to numerous fires on training grounds using several ammunition types, an improved formula needed to be developed.

The author^[27] developed a series of smoke compositions based on both titanium and zirconium. With the application of zirconium and/or titanium as an additional fuel, the side reaction products TiP and ZrP are metallic type phosphides that do not react with moisture or even dilute acids such as "acid rain".^[28] Hence smoke compositions based on red phosphorus and Ti or Zr do not yield poisonous combustion products.

The constituents of the combustion products of several smoke compositions, based on red phosphorus, sodium nitrate, organic binder and magnesium have been investigated by Klusáček and Navrátil^[29] by means of ³¹P-NMR-spectroscopy. In systems having magnesium as an additional fuel, the major combustion/hydrolysis product is hydrogen phosphate (HPO₄²⁻) along with modest amounts of diphosphate (P₂O₇⁴⁻) and minor amounts of dihydrogenphosphate (H₂PO₄⁻) and *cyclo*-triphosphate ((OHPO)₃³⁻). In contrast magnesium-free systems provide a mixture of *cyclo*-(tri-, tetra- and hexa-)phosphates as the major combustion/hydrolysis products and modest amounts of both dihydrogen phosphate

and dihydrogendiphosphate (H₂P₂O₇²⁻). Freiwald and coworkers^[30,31] also investigated the combustion constituents of RP based smoke compositions.

Combustion of Phosphates with Metals

The potential of alkali metal and alkaline earth salts of oxyacids such as carbonates, phosphates and sulfates to act as single oxidizers in stoichiometric magnesium-based pyrotechnic systems has been impressively demonstrated by Shimizu.^[32,33] In this context calcium orthophosphate (Ca₃(PO₄)₂) [7758-87-4] (Δ_rH: -4120 kJ mol⁻¹), calcium dihydrogenphosphate (Ca(H₂PO₄)₂) [7758-23-8] (Δ_rH: -3104 kJ mol⁻¹) and phosphorus pentoxide (P₄O₁₀) have been evaluated as oxidizers in stoichiometric mixtures with magnesium. An intimate mixture of P₄O₁₀ and Mg ignites with a bright flash when contacted with water. A pulverized mixture of magnesium with Ca(H₂PO₄)₂ ignites at ~ 330 °C. Even consolidated, this mixture burns fiercely to produce a luminous flame. Although calcium orthophosphate/Mg mixtures ignite in the pulverized state, they do not ignite in the pressed form.^[32]

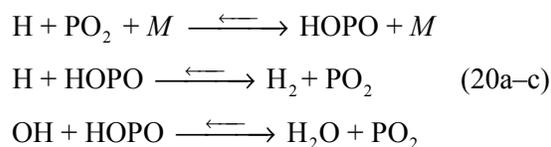
Combustion products of calcium orthophosphate aluminum mixtures contain Ca₃P₂, which subsequently reacts with water and humidity to produce toxic phosphane (PH₃).^[34]

Combustion of Phosphorus Sulfides with Oxidizers

In strike anywhere (SAW) matches, red phosphorus has been replaced by tetraphosphorus trisulfide (P₄S₃) [1314-85-8] (Δ_rH: -224 kJ mol⁻¹). P₄S₃ is a light yellow crystalline that melts at 174 °C and vaporizes at 408 °C. It displays a chemiluminescence at temperatures from 40 to 60 °C comparable to that of WP and ignites at ~ 100 °C. It is very soluble in carbon disulfide (CS₂). Its friction sensitivity surely is due to high strain of the three-membered phosphorus ring present in the molecule.

Inhibiting Combustion with Phosphorus

Although highly flammable, red phosphorus is also a very potent flame retardant. Thus many commercial polymers in structural units subjected to thermal stress are often loaded with red phosphorus and also organic phosphorus compounds such as dimethyl methylphosphonate (DMMP, C₃H₉O₃P) and trimethyl phosphate (TMP, C₃H₉O₄P). In fact the largest amount of red phosphorus produced today is used in applications as flame retardants. The mechanism is based on the flameless recombination of H and OH radicals in hydrocarbon flames. The actual process has been recently elucidated to occur via the following sequence:



Thus the intermediate phosphorus dioxide (PO₂) scavenges hydrogen radicals to successively yield water and the PO₂ again. It is said that the termolecular reaction is the most efficient one in removing H radicals (with *M* being an inert collision partner).^[35]

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