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Research Article

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Action of Organophosphorus Flame Retardants: Impact of Structure and Mode of Thermal Degradation

Bob A Howell*

Science of Advanced Materials Center for Applications in Polymer Science Department of Chemistry and Biochemistry Central Michigan University Mt. Pleasant, MI 48859-0001

***Corresponding author:**
Bob A Howell, Science of Advanced Materials Center for Applications in Polymer Science Department of Chemistry and Biochemistry Central Michigan University Mt. Pleasant, MI 48859-0001.

ABSTRACT

The rapid development of organophosphorus flame retardants has been driven by demands for sustainability, environmental protection and low toxicity as well as broad effectiveness and modest cost. This development has been facilitated by an increasing understanding of both polymer combustion and flame-retardant mode of action. The activity of organophosphorus flame retardants is largely determined by the mode of decomposition in a degrading polymer matrix. This is strongly dependent on structure, primarily the oxidation level at phosphorus. Other structural features which provide a strong thermodynamic driving force and a facile pathway for the extrusion of the PO radical may also play a role. It has been demonstrated that organophosphorus compounds containing phosphorus at high oxidation level (e.g., phosphates) undergo thermal decomposition to form acidic species which promote cationic crosslinking and char formation. The presence of a char layer at the surface of the degrading polymer acts as an insulation barrier to inhibit heat feedback from the combustion zone which reduces the rate of polymer pyrolysis and consequent formation of volatile fuel fragments. In contrast, organophosphorus compounds containing phosphorus at low oxidation level (e.g., phosphonates) undergo thermal degradation at somewhat high temperature but do so to generate PO radicals some of which escape reaction with components of the matrix and are evolved to the gas phase. These radicals are sufficiently reactive to efficiently scavenge combustion propagating radicals. In general, these are more effective than counterparts that function in the solid phase.

Keywords: Flame Retardant Decomposition, Flame Retardant Activity, Biobased Flame Retardants, Nonmigrating Flame Retardants, Active Flame Retardant Species, Oxidation Level at Phosphorus.

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Abbreviations

IDEA: 3,6-bis-(diethylphosphato)isorbide
IDPA: 3,6-bis-(diphenylphosphato)isorbide
IOPA: 3,6-bis-(diphenylphosphido) isosorbide
IDOPYL: 3,6-bis-(didopyloxy)isosorbide
DOPO: 9,10-dihydro-9-oxa-10-phosphenthrene 10-oxide

Introduction

The recognition that traditional flame retardants are persistent, lead to environmental degradation and pose risks to human health has led to a focus on the development of new effective, low-cost, sustainable, nonmigratory and nontoxic additives for the control of polymer flammability [1]. In the main, these have been organophosphorus compounds. Biobased phosphorus derivatives have been particularly attractive [2,3]. Biobased precursors (compounds derived from biomaterials) are renewable, readily available, modest in cost, easily converted to useful organophosphorus compounds using simple methods, and nontoxic. Most organophosphorus flame retardants are esters, often simple phosphates. These compounds lie near the nontoxic end of the range of organophosphorus materials [4]. These materials are solid-phase active, i.e., they decompose in a degrading polymer matrix to

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generate species which promote the formation of insulating char layer at the surface of the polymer.

Alone these agents must be present at relatively high levels to ensure a suitable reduction in flammability. An adjuvant, an organonitrogen compound, is often incorporated into the polymer matrix along with the primary flame retardant. In fact, this mixture is currently the most widely used flame retardant system for polymeric materials. The organonitrogen compounds act in parallel with the phosphorus entity to decompose with the formation of volatile inert species which escape the polymer matrix and dilute the fuel load in the combustion zone. This combination of agents functions as an effective cooperative flame-retardant system.

Another set of compounds, most notably, 9,10-dihydro-9-oxa-10-phosphaphenthrene 10-oxide (DOPO), act in an entirely different manner and are more effective flame retardants. Literally dozens of DOPO derivatives have been prepared and evaluated as flame retardants, particularly for epoxy resins [5]. These decompose thermally in a degrading polymer matrix to form PO radicals, some of which escape reaction with components of the matrix and are evolved to the gas phase [6,7]. These radicals efficiently scavenge combustion propagating radicals.

For some time, evidence that the mode of action of organophosphorus flame retardants is strongly dependent on structure, particularly the oxidation level at phosphorus, has been accumulating [8]. This has been put on a sound foundation by a careful analysis of the thermal degradation of phosphorus esters of isosorbide containing phosphorus at different oxidation level [8].

Materials and Methods

Materials and methods have previously been described in detail [10]. Thermogravimetry was performed using a TA Instruments Q500 instrument, platinum sample pans and a constant purge of dry nitrogen. Infrared spectra were obtained using attenuated total reflectance and a Thermo Scientific Nicolet 380 FT-TR spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained using a Varian Mercury 300 MHz spectrometer and approximately 10% solutions in deuterochloroform. 1H and 13C chemical shifts are reported in parts-per-million with respect to the resonance for the tetramethlysilene (TMS) as internal reference (δ = 0.00), 31P chemical shifts with respect to the resonance for triphenyl phosphate (δ = -18.00) as internal reference. Electrospray (ESI) chemical ionization mass spectrometry was carried out using a Waters micro mass LCT Premier XE orthogonal acceleration time-of-flight (TOF) mass spectrometer.

Results/Observations

To better understand the behavior of organophosphorus flame retardants in a degrading polymer matrix, the thermal decomposition of four bis-phosphorus esters of isosorbide has been examined in detail (structures displayed in Figure 1) [9]. Two of these, IDEA and IDPA, are phosphates (high oxidation level at phosphorus), one, IDPO, a phosphinate and one, IDOPYL, a phosphonate (low oxidation level at phosphorus). That the thermal decomposition behavior of these esters varies strongly as a function of oxidation level at phosphorus is apparent from the plots displayed in Figure 2. Those containing phosphorus at high oxidation level (phosphates) undergo decomposition at relatively low temperature with formation of substantial residual material. The diethyl ester, IDEA, undergoes two-step decomposition with an initial event at very low temperature (Tonset 245° C). The diphenyl ester, IDPA, is more stable (Tonset 289° C) and degrades in a single step. Both the esters containing phosphorus at low oxidation level, IDPO and IDOPYL, degrade at high temperature (Tonset 338° C and Tonset 323° C, respectively) and produce little residual material. This disparity in thermal stability is more apparent from the plots displayed in Figure 3 which reflects isothermal degradation at 200° C. The phosphate esters undergo rapid degradation while the phosphinate and, in particular, the phosphonate, undergo degradation much more slowly (95% of the initial sample mass for IDOPYL remains after 4 hours at 200° C; 88% after 10 hours at 200° C).

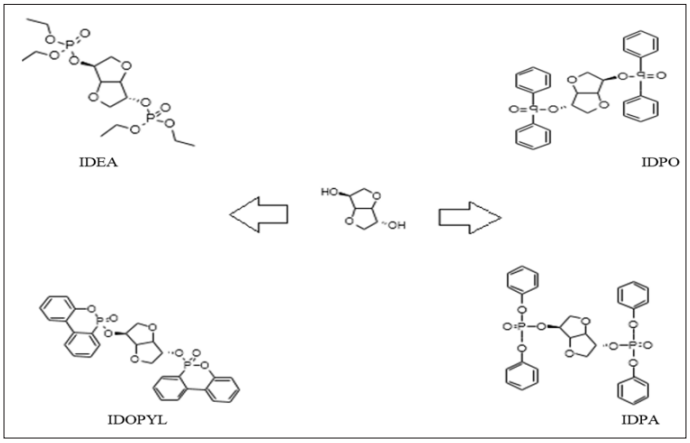

Figure 1: Structures of Isosorbide bis-Phosphorus Esters

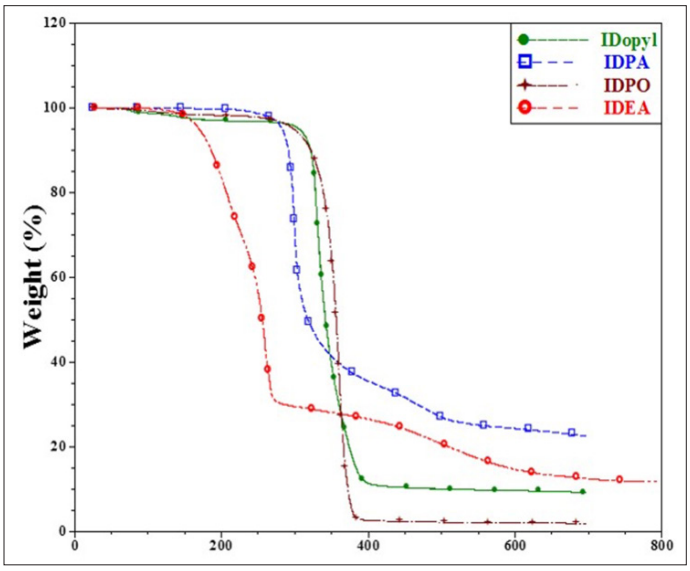

Figure 2: Thermal Decomposition of Isosorbide bis-Phosphorus Esters

The degradation process may be better defined by observation of the infrared spectra of compounds undergoing thermal decomposition. The first major change is the loss of C-H absorption in the 3000 cm-1 region and the appearance of

a broad band characteristic of a phosphorus acid in the same region. Another significant change is the growth of a band at 1644 cm-1 characteristic of a well-known diene previously prepared by ester pyrolysis. Analysis of extracts from the decomposition residues using ESI-MS confirmed the presence of the appropriate phosphorus acid. In the case of the IDOPYL ester, the corresponding DOPO acid sublimed from the degrading mixture, was isolated, and fully characterized using NMR spectroscopy. Most notably, the 31P spectrum contains a single sharp peak at **δ** 13.1.

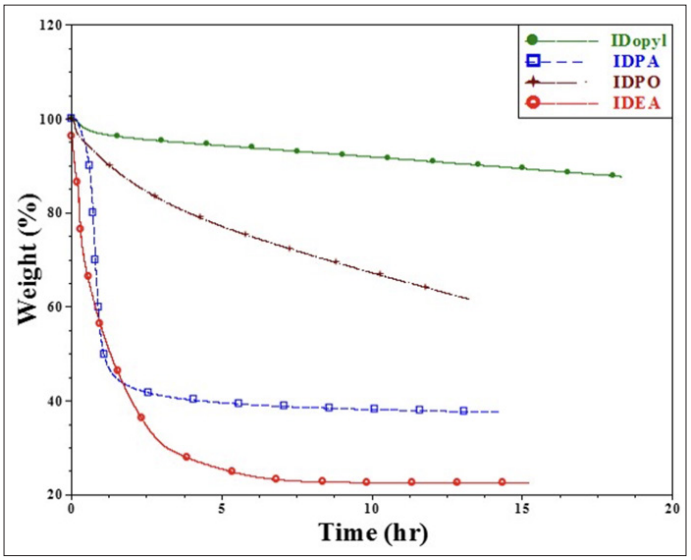

Figure 3: Thermal Degradation of Isosorbide bis-Phosphorus Esters at 200° C.

Discussion

It is clear that the phosphorus esters containing phosphorus at high oxidation level undergo thermal decomposition at relatively low temperature to form stable phosphorus acids. In the case of the diethyl phosphate initial elimination, as might be expected, occurs in the ethyl groups (Tonset 156° C) to liberate ethylene. A second event (Tonset 245° C) corresponds to elimination in the isosorbide unit to provide a residue of phosphoric acid. The diphenyl phosphate behaves in a similar manner but with the elimination in the isosorbide unit at somewhat higher temperature (Tonset 289° C) to afford a residue of the diphenyl-substituted acid. The initial degradation of the esters containing phosphorus at low oxidation level also corresponds to elimination. However, in these cases, the phosphorus acids formed are thermally unstable and degrade further to form volatile species such that little residue is generated. The initial degradation of the esters is depicted in Figure 4. The further degradation of the phosphinate and phosphonate acids is displayed in Figure 5. This further decomposition is spurred by a strong thermodynamic driving force (the formation of a stable organic product, biphenyl or dibenzofuran) and an accessible kinetic pathway for expulsion of small reactive species.

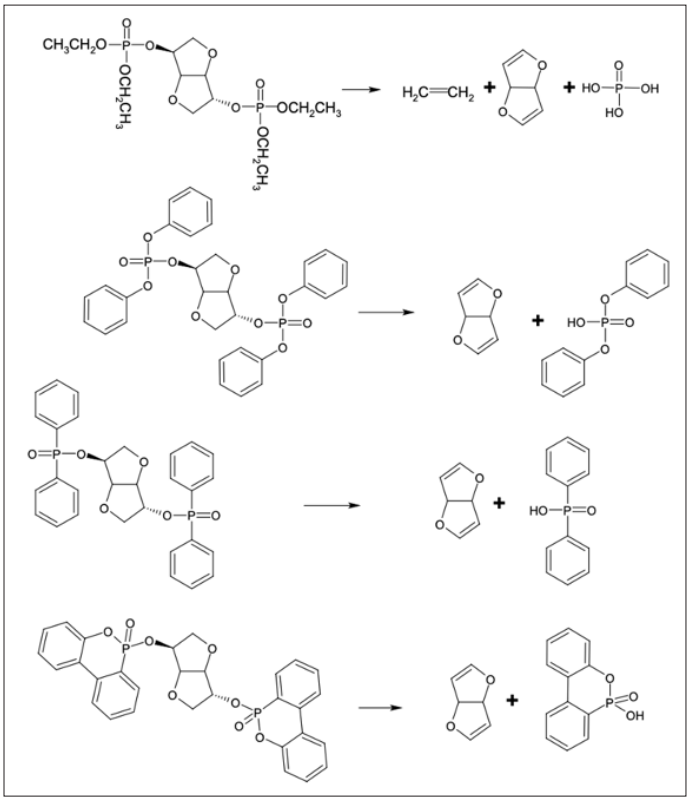

Figure 4: Initial Degradation of Isosorbide bis-Phosphorus Esters.

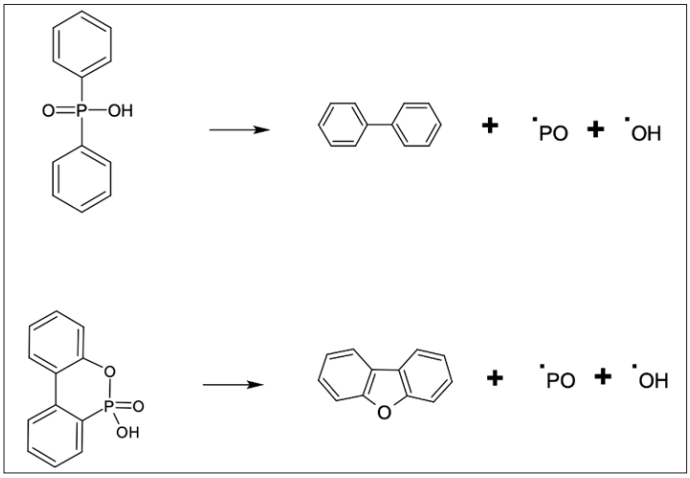

Figure 5: Thermal Degradation of Phosphinate and Phosphonate Derived Acids.

The mode of flame-retardant action for these compounds may be understood in terms of the simple diagram presented in Figure 6. As depicted, any polymer when heated to a sufficiently high temperature will begin to degrade thermally. This process generates small volatile fuel fragments which escape to the gas phase where they mix with oxygen and, if the temperature is at or above the ignition temperature, combustion may occur. Combustion is a radical chain process which produces heat, light (flame) and, if combustion is incomplete, particulates (soot, smoke) and noxious carbon monoxide. As may be seen, there are two opportunities to interrupt the overall process. The first is in the solid phase, i.e., to reduce the rate of polymer pyrolysis and consequent formation of volatile fuel fragments. Phosphorus compounds containing phosphorus at high oxidation level

function in the solid phase. In the degrading polymer matrix, they decompose to form phosphorus acids which promote cationic crosslinking and char formation at the surface of the polymer. This char layer acts as an insulation barrier to inhibit heat feedback to the polymer and reduce the rate of formation of volatile fuel fragments. Phosphorus compounds containing phosphorus at low oxidation level degrade further, in this case, to generate hydroxyl and PO radicals. The hydroxyl radicals are rapidly consumed by reaction with components of the degrading polymer matrix.

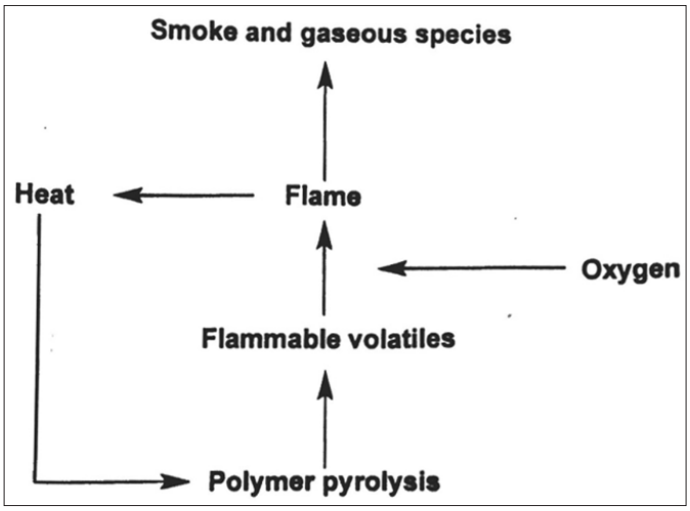

Figure 6: The Polymer Combustion Process.

Some of the PO radicals meet the same fate but, being less reactive, some survive and escape to the gas phase. These species very efficiently scavenge propagating radicals in the combustion zone. Thus, depending on structure, principally the oxidation level at phosphorus, organophosphorus flame retardants may be either solid-phase or gas-phase active. The impact of phosphorus oxidation level on the mode of action of organophosphorus flame retardants has been supported by theoretical considerations [11]. The great utility of DOPO derivatives as flame retardants lies in structural features which facilitate thermal decomposition to generate the PO radical.

In the design and synthesis of new, broadly useful flame retardants, such structural features should be given appropriate attention. Further, to meet expectations for sustainability, environmental integrity and regard for human health these should be derived from biobased substrates [1]. Further, they should be either reactive or oligomeric. Oligomeric organophosphorus flame retardants based on hyperbranched poly(ester)s generated from renewable, abundantly-available, nontoxic bio monomers are particularly attractive. These materials offer both a high degree of branching and ester functionality both of which enhance compatibility with a range of polymer matrices [12]. Now that these materials can be prepared in any desired molecular weight without gelation and with control of end group identity (Martin-Smith procedure), a wide variety of opportunities for preparation of useful and benign flame retardants is available [13].

Conclusion

The present study demonstrates that the flame-retardant activity of organophosphorus compounds is strongly influenced by their molecular structure, particularly the oxidation level at the phosphorus atom. Phosphorus esters with a high oxidation state (such as phosphates) decompose at relatively lower temperatures and form stable phosphorus acids, which promote char formation and cross-linking in the polymer matrix. The resulting char layer acts as a thermal barrier, reducing heat transfer and slowing the release of combustible volatile fragments from the polymer.

In contrast, compounds with a lower oxidation state (such as phosphinates and phosphonates) decompose at higher temperatures and produce reactive PO radicals. Some of these radicals migrate into the gas phase where they effectively quench flame-propagating radicals, interrupting the combustion chain reaction. Thus, depending on their structure, organophosphorus flame retardants can function through solid-phase mechanisms (char formation) or gas-phase radical scavenging mechanisms.

Understanding the relationship between molecular structure, thermal degradation behavior, and flame-retardant mechanism is essential for the rational design of new materials. Future flame-retardant systems should emphasize biobased, environmentally benign, and non-migratory organophosphorus compounds, particularly oligomeric or reactive derivatives derived from renewable resources. Such materials can provide effective fire protection while meeting modern requirements for sustainability, safety, and environmental compatibility.

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