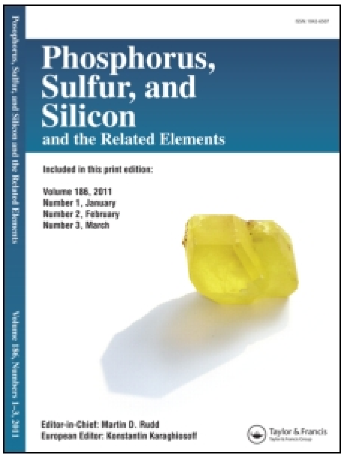

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OLIGOMERIC PHOSPHATE ESTERS AS FLAME RETARDANTS

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Abstract. In this paper, some Akzo Nobel contributions to organophosphorus flame retardant chemistry are discussed in the context of some current and future issues affecting various end use applications. Current issues of greatest concern include toxicity, environmental impact and performance characteristics such as fogging in automotive applications. Future concerns will no doubt focus on environmental issues and recycling as well as new indices of fire performance such as rate-of-heat release. One approach to the right molecules is through oligomeric phosphate esters. Specifically, those that are formed by the reaction of oligomeric pyrophosphates with cyclic ethers.

As a consequence of the current technological revolution, synthetic polymers and composites continue to replace traditional materials such as metal, wood, glass, etc., especially in electrical, electronic, transportation, construction and home furnishings applications. Once it was established that synthetics could do the job, another wave of change began in which lower cost polymers are being formulated and "engineered" to replace higher cost polymers by improving properties and pushing service capabilities to higher performance levels. One particular characteristic of synthetic polymers that has always needed improvement has been and continues to be fire performance.

Factor in the present worldwide concern for the environment and the rapidly growing emphasis on recycling and we get an exciting challenge to produce cost-effective, halogen-free flame retardants. Certainly, high on the list of candidate compounds to meet these challenges are organophosphorus compounds.

In some areas, such as the flame retarding of polyurethane foams, organophosphorus materials have a longstanding history of use. The compounds used though have generally contained combinations of phosphorus and halogens in the form of simple haloalkyl phosphates. In recent years, concern for the health and safety of workers and consumers brought about greater emphasis on the toxicity of materials. Several years ago tris(dibromopropyl) phosphate was found unacceptable due to its chronic toxicity. More recently tris(chloroethyl) phosphate has also come under attack for toxicity reasons. Tris(chloroethyl) phosphate now falls into labeling category R40 in Europe. This label carries the words "possible risk of irreversible effects".

From a performance perspective, tris(chloroethyl) phosphate and tris(monochloroisopropyl) phosphate are too volatile for today's more stringent automobile seat cushion requirements. They will fail the new fogging test criteria which measures the propensity of additive materials in flexible polyurethane foam to volatilize and collect on vehicle windows. Tris(chloroethyl) phosphate can also cause unacceptable discoloration in polyurethane foams, especially in the new, more efficient production techniques which make larger and less dense foam buns. Even though tris(monochloroisopropyl) phosphate is more volatile than its chloroethyl analog this is generally not a problem when it is used in rigid polyurethane foams.

A few higher molecular weight chloroalkyl phosphates have been commercialized over the years. Even though they are more permanent, they can cause problems in some disposal or recycling schemes. The potential disposal problems and the toxicity testing likely to be required for registration on the various international chemical inventories such as the EINECS, the TSCA or the MITI lists discourages further exploration of any new chloroalkyl phosphate compounds. Simple molecules containing only phosphorus and no halogens such as dimethyl methylphosphonate, often referred to as DMMP, are also very effective flame retardants, but their low molecular weight results in relatively high volatility. DMMP also falls into the European labeling class R46 which carries the warning "may cause heritable genetic damage". Similarly, triphenyl phosphate and its various alkylated derivatives, though nonvolatile enough to pass the automotive fogging test requirements, are still volatile enough to collect in exhaust hoods over thermoplastic processing equipment when they are used in various engineering plastics. This evidence of volatility together with the discovery a decade ago of a unique but apparently harmless monocyte esterase inhibition in some workers exposed to these polymer processing operations [1] has encouraged the search for even less volatile materials.

The pursuit of reduced volatility of organophosphorus flame retardants has taken numerous paths over the years. In one approach, virtually nonvolatile salts are prepared from highly volatile precursors such as DMMP . At least one of these compounds has been reported to be in commercial development but does not seem to have found much actual use.

A second approach, making reactive molecules that become part of the polymers in which they are used, has enjoyed some commercial success over the years [2], most notably in polyester fibers, and in polyurethane foams. This approach can be expensive and leads to specific, niche compounds rather than to materials with broad applicability.

A third approach, one that we at Akzo Nobel have emphasized, is the preparation of higher molecular weight compounds, specifically oligomeric versions of some of the simple compounds mentioned earlier, such as dimethyl methylphosphonate and trischloroethyl phosphate. Earlier phases of our work in this area have been reported at a previous International Conference on Phosphorus Chemistry by Weil [3]. The work previously reported covered aliphatic oligomeric phosphates and phosphonates. I will discuss our extension of this work into aromatic analogs.

As previously described, we approach the oligomeric phosphates by reacting simple trialkyl phosphates or phosphonates with phosphorus pentoxide to obtain alkyl esters of a mixture of oligomeric metaphosphoric and metaphosphonic acids also referred to as metaphosphates and metaphosphate/phosphonates. This mixture is then reacted with ethylene oxide until all of the pyrophosphate groups disappear and are replaced by ethyleneoxy bridges. This appears to be easily explained by the insertion of ethylene oxide into the pyrophosphate bond as suggested by Weil et al [3].

Bright, Jaffe and Walsh [5] point out that this suggestion was based, in part, upon the diagnostic chemistry and, in part, upon infrared monitoring of the reduction in the concentration of the pyrophosphate bonds resulting from the processing and that the reduction in concentration or the disappearance of the anhydride groups is not unequivocal evidence that ethylene oxide inserts into the anhydride bond. Since the more stable of these linkages may resist titration by the usual alcoholic KOH method, measurement of the HCl acid number is very useful [4]. In this procedure, residual pyro moieties and labile five-membered cyclic ester groups are hydrolyzed with a measured amount of excess HCl and then back-titrated.

Walsh also points out that in this oligomeric system, there are other pathways for the opening of the anhydride linkages and, there was no clear identification of the formation of the products expected from an insertion reaction of ethylene oxide into the anhydride linkage.

Weil suggests [3] that ethylene oxide inserts into the anhydride linkages formed in a side reaction during the condensation of tris(2-chloroethyl) phosphate. However, insertion is not the only pathway available for removal of the anhydride linkage and, perhaps because of the difficulty in analyzing such reaction mixtures, a product of such a reaction was not unequivocally identified.

Extending this chemistry to the aryl phosphates we have demonstrated clearly and unequivocally the insertion reaction of epoxides into the pyrophosphate linkage [6]. Under carefully controlled conditions, ethylene oxide was added to tetraphenyl pyrophosphate to form ethylene bis(diphenyl phosphate) as the sole reaction product. The reaction proceeds at 70°C when ethylene oxide is added to molten tetraphenyl pyrophosphate during a 10-hour period. Pyridine was found to be an effective catalyst. The yield is 87.4%; m.p., 38-40°C; purity, 97.2 by HPLC.

Similarly the reaction of tetraphenyl pyrophosphate with propylene oxide leads to an 80% yield of the corresponding insertion product, as an oily liquid. The reaction time was six hours at 70°C; purity, 96.7% by HPLC. Magnesium chloride and stannous octoate were also shown to be effective catalysts for this insertion reaction.

The tetraphenyl pyrophosphate was prepared by hydrolytic condensation of diphenyl chlorophosphate and the subsequent alkylene bis(diphenyl phosphates) form a series of mixed aliphatic aromatic phosphates. These are "dimeric" versions of the commercial "monomeric" alkyl diaryl phosphate plasticizers which are noted for their low-smoke-generation characteristics but this "dimeric" series is higher in phosphorus content and in molecular weight.

The high reactivity of the strained three-membered epoxide ring suggested that the insertion into pyrophosphoric linkages might be unique for epoxides. This is not true and the insertion reaction is not restricted to epoxides. Four-membered-ring cyclic ethers, oxetanes, will also insert into the pyrophosphate bond of tetraphenyl pyrophosphate [6].

Neopentyl glycol bis(diphenyl phosphate) and dichloroneopentyl glycol bis(diphenyl phosphate) were prepared in 89% and 75% yield respectively by reaction of 3,3-dimethyl oxetane and 3,3-bis(chloromethyl)oxetane with tetraphenyl pyrophosphate using pyridine as catalyst. The oxetane ring may be slightly less reactive than the epoxide ring as suggested by the higher reaction temperature, 120°C, used in these reactions.

In retrospect, the reaction of aliphatic ethers with pyrophosphoric linkages may be a general reaction resulting in the formation of two phosphoric ester linkages. When the ether is a cyclic ether, the result is insertion of one molecule. By contrast when the ether is acyclic, the result is more complex. A well known example fitting this model is the autoclave reaction of diethyl ether with phosphorus pentoxide which results in a metaphosphate mixture from which triethyl phosphate is reactively distilled [7][8].

Aliphatic bridged oligomeric aryl phosphates have the desired low volatility and a reasonable phosphorus content but are still limited by the thermal stability of the aliphatic phosphate ester link. To overcome this shortcoming and better address the needs of the marketplace we have focussed on the development of a totally aromatic oligomeric phosphate. The current state of the art in thermally stable, easily recycled, halogen-free, non-volatile flame retardants is resorcinol bis(diphenyl phosphate). The commercially available products are mixtures of resorcinol-bridged diphenyl phosphate moieties containing oligomeric species with two to five phosphorus atoms per molecule. This mixture is reportedly made by reacting resorcinol with an excess of phosphorus oxychloride [9], then stripping off the excess phosphorus oxychloride and reacting the residue with phenol. The oligomer distribution is controlled by the amount of excess phosphorus oxychloride used initially. This oligomeric flame retardant, sold by Akzo Nobel as Fyrolflex®RDP, is very effective in polycarbonate blends with styrenic polymers, notably ABS [10] and in polyphenylene ether blends with high impact polystyrene [11]. Thin-walled, light-weight computer housings meeting the stringent UL94 V0 flammability test criteria incorporating this material have gained widespread commercial acceptance.

Another approach to achieving high molecular weight, oligomeric phosphorus compounds is based on the high temperature transesterification of dialkyl or diaryl methyl phosphonates [12][13][14]. Despite a flurry of patent activity in this area in recent years, no commercial products based on this technology have yet evolved.

As you can see there are several good synthetic approaches to building structures that will function as thermally stable and effective flame retardants. The problem is that any new flame retardant compound must also demonstrate minimal effects on the physical properties of a variety of polymers. This requires extensive testing and evaluation by compounders and end users. New compounds must also be listed on the various chemical inventories around the world. Unfortunately, there is not one but three sets of testing protocols necessary to gain acceptance worldwide. These are the requirements for listing on the EINECS (Europe) inventory, the TSCA

(US) inventory and the MITI (Japan) inventory. Many other countries have their own inventories but will usually accept test results acceptable for listing on one of the main three. In the past you could restrict yourself to a limited geographic market and concentrate on the listing requirements of that market. But today, and especially in the future, with the globalization of products and markets it is necessary to consider worldwide registration requirements. This is particularly true in those applications with the greatest growth, such as in electronic equipment and computers. The use of new polymers to replace metal and even other polymers requires flame retardants acceptable in any jurisdiction. It is not uncommon to have components made in many different countries, assembled in still other countries and finally sold everywhere. The problem does not stop there, because it is likely that each country or regional trading bloc will have its own rules on disposal and recycling of obsolete equipment. We are already seeing this in the still voluntary ecolabeling programs established in Germany (Blue Angel) and in Sweden (White Swan).

It is clear that the defining parameters for future flame retardant candidates present formidable challenges even before chemistry is considered. It is also likely that no other class of compounds has a better chance of meeting these challenges than organophosphorus compounds.

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