Sustainable Industrial Phosphorus Chemistry

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Phosphorus plays an important role not just in food production, but also in various industrial applications. The presentation will focus on options to make these industrial uses of phosphorus more sustainable, contributing to a circular economy.

Real World Applications of Organophosphorus Chemistry.

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Organo phosphorus process chemistry starts with the manufacture of white phosphorus, (P_4) from phosphate rock ; P_4 is converted into primary derivatives such as phosphorus halides, phosphorus pentoxide and phosphine – secondary downstream organo P derivatives play an important part in the world we live in and affect us all daily. This presentation will outline by example, the extremely diverse applications chemistry of phosphorus technology.

- Flame retardants, in thermo plastics, PU foams, textiles.
- Surface modification – dispersion of minerals in plastic, adhesive bonding in metallurgy.
- Mining, mineral flotation and metal extraction.
- Scale and corrosion control in water treatment.
- PH_3 in Electronics and fumigation
- Biocides
- Agriculture – herbicides, pesticides and growth regulators
- Catalysts in industrial processes.
- Medicine – bisphosphonates in bone diseases, antivirals, antibiotics.

New developing applications

- Oligo nucleotides
- Antisense drugs, DNA data storage, RNA pesticides.
- Manufacture of quantum dots used in flat screen displays.

Catalysis with P-ligands at BASF and new developments at CaRLa

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Homogeneous Catalysts with phosphine based ligands are used at BASF on a large scale like in hydroformylations, carbonylations, asymmetric hydrogenations or cross-couplings.

At the Catalysis Research Laboratory (CaRLa) in Heidelberg, a joint laboratory between the university of Heidelberg and BASF SE, we are working on new catalytic systems for industrial applications. In this presentation, an overview on the catalysis with P-ligands at BASF as well as two projects for the developments on new P-ligand based catalysts at CaRLa will be given.

One example will be the current work on the development of new catalysts for the hydrogenation of esters[1] and the other the synthesis of sodium acrylate based on CO_2 and ethylene using nickel- and palladium phosphine complexes as catalysts.[2]

CaRLa (Catalysis Research Laboratory) is cofinanced by the Heidelberg University and BASF SE.

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Poly(alkylene phosphates)

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Most commercial phosphorus derivatives are based on well established chemistry, alkyl phosphate esters[1] being an example. However, industrial development efforts driven by rising demands on performance and sustainability may yield innovative products even in mature areas. As part of a program directed at the development of new, halogen-free flame retardants a new synthesis for poly(alkylene phosphates)[2] was explored.

Phosphoryl chloride was found to undergo polycondensation with diols. The intermediates obtained can readily be converted into a variety of poly(alkylene phosphate) esters.[3] The oligomeric nature of these products was established analytically.[4] Their properties can be modified easily to address requirements of various applications. As an example, the utility of the new poly(alkylene phosphate) esters as flame retardants in polyurethane foams is highlighted.

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IONQUEST for Solvent Extraction:
Industrial scale-up of diverse P-chemistries

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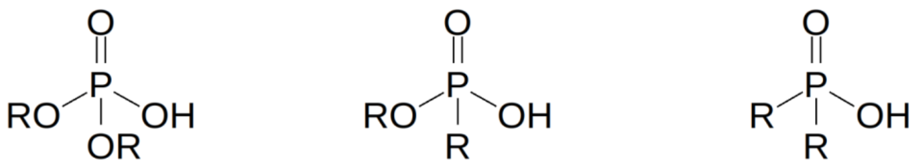
Performing sensitive chemistry with reactive and toxic reagents in a glove-box is one thing, doing it routinely in a multi-ton reactor inside a chemical plant is a whole other. Italmatch Chemicals, renowned speciality chemicals producer has a complex global production and logistics operation of 1000s of tons of different chemicals, intermediates and precursors.

Mining and refining chemicals is a relatively young but rapidly growing branch of the Water and Oil Performance Additives business unit. The solvent extraction reagents form the core of this business. Italmatch produces IONQUEST IQ-290, an extremely pure phosphinic acid reagent mostly used for cobalt extraction. Complementing this reagent, two other related chemistries, the phosphoric and the phosphonic acid are known in industry, marketed by Italmatch as IONQUEST IQ-220 and IONQUEST IQ-801 respectively.



Phosphoric Acid IONQUEST® IQ-220 | Phosphonic Acid IONQUEST® IQ-801 | Phosphinic Acid IONQUEST® IQ-290

In this talk we will describe how these three reagents were scaled-up within different factories of Italmatch Chemicals. Through these examples of related P-containing chemistries we will have a look at possible synthetic pathways and which to favour during scale-up based on available raw-materials, plant capability and capacity as well as regulatory and health and safety issues that arise when taking such chemistries from bench-scale to multi-ton reactor scale.

Acylphosphine Oxide Photoinitiators: Some Recent Developments

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Bis(acyl)phosphine oxides (BAPOs) are among the most important members of highly active photoinitiators used in industry. Upon irradiation, the phosphorus - acyl carbon bond in these compounds is homolytically cleaved into radicals which initiate the emission-free polymerization of monomeric or oligomeric polymer precursors for various applications.

After a short summary on the history, properties, and uses of acylphosphine oxide photoinitiators, the chemical process development which led to the current manufacturing procedure of the prominent BAPO Irgacure® (Omnirad®) 819 as well as recent work directed at the synthesis of novel functionalized BAPO derivatives is outlined.

The current demand for BAPOs with well-defined properties such as activity, absorption region, water-solubility, state of matter, suitable for the use in specific applications has triggered the search for new processes and led to new patent applications. More specifically, bis(acyl)phosphinic acid derivatives could play an important role as building blocks for new phosphorus-based custom-tailored photoinitiators. The chemistry of recent approaches to this class of acylphosphinates is critically discussed.

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Building blocks containing phosphorus for atom efficient syntheses

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It is a formidable challenge for chemistry to create processes which can be considered as truly sustainable. This does not only require to develop processes which are highly efficient but also take into account the availability of starting materials. On top of that, the fate of a chemical product after its use has to be taken into account. In other words, when a product with a certain function has turned into waste its maximal recyclability into usable chemicals has to be considered and designed from the beginning into the production process.[1] In this area of conflict, chemistry has therefore the task to generate products of high functionality, quality, and sufficiently long life-time from cheap and readily available resources which in addition can be completely recycled. At the same time, research must also focus on the finding of entirely new molecules and materials. Only these offer the chance to find even better products which surpass the properties of known species. These considerations have to be made especially for so called specialty chemicals which mostly have highly specific functions but because of their high market value are often prepared using procedures which are far off the principles of sustainable chemistry. Considering the principles of atom economy for the synthesis of such compounds, we have developed building blocks from simple and easily available starting materials. On one side, these building blocks - like sodium phosphaethynolate, Na(OCP) - allow to assemble a variety of new molecules in a short time using simple processes which open up the opportunity to find new applications.[2] On the other side, they also allow to streamline processes to known molecules and materials and reduce waste and cost. One example are photoinitiators applicable for a wide range of established coating processes but also in emerging technologies such as 3D printing or as additives in composite materials.[3] Using mostly examples from our own research efforts, the lecture will illustrate the value taking the effort of developing new functional groups and building blocks in phosphorus chemistry.

Acknowledgements

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