

Toxicity as a Function of Structure: Organophosphorus Flame Retardants

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Abstract

The rapidly increasing development of new organophosphorus flame retardants presents a need for toxicity assessment. To date, toxicity studies have included compounds of very heterogeneous structure which has led to the generation of muddled results. Careful studies which focus on compounds of similar structure, e.g., linear alkyl phosphates, branched alkyl phosphates, aryl phosphates, substituted aryl phosphates, phosphonates, phosphonates, phosphine oxides, are needed to provide data to support the synthesis and use of new effective nontoxic organophosphorus flame retardants.

Keywords: Organophosphorus flame retardants; Heterogeneous structure; Bioaccumulator; Nontoxic bio-sources; Synthesis

Need for Organophosphorus Flame Retardants

The development of polymeric materials during the mid-twentieth century has permitted huge enhancement of the standard of living of peoples in most areas of the world [1,2]. Despite their many attractive features these materials are, in the main, quite flammable and must be flame retarded for most applications [3]. Over the decades, many substances have been utilized as flame retardants, most often as additives that could be introduced into a polymer matrix during processing. Among a wide range of potential flame-retarding agents, two have been most prominent. Both are organic: organo-halogen, particularly brominated aryl ethers, and organophosphorus compounds [4-6]. Traditionally, organo-bromine flame retardants have been industrial favorites. On an elemental basis alone, bromine is much more available, and much less expensive than phosphorus. Phosphorus compounds are also in high demand for other applications such as fertilizer and food additives [7,8]. The popular, decabromodiphenyl ether, is derived from a byproduct of phenol production [9]. Cost alone does not account for the widespread use of bromo-aromatics. They function as very effective flame retardants. They undergo decomposition in the temperature range for degradation of a range of polymers to liberate hydrogen bromide to the gas phase where it serves as an effective scavenger for combustion propagating radicals.

Unfortunately, despite the effectiveness of these compounds, they display several features which negatively impact their use [4]. Decomposition at high temperature is accompanied by the formation of volatile, very toxic dioxins [10]. More importantly, they tend to migrate from a polymer matrix into which they have been incorporated. This is particularly a problem for items discarded in a landfill [11]. These materials enter the environment, tend to bioaccumulate and may enter the human food chain. Human exposure to organo-halogen flame retardants can lead to a range of disease states, most associated with endocrine disruption [12]. For this reason, both regulatory and societal pressure have stimulated a reduction in the use of these materials. Organophosphorus compounds have risen to prominence as replacements. In particular those derived from renewable, readily available, low-cost nontoxic bio-sources have gained attention [13,14]. Those that may be covalently incorporated into the polymer structure or that are highly branched oligomeric compounds seem to hold great promise [15,16]. Not only do these materials provide efficient flame retardancy but are not prone to migration and loss to the surroundings.

Phosphorus Compounds

Phosphorus compounds have long had a prominent impact on society. From the earliest establishment of organized communities,

phosphorus compounds have been utilized as nutrients for crop production [17]. They have also been widely used as additives in both animal feed and food for human consumption. Huge amounts of these compounds are consumed annually. Phosphorus compounds are required for both plant and animal growth and development.

Phosphorus compounds have been hugely impactful in other areas as well. While the volumes have been much smaller than that in the nutrient area, they nonetheless have had major societal influence. At one extreme lie the organophosphorus warfare agents [18,19]. These compounds often contain a P-F bond. More important, of lesser but significant toxicity, are the pesticides [20]. Many of these compounds contain a P=S bond. Hugely significant has been the development of herbicides [21]. Glyphosate [N-(phosphonomethyl)glycine] has been the most widely used and effective of the organophosphorus herbicides. It acts on a pathway not available in mammals and therefore displays little human toxicity. It has been extremely successful when used with herbicide-resistant crops [22]. The development of effective pesticides and herbicides has revolutionized agriculture and permitted the production of food to sustain an ever-increasing world population. An important, but still smaller in production volume, class of organophosphorus compounds are flame retardants. These have permitted the utilization of many materials that, while displaying several desirable features, are highly flammable without modification.

Toxicity of Organophosphorus Flame Retardants

The development and use of organophosphorus flame retardants is currently of great interest. These materials provide great potential for polymer modification to reduce flammability. This without the toxicity problems associated with the use of organo-bromine counterparts. This is particularly true for organophosphorus compounds derived from renewable, readily-available, nontoxic biobased precursors. Now that organophosphorus flame retardants are becoming more prominent, human exposure to these materials and potential toxic effects have begun to be of concern [23-27]. Thus far toxicity assessment results are not definitive. The earliest organophosphorus flame retardants were simple phosphate esters. In general, these display low toxicity, most usually adverse neurodevelopment in children. However, toxicity is strongly structure dependent. Often sets of compounds for toxicity assessment contain esters of varied structure - linear alkyl, branched alkyl, variously substituted aryl or even haloalkyl [27,28]. Not surprisingly, haloalkyl phosphorus esters display greater toxicity than do nonhalogenated analogs (these compounds should more properly be treated as organo-halogen flame retardants containing a phosphorus atom). Systematic studies, with appropriate attention to dose level, of independent classes of organophosphorus esters-linear alkyl esters of varying chain length, branched alkyl esters, aryl esters containing various substituents-should be conducted to provide meaningful data to guide the synthesis and use of these compounds.

It has been noted that organophosphorus flame retardants with low levels of oxygenation at phosphorus, particularly DOPO (9,10-dihydro-9-oxa-10-phosphaphenathrome-10-oxide) esters, display little toxicity [29,30]. This observation needs to be examined in detail. Can toxicity of these compounds be correlated with the level of oxygenation at phosphorus. A systematic, careful study of toxicity versus level of oxygenation at phosphorus could provide, not only guidelines for selection of the most appropriate compounds for use but also direction for the synthesis of effective, nontoxic organophosphorus agents.

Conclusion

Organophosphorus flame retardants for polymeric materials are rapidly replacing traditional organo-halogen compounds which are persistent in the environment and display significant toxicity. In the main, organophosphorus flame retardants exhibit low toxicity. However, toxicity studies have yielded mixed results. This has largely arisen from the inclusion of compounds of quite varied structure within sample sets of compounds to be evaluated. Careful studies with attention to structure and dose level are needed to provide useful data. This information is needed to provide meaningful guidelines for the synthesis and use of new organophosphorus flame retardants.

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