

Reducing the P-Cycle by Grinding

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A room temperature synthesis of phosphite from the reduction of polyphosphates with potassium hydride in a ball-milling reaction.

In this issue of *ACS Central Science*, Cummins and co-workers report a facile and selective reduction of polyphosphates to phosphite with potassium hydride via mechanosynthesis, a potential solution toward a “greener” phosphorus industry.¹ Phosphorus generally exists in its highest oxidation state in nature and is a vital element for living organisms. It constitutes approximately 1% of the human body weight as a component of bone, membrane, nucleic acids, and high-energy phosphates. It is also one of the three major plant nutrients in agriculture, in company with nitrogen and potassium. The growth of the global population from 3.7 billion in 1970 to 7.9 billion in 2021 has led to an exponentially increased demand for phosphate rock, the primary source of phosphorus, and more so since World War II. According to the 2020 US Geological Survey’s (USGS) 2021 annual report on world phosphate mine production and reserves, there seems to be no need to worry about the shortage of phosphorus for the next 300 years.² However, the global distribution of phosphate ore resources is highly polarized, and rock phosphate is nonrenewable.³ The industrial process is not environmentally sustainable either.

Phosphate rock mining activities create air and water pollution and solid wastes containing toxic metals and radioactive elements (Figure 1).⁴ The majority of the phosphate rock that is mined for phosphate fertilizers is manufactured in a wet-process involving sulfuric acid. Industry applications of phosphorus rely on chemicals derived from elemental phosphorus. White phosphorus (P₄), a common starting material of phosphorus chemicals, is also obtained from phosphate rock with a thermal process that involves the reduction of rock

phosphate with coke at temperatures up to 1500 °C.⁵ It is then oxidized by Cl₂ to PCl₃ for the production of a variety of P(III) chemicals. A synthetic route that avoids the high-energy-consuming P(V) to P(0) reduction process and the use of strong oxidizing chlorine gas would be an essential step toward a more environmentally friendly phosphorus industry. In 2018, Cummins’ group also reported a way to bypass the energy-intensive white phosphorus synthesis process with a highly reactive bis(trichlorosilyl)phosphide anion obtained from the reduction of trimetaphosphate, a dehydration product of phosphoric acid, with trichlorosilane.⁶ However, renewable phosphorus sources and recyclable phosphorus chemicals remain indispensable to the establishment of a sustainable phosphorus cycle.⁷ Most of the mined rock phosphate is lost during mining and fertilizer production, plant or animal cultivation, and excretion. The anthropogenic inputs of phosphates to the environment enrich nutrients in freshwater, which contributes to the excessive growth of algae and eutrophication. A direct transformation of the condensed phosphates, recycled from the environment, to valuable phosphorus fine chemicals at room temperature would be a blueprint for sustainable phosphorus management.⁸

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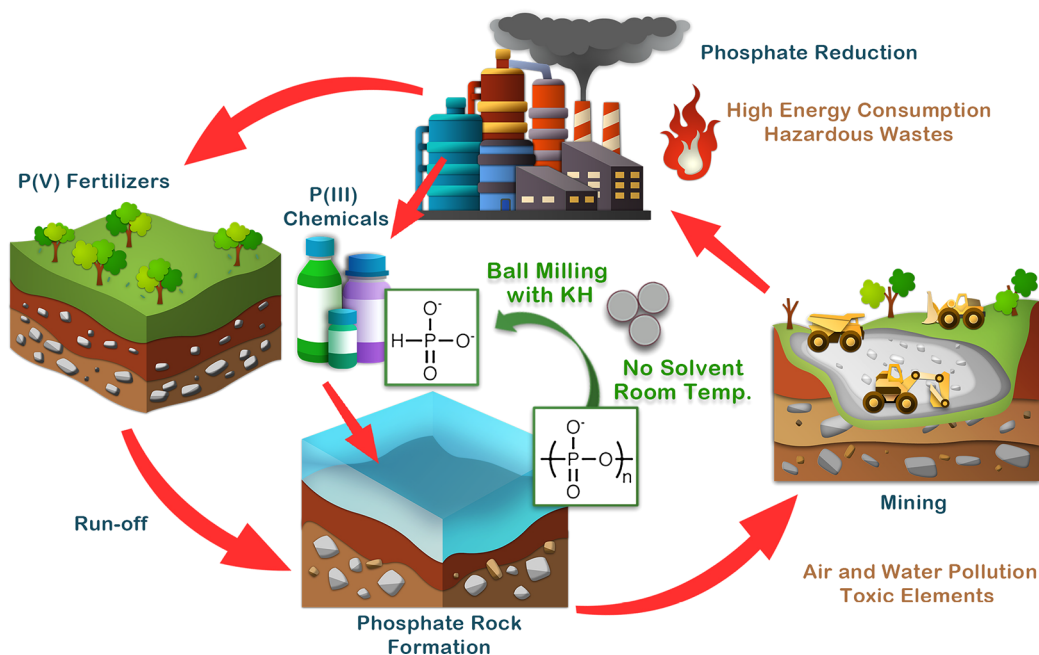
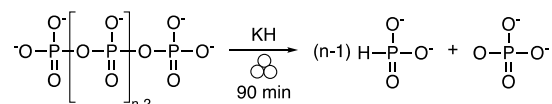


Figure 1. Anthropogenic impacts on the phosphorus cycle and the breakthrough of Cummins and co-workers.¹

To synthesize P(III) chemicals from phosphates with reagents that are easy to handle, Cummins and co-workers now report the reduction of polyphosphates with potassium hydride under solvent-free conditions.¹ Grinding the polyphosphate/hydride mixture in a ball mill is the key to achieving a high yield of phosphite. The friction and impact generated during milling promote the reaction between solid polyphosphates and potassium hydride at room temperature that produces phosphite with good selectivity. For each linear $[\text{P}_n\text{O}_{3n+1}]^{(n+2)-}$ source, a maximum $(n - 1)$ equiv of phosphite can be obtained with 1 equiv of orthophosphate byproduct (Scheme 1). Surprisingly, the reaction of polyphosphate with substoichiometric KH increased the yield of the over-reduction product, hypophosphite, that contains phosphorus in the +1 oxidation state. This finding is counterintuitive to what is expected in a substoichiometric reaction. Mechanistic studies reveal that phosphite phosphorylation occurs when a substoichiometric amount of KH is applied leading to the formation of phosphorylated phosphite and the over-reduction products.

The mechanosynthesis of phosphite is not limited to commercially available, analytically pure inorganic polyphosphates. A long-chain polyphosphate mixture that is isolated from yeasts incubated in a phosphate-enriched medium can also be utilized as the feedstock of phosphite.

Scheme 1. Reduction of Polyphosphate to Phosphite with Potassium Hydride



The mechanosynthesis of phosphite is not limited to commercially available, analytically pure inorganic polyphosphates. A long-chain polyphosphate mixture that is isolated from yeasts incubated in a phosphate-enriched medium can also be utilized as the feedstock of phosphite. Although the efficiency is reduced due to the impurities in the biosynthesized starting materials, this experiment demonstrates the potential to build a sustainable phosphorus industry with this solvent-free room temperature mechanosynthetic protocol for phosphite.

As the 11th most abundant element on earth, it might be difficult to recognize the fact that we are facing global phosphorus scarcity. With more than 80% of phosphate rock reserves located in one country, the use of phosphorus must be more efficient, and finding alternative renewable sources is pressing. The recovery of phosphorus from local wastes could be the solution to mitigate water pollution, reduce the dependence on finite phosphorus resources, and lead to a more sustainable phosphorus society.

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REFERENCES

- (1) Zhai, F.; Xin, T.; Geeson, M. B.; Cummins, C. C. Sustainable Production of Reduced Phosphorus Compounds: Mechanochemical Hydride Phosphorylation Using Condensed Phosphates as a Route to Phosphite. *ACS Cent. Sci.* **2022**, in press. DOI: 10.1021/acscentsci.1c01381.
- (2) U.S. Geological Survey on Phosphate Rock Statistics and Information. <https://pubs.usgs.gov/periodicals/mcs2021/mcs2021-phosphate.pdf>.
- (3) Elser, J.; Bennett, E. A broken biogeochemical cycle. *Nature* **2011**, *478*, 29–31.
- (4) Reta, G.; Dong, X.; Li, Z.; Su, B.; Hu, X.; Bo, H.; Yu, D.; Wan, H.; Liu, J.; Li, Y.; Xu, G.; Wang, K.; Xu, S. Environmental impact of phosphate mining and beneficiation: review. *Int. J. Hydro.* **2018**, *2*, 424–431.
- (5) de Boer, M. A.; Wolzak, L.; Slootweg, J. C. Phosphorus: reserves, production, and applications. In *Phosphorus recovery and recycling*; Springer, 2019; pp 75–100.
- (6) Geeson, M. B.; Cummins, C. C. Phosphoric acid as a precursor to chemicals traditionally synthesized from white phosphorus. *Science* **2018**, *359*, 1383.
- (7) Jupp, A. R.; Beijer, S.; Narain, G. C.; Schipper, W.; Slootweg, J. C. Phosphorus recovery and recycling – closing the loop. *Chem. Soc. Rev.* **2021**, *50*, 87–101.
- (8) Geeson, M. B.; Cummins, C. C. Let's make white phosphorus obsolete. *ACS Cent. Sci.* **2020**, *6*, 848–860.