Flame Retardation by Phosphorus Compounds

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Most organic materials are thermodynamically unstable with respect to their combustion products. In an oxygen-containing atmosphere, they are therefore susceptible to flaming combustion if ignited.

The often disastrous consequences of unwanted combustion long ago prompted attempts to reduce the fire hazard of combustible materials by combining them with chemical compounds that act as flame retardants. Research in this area dates back to the early 19th century. For example, Gay Lussac, in 1821, described a procedure to flame-retard theater curtains by impregnation with ammonium phosphate solution.[1]

In recent years, interest in flame retardation has increased dramatically because of the large-scale introduction of synthetic macromolecular materials which are often more flammable than the original materials they replace. As a result of this effort, thousands of flame-retardant compounds have been developed for use in a wide variety of inherently flammable, polymeric materials.[2]

Chemically, the large number of flame-retardant compounds reported in the literature may be grouped according to the "flame-retardant element" which they contain. The two most prominent classes of flame retardants are based on either halogen or phosphorus. Among the halogen-containing compounds, bromine compounds are usually the most effective. The mode of action of halogen-based flame retardants has been thoroughly investigated and is assumed to involve, in most cases, inhibition of gas-phase chain reactions which occur in the combustion zone of the polymer flame.[3] The flame-retardant activity of halogen compounds is often dramatically increased when they are used in combination with antimony compounds, usually Sb_2O_3. This synergistic effect of antimony most probably results from the formation of volatile antimony–halogen compounds, such as $SbBr_3$, which act as efficient inhibitors of the gas-phase oxidation in the flame.[4]

Phosphorus-based flame retardants are of at least equal importance. Members of almost every class of

organophosphorus compounds have been proposed for a wide range of materials and end-use applications. Inorganic phosphorus flame retardants include ammonium phosphates and elemental red phosphorus.[2] The flame-retardant activity of elemental phosphorus may appear somewhat surprising, since its highly negative oxidation enthalpy is the basis of the chemiluminescence of the white phosphorus allotrope which originally led to the name "phosphorus".

This example shows that by no means do effective phosphorus-based flame retardants have to be "noncombustible". In many cases, active compounds contain phosphorus in low oxidation states and are, therefore, readily oxidized. The performance of a particular phosphorus compound depends strongly on the nature of the matrix polymer. For this reason, it is not possible to make generalized statements concerning the relative effectiveness of two phosphorus compounds without indicating the polymer with which they are used. However, for chemically similar compounds, the flame-retardant activity in a given polymer often increases with increasing phosphorus content.

Although empirical research has led to the development of highly effective, phosphorus-based flame-retardant systems, there exists, at present, no unified theory which is able to explain the flame-retardant action of phosphorus compounds in terms of chemical mechanism. Consequently, this Account must be limited to a discussion of the various principles which have been used to rationalize the flame-retardant effects of different phosphorus-based systems. Many of the ideas relating to the mechanism of flame retardation by phosphorus compounds still lack definite experimental proof and may, therefore, have only the tran-

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(1) J. L. Gay Lussac, *Ann. Chim.*, 18 (2), 211 (1821).
(2) J. W. Lyons, "The Chemistry and Uses of Fire Retardants", Interscience, New York, N.Y., 1970.
(3) R. M. Fristrom and R. F. Sawyer, "Flame Inhibition Chemistry", presented at the 37th AGARD Symposium on Aircraft, Fuels, Lubricants and Fire Safety, The Hague, Netherlands, May 1971.
(4) J. W. Hastie, *J. Res. Natl. Bur. Stand., Sect. A*, 77, 733 (1973).

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sient merit of stimulating further research in the area.

Models of Polymer Combustion

In order to appreciate possible modes by which flame retardants may reduce the flammability of polymeric materials, one must discuss the models which have been developed to explain the mechanism of polymer combustion.

According to the widely accepted "two-stage theory of polymer combustion", the polymer must be volatilized before combustion can occur. The vaporization behavior of polymeric materials is basically different from that of low-molecular-weight compounds. For the latter, the heat of volatilization, which is a measure of the strength of the intermolecular forces, is usually much lower than the energy required to break the weakest bond in the molecule. Low-molecular-weight compounds, therefore, generally volatilize without prior decomposition.

In the case of polymeric materials, the intermolecular forces exceed the strength of the weakest chemical bonds in the polymer. Vaporization is therefore preceded by decomposition of the polymer into low-molecular-weight fragments. The thermal degradation is generally endothermic and requires the transfer of energy to the polymer, either by heat conduction or by absorption of radiant energy from an extraneous source. As soon as the rate of pyrolysis becomes high enough to provide a steady concentration of gaseous fuel in the air layer above the polymer surface in excess of the lower explosion limit of the fuel–oxidant mixture, ignition can occur, either by an outside source or, if the temperature is sufficiently high, by spontaneous autoignition. Once ignition has taken place, the generation of gaseous fuel is maintained by an energy feedback from the flame to the polymer surface. If this feedback is sufficient to maintain the composition of the oxidant–fuel mixture above its lower explosion limit, the combustion of the polymer becomes self-propagating and proceeds until the entire material has been consumed. In the case of inadequate feedback, the rate of pyrolysis decreases until the flame becomes unstable and extinction occurs.

While the condensed-phase reactions which lead to the formation of the gaseous pyrolysis products are, in most cases, not yet fully understood, knowledge of the gas-phase combustion of the pyrolysis products is more detailed: polymer flames have the physical characteristics of diffusion flames. However, in contrast to conventional diffusion flames, the rate of fuel generation is not an independent variable but is determined by the heat flux back to the polymer. This heat flux depends on the temperature of the polymer flame which, in turn, is determined by the oxygen concentration of the atmosphere. Chemically, the flames of polymers containing only carbon, hydrogen, and oxygen can be compared to the well-studied hydrocarbon/oxygen diffusion flames.[5]

Based on the two-step model of polymer combustion, different modes of action for a flame retardant may be visualized: A flame retardant may act in the gas phase by inhibiting exothermic oxidation reactions in the flame, thus reducing the energy feedback to the polymer surface which, in turn, renders the material less flammable. A second possible way of imparting flame retardance involves formation of a thermal barrier between the condensed and the gaseous phases which prevents heat transfer back to the pyrolyzing polymer and inhibits the generation of gaseous fuel. Flame retardants which act in this way usually catalyze the formation of a visible char on the polymer surface. Finally, a flame retardant may act by modifying the pathway of pyrolytic decomposition of the polymer either by changing the composition of the gaseous fuel or by affecting the rate of its formation.

In the case of phosphorus, flame retardation according to each of these basic mechanisms has been invoked to explain experimental results obtained for different polymeric systems. Specific examples will be presented in later sections of this Account.

Measuring Flammability

To determine the efficiency of flame retardants, reliable tests must be available which permit the measurement of the flammability for a given material in the presence and absence of the flame retardant. Although this requirement may appear trivial, it has not been possible to develop a universal, small-scale flammability test capable of predicting the performance of a material in a "real fire". This failure results from the conceptual difficulty of defining a standard fire situation.

In spite of this inherent limitation, it is possible to measure the relative flammabilities of materials under carefully controlled conditions. For this purpose, the so-called oxygen index method has been widely used. In this test, the sample is burned in a vertically downward mode in an oxygen/nitrogen atmosphere of controlled composition. The oxygen content of the gas mixture is gradually reduced until the atmosphere is no longer able to support the combustion of the sample and extinction occurs. This limiting oxygen concentration is termed the oxygen index (O.I.) of the material.[6] The O.I. is material specific and relatively insensitive toward changes in the sample dimensions; its value decreases with increasing temperature of the sample. Most common polymers have an O.I. < 21 at room temperature, which means that they will burn in air. Since the temperature in a fire situation is almost always above ambient, and the burning is most likely to occur in an upward mode, the true flammability hazards are usually greater than reflected by the O.I. value.

Combination with a flame retardant increases the O.I. compared with the unprotected polymer. The slope of the curve obtained by plotting O.I. vs. flame-retardant concentration is a measure of the flame-retardant activity in the particular system. The O.I. method is valuable for establishing positive interactions among several different flame retardants in the same polymer system: If the O.I. increase produced by a mixture of flame retardants is equal to the combined effects of the individual components, no interaction is taking place. On the other hand, if synergistic interactions occur, the O.I. increase of the mixture exceeds the additive effects of the components. Synergistic systems are obviously of great practical importance;[7] examples of synergism

(5) R. M. Fristrom, *J. Fire Flammability*, 5, 289 (1974).

(6) C. P. Fenimore and F. J. Martin, NBS Symposium, "The Mechanism of Pyrolysis, Oxidation and Burning of Organic Materials", *Natl. Bur. Stand. (U.S.) Spec. Publ.*, **No. 357**, 159 (1972).

involving phosphorus-based flame retardants are discussed below.

Aside from providing a measure of flammability, the O.I. method has also been used as a probe to elucidate the mode of action of a flame retardant: If a compound acts as a gas-phase inhibitor, its activity should be confined to combustion in an oxygen-containing atmosphere, while no activity is expected if another oxidant, such as N_2O, is used to burn the sample, since, in this case, the flame chemistry is different. On the other hand, if the flame retardant acts via a condensed-phase mechanism, its effectiveness should not be affected by a change of the oxidant, since the inhibition involves changes in the pyrolysis pattern which are specific for the particular polymer but independent of the oxidant. Using these criteria, one can discriminate between gas- and condensed-phase activity of a flame retardant by measuring the O.I. and the N_2O index as a function of the flame-retardant concentration.[8]

Gas-Phase Inhibition by Phosphorus Compounds

Empirically, it has been found that in many cases effective phosphorus compounds have to volatilize below 450 °C, which is the typical surface temperature of a burning polymer. Volatilization of the pure flame-retardant compound in the appropriate temperature range is, however, not sufficient evidence that a flame-retarded polymer is capable of releasing the flame retardant into the gas phase during actual burning, since the mass flux of the retardant into the gas phase may be limited by its transport through the phase boundary.[9] The presence of phosphorus-containing moieties in the combustion zone of the flame may be inferred from the characteristic emission in the range of 500 to 600 nm, which is presumably caused by excited HPO species in the flame.[10] A quantitative correlation between emission intensity and concentration of a volatile phosphorus compound in the flame fuel has been obtained in the case of trimethyl phosphate admixed to a fuel-rich hydrogen/oxygen flame.[11]

Recently it has also been possible to monitor phosphorus-containing species by direct mass spectrometric probing of flames with admixture of either triphenyl phosphate or triphenylphosphine oxide.[9] In both cases, the concentration of the parent phosphorus compound decreases in the direction toward the flame front, while a concomitant buildup of other phosphorus-containing species occurs. The most abundant of these is PO, while HPO_2, PO_2, and P_2 are found in lesser concentrations. These results show unequivocally that phosphorus species resulting from the thermal breakdown of volatile phosphorus compounds are capable of reaching the reaction zone of a gas diffusion flame. In the case of polymers which are flame-retarded by volatile phosphorus compounds, the characteristic flame emission is likewise observed, although, to our

knowledge, direct quantitative measurements have not been reported.

The ability of phosphorus to act as a flame quencher has been verified experimentally: a comparison of the quenching efficiency of PCl_3 with phosphorus-free hydrogen compounds shows that, on a molecular basis, phosphorus is about 12 times as effective as chlorine and more than twice as effective as bromine.[12] The quenching experiments were carried out in an oxygen/hydrogen flame by adding the quenchers on the oxidant side of the diffusion flame. Since in the case of a flame-retarded polymer the volatilized flame retardant enters the combustion region from the fuel side, these relative quenching efficiencies may not be valid quantitatively.

The mechanism of the gas-phase inhibition can be deduced from the dependence of the quenching on the phosphorus concentration: significant quenching is observed only if the concentration of the phosphorus species becomes comparable to the concentration of hydrogen atoms in the flame, which is in the order of 10^{-3} M. This suggests that gas-phase inhibition involves a destruction of hydrogen atoms which leads to an interruption of the combustion chain. Reduction of the hydrogen atom concentration appears to be a particularly effective way of inducing gas-phase inhibition, since hydrocarbon flames, including most polymer flames, are limited by the branching step of the combustion chain, eq 1, which depends on the presence of hydrogen atoms. This main branching step also provides the principal attack on molecular oxygen. For a flame reaction, the activation energy, $E = 16.5$ kcal/mol, is rather high, and the reaction is rapid only for temperatures above 1100 K.[5]

$$H + O_2 \rightarrow OH + O \tag{1}$$

On a molecular basis, the phosphorus species act via a third-body mechanism, catalyzing the recombination of hydrogen atoms according to eq 2.

$$PO + H \rightarrow HPO \tag{2a}$$

$$HPO + H \rightarrow H_2 + PO \tag{2b}$$

The inhibition cannot involve a chemical scavenging of H atoms with consumption of phosphorus species, since this type of mechanism would require a much higher inhibitor concentration in the flame to produce a retarding effect.

This shows that, in the case of volatile phosphorus compounds, gas-phase activity can be a contributing factor to the overall flame-retardant effect. However, as will be seen in the following sections of this Account, the mode of action of flame-retardant systems with practical importance generally involves inhibition of polymer-specific, condensed-phase reactions. An example of the superimposition of general gas-phase and specific condensed-phase action has been found in the case of flame retardation by elemental red phosphorus.[13]

Flame Retardation of Polypropylene

Isotactic polypropylene, which has an O.I. of 17.4, can be used as an example for the flame retardation of a polyolefin by phosphorus compounds. Flame-retardant

(7) E. D. Weil, "Additivity, Synergism, and Antagonism in Flame Retardancy", in "Flame Retardancy of Organic Materials", W. C. Kuryla and A. J. Pappa, Ed., Marcel Dekker, New York, N.Y., 1975, pp 185–243.

(8) C. P. Fenimore and G. W. Jones, *Combust. Flame*, **10**, 295 (1966).

(9) J. W. Hastie and C. L. McBee, *Nat. Bur. Stand (U.S.) Interagency Rep.*, **No. 75-741** (1975).

(10) L. T. My and M. Peyron, *J. Chim. Phys. Phys.-Chim. Biol.*, **60** 1289 (1963).

(11) C. P. Fenimore and G. W. Jones, *Combust. Flame*, **8**, 133 (1964).

(12) G. Lask and H. G. Wagner, "Eighth Symposium (International) on Combustion", Williams and Wilkins Co., Baltimore, Md., 1962, p 432.

(13) A. Granzow and J. F. Cannelongo, *J. Appl. Polym. Sci.*, **20**, 689 (1976).

requirements for this polymer are generally similar to those for other polyolefins such as high-density polyethylene and polybutylene. Polypropylene starts to degrade thermally above 290 °C. In the case of linear high-molecular-weight polypropylene, the decomposition rate goes through a maximum, indicating that the polymer degrades via a random scission mechanism.[14] At 400 °C, a complex mixture of gaseous pyrolysis products is formed which consists mostly of C_5, C_6, and C_4 hydrocarbon fragments with only small amounts of propylene monomer present.[15] The degradation occurs by thermal scission of the carbon–carbon bonds in the polymer backbone which requires an activation energy of about 55 kcal/mol. This primary cleavage is accompanied by a hydrogen transfer which preferentially involves breaking a tertiary carbon–hydrogen bond according to eq 3.[16]

(3)
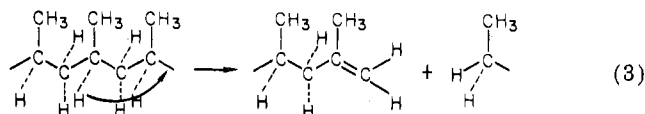
Additive-type flame retardants for polypropylene have to be thermally stable at the processing temperature of about 250 °C. In the case of phosphorus-based compounds, this requirement limits the choice of potential flame retardants to phosphonium salts, phosphine oxides, and phosphonic acids, classes which generally exhibit a high degree of thermal stability.[17] In the case of heat-stable phosphine oxides, compounds containing cyanoethyl groups such as structure I have been found to be particularly effective flame retardants. The activity of this compound has been shown to increase in the presence of inorganic phosphorus in the form of ammonium polyphosphate (II).[18]

I

II
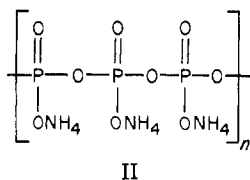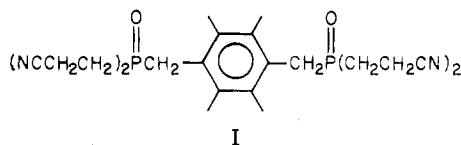
The shapes of the O.I. vs. concentration plots for compounds I and II are different: II gives a linear efficiency plot, while I shows a leveling off at high concentrations, indicating that the modes of action of the two compounds probably are different. This is supported by the results of combustion experiments in an atmosphere containing N_2O instead of oxygen. The efficiency of I is greatly reduced, while the flame retardancy of II remains intact, suggesting that I acts as a gas-phase and II as a condensed-phase flame retardant. This complementary behavior may be the basis

of the strongly increased flame retardance observed when mixtures of the two compounds are added to polypropylene. The extent of the synergistic action of such mixtures can be demonstrated by the following comparison. A thermally thin sample of polypropylene containing 15 wt % of I + 15 wt % of II has an O.I. of 34, while the O.I. calculated from the contributions of the two individual components is only 23.[19] Although only II may be considered a condensed-phase flame retardant, the synergistic effect of the mixture appears to be exclusively caused by condensed-phase reactions, since the synergism is not suppressed if the oxidant is changed to N_2O.

The flame-retardant mechanism responsible for the synergism may be deduced from the following observations. If polypropylene containing a mixture of I and II is burned in an atmosphere the oxygen concentration of which surpasses the O.I. for that particular formulation, a large amount of char is formed which contains almost the entire amount of phosphorus initially present in the sample. On the other hand, one observes no significant char formation during combustion of samples containing either I or II alone. Consequently, we have to assume that formation of this char layer is related to the observed flame-retardant synergism. Experimentally, it has been shown that the char acts as a thermal barrier which inhibits the heat transfer from the flame to the unburned polypropylene and in this way reduces the pyrolysis rate so that stable burning conditions can no longer be maintained. The insulating effect of the char is demonstrated by the considerable temperature lag experienced by a thermocouple embedded in the center of the flame-retarded sample when the surface of this sample is subjected to charring combustion.[20]

Flame Retardation of Poly(ethylene terephthalate)

Recently, the flame retardation of poly(ethylene terephthalate) fibers for textile applications has become an important area of research. Poly(ethylene terephthalate) has an O.I. of about 20 and can be effectively flame-retarded by phosphorus compounds. The flame retardant can be applied in two different ways. The first type of flame retardant is introduced into the spun fiber by a thermosol process. Compound III is the most

III

IV

$Ph_3P=O$

V

widely used flame retardant applied in this manner. Because of the additive effects of phosphorus and bromine, the flame-retardant activity of III is high. Recently, however, this compound has become suspect as a carcinogen and is no longer used.[21]

(14) L. A. Wall and S. Straus, *J. Polym. Sci.*, **44**, 313 (1960).
(15) S. L. Madorsky and S. Straus, *J. Res. Natl. Bur. Stand.*, **53**, 361 (1954).
(16) S. L. Madorsky, "Thermal Degradation of Organic Polymer", Interscience, New York, N.Y., 1964, p 93.
(17) A. E. Sherr, H. C. Gilham, and H. G. Klein, *Adv. Chem. Ser.*, **No. 85**, 307–325 (1968).
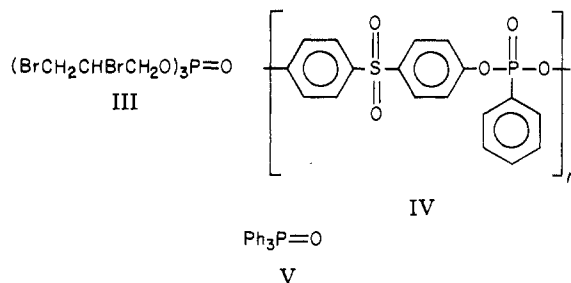(18) J. A. Hoffman, U.S. Patent 3 835 119 (1974).
(19) C. Savides, A. Granzow, and J. F. Cannelongo, submitted for publication to *J. Appl. Polym. Sci.*
(20) C. Savides, A. Granzow, and J. F. Cannelongo, SPE RETEC, Polyolefins, Houston, March 1975.

Flame retardants of the second type are added to the polyester melt before spinning. The choice of phosphorus compounds is therefore restricted to those which are thermally stable at the processing temperature of poly(ethylene terephthalate) around 300 °C; but to be effective, the additive has to decompose rapidly around 400 °C, the surface temperature of burning polyester. The activation energy for the decomposition of the additive, therefore, has to be high, and the decomposition ranges of the additive and polymer have to overlap. Aside from these thermal stability constraints, good physical compatibility with the polyester melt and the absence of any detrimental effects on the spinnability are mandatory. Polymeric phosphonates such as IV have been found to be particularly suitable in meeting these various requirements.[22]

The mode of action of phosphorus-based flame retardants in polyester is still controversial. However, it is apparent that in the case of low-molecular-weight compounds such as V, which volatilize without prior decomposition, the flame retardancy exclusively involves gas-phase inhibition, since no effect by the additive on the thermal decomposition of the polyester is observed; this conclusion is supported by the fact that the change to N_2O as the oxidant totally eliminates the flame-retardant effect.[23] The flame retardancy of volatile compounds of this type is only modest, as expressed in terms of the O.I. increase, indicating that condensed-phase processes have to account for the much higher activity of compounds such as IV which, unlike V, decompose rather than evaporate upon heating.

Comparison of the flame retardance of a large number of thermally stable phosphorus compounds on the basis of equivalent phosphorus content shows marked differences in activity. No phosphorus organic compound has been found to exceed the effectiveness of elemental red phosphorus,[24] perhaps because only the pure "flame-retardant element" is added, and no additional fuel resulting from the nonphosphorus part of the additive is introduced. Red phosphorus is a polymeric material which starts to decompose around 450 °C to form P_4 molecules which, in turn, can dissociate into P_2 molecules at flame temperatures. Because of its high activity and favorable thermal properties, elemental red phosphorus may, therefore, be considered as a useful model compound to study the effects of phosphorus-based flame retardants on the pyrolysis and combustion of poly(ethylene terephthalate).[13,25]

The O.I. vs. concentration curve for flame retardation by elemental red phosphorus is nonlinear; replacing oxygen by N_2O does not change the shape of the efficiency curve but partially suppresses the flame retardance, indicating that both gas- and condensed-phase processes are operative.[13] The importance of condensed-phase reactions is demonstrated by the effect of red phosphorus on the isothermal pyrolysis of poly(ethylene terephthalate) at 400 °C: the pyrolysis rate of phosphorus-containing samples decreases pro-

Scheme I
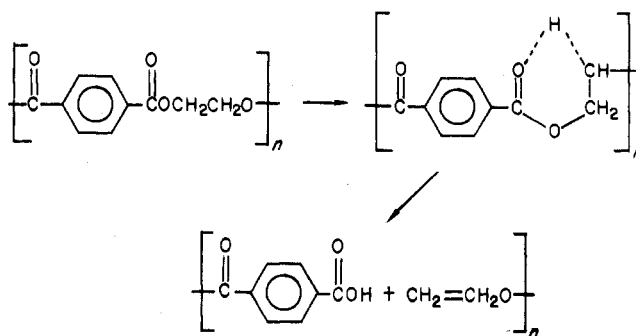
gressively with increasing phosphorus concentration, and the total amount of gaseous products diminishes, while the weight fraction of nonvolatile residue increases. The flammability results can be correlated with the isothermal pyrolysis data: the relative increase of the O.I. is directly proportional to the relative decrease of the maximum pyrolysis rate for a given phosphorus concentration.[25] Since the pyrolysis experiments apply to an inert gas atmosphere, one has to assume that the degradation of the polyester under actual burning conditions is purely pyrolytic rather than thermooxidative.

The condensed-phase activity of phosphorus in poly(ethylene terephthalate) must, therefore, involve an inhibition of the pyrolytic decomposition, which is known to occur by a random scission process with initial breaking of the ester linkage by way of a β-hydrogen-type alkyl–oxygen fission according to Scheme I. This reaction is believed to involve a concerted cyclic transition state. The vinyl ester end groups resulting from the primary chain scission are subsequently destroyed either by secondary scissions or by disproportionation reactions which ultimately lead to volatile, low-molecular-weight fragments or, alternatively, form a nonvolatile charlike residue.[26]

At 400 °C, the volatiles consist mainly of acetaldehyde, methane, and carbon monoxide, the latter two gases probably being formed by the secondary breakdown of acetaldehyde.[27] In the presence of phosphorus, the composition of the pyrolysis gases remains unchanged. Therefore, the flame-retardant activity seems to be connected with a shift in the ratio of volatile to nonvolatile pyrolysis products rather than with a basic change of the pyrolysis pattern. This is supported by the pyrolysis kinetics measured by thermogravimetry: the weight loss curve for pure poly(ethylene terephthalate) at 400 °C is exponential after a brief induction period, indicating that, for most of the decomposition, the initial chain scission is rate limiting, while the subsequent breakdown to smaller voltile molecules is significantly faster. In phosphorus-containing samples, the rate of volatilization is reduced, and the apparent kinetic order is changed to zero. This change in pyrolysis kinetics suggests that phosphorus inhibits the secondary reactions which lead to volatile products so that this process now becomes rate limiting. Inhibition involving primary chain scission should simply reduce the rate constant for the exponential weight loss without affecting the kinetic order.[25]

(21) A. Blum and B. N. Ames, *Science*, 195, 17 (1977).
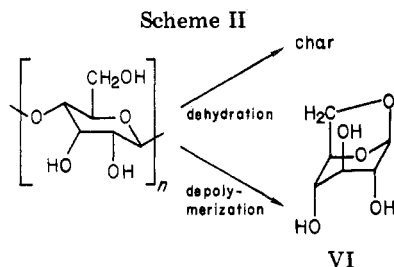
(22) Toyobo Co., U.S. Patent 3 719 727 (1974).

(23) J. E. Bostic, Jr., K. Yeh, and R. H. Barker, *J. Appl. Polym. Sci.*, 17, 471 (1973).

(24) A. Granzow, C. Savides, and J. F. Cannelongo, unpublished.

(25) A. Granzow, R. G. Ferrillo, and A. Wilson, *J. Appl. Polym. Sci.*, 21, 1687 (1977).

(26) P. D. Ritchie, *SCI Monogr.*, No. 13, 107–131 (1961).

(27) E. P. Goodings *SCI Monogr.*, No. 13, 211–228 (1961).

Scheme II

VI

Scheme III

$$\overset{+}{P}(CH_2OH)_4 \rightarrow P(CH_2OH)_3 + CH_2O + H^+$$

$$CH_2O + H_2NCONH_2 \rightarrow HOCH_2NHCONH_2$$

$$HOCH_2NHCONH_2 + H^+ \rightarrow \overset{+}{C}H_2NHCONH_2 + H_2O$$

$$\overset{+}{C}H_2NHCONH_2 + P(CH_2OH)_3 \rightarrow$$
$$\overset{+}{P}(CH_2OH)_3CH_2NHCONH_2, \text{ etc.}$$

The fact that elemental phosphorus is an effective flame retardant only for oxygen-containing polymers, such as polyesters, polyamides, and polyurethanes, while only marginally active in oxygen-free polymers, such as polystyrene or polypropylene, may suggest that, on a molecular basis, its mode of action involves scavenging of oxygen-containing radicals which act as chain carriers in the secondary pyrolysis steps that lead to generation of gaseous fuel species.

Flame Retardation of Cellulose

Natural cellulose is a linear polymer whose primary structure consists of β-glucopyranose units linked together by 1,4-glycosidic bonds, with the number of monomer units ranging up to about 5000. Since the strength of the C–O bond is lower than that of the C–C bond, pyrolytic degradation of cellulose will preferentially involve primary scission of C–O bonds. Bond-breaking may occur either within the ring or at the glycosidic linkage between the individual monomer units. The first case leads to a complete breakdown of the molecular structure with carbon dioxide, carbon monoxide, water, and a carbonaceous char as the main products, the overall result being a dehydration of the cellulose. This dehydration reaction is favored at low pyrolysis temperatures.

The second pyrolysis pathway involves intramolecular transglycosylation with breaking of the glycosidic linkage. The reaction is probably heterolytic and leads mainly to the formation of levoglucosan (1,6-anhydro-β-D-glucopyranose, VI).[28] The depolymerization pathway of pyrolysis is favored at high temperatures. The two parallel pathways of degradation are shown in Scheme II.

The main exothermic process in the combustion of cellulose is the oxidation of carbon monoxide to carbon dioxide; formation of a carbon-rich char by way of the dehydration mechanism reduces the amount of carbon oxidized to carbon dioxide and lowers the overall exothermicity of the combustion as compared with decomposition via the depolymerization mechanism. In the latter case, levoglucosan is completely oxidized in the gas phase, and the heat production of the combustion process is higher.

Phosphorus compounds, which are the most widely used flame retardants for cellulose, presumably act by reducing the pyrolysis temperature of cellulose, thus favoring the dehydration pathway of decomposition. Experimentally, it is found that phosphorus-based flame retardants increase the char yield, with a large part of the phosphorus being retained in the residue. There is, therefore, little doubt that in the case of cellulose the flame-retardant action occurs exclusively in the condensed phase.
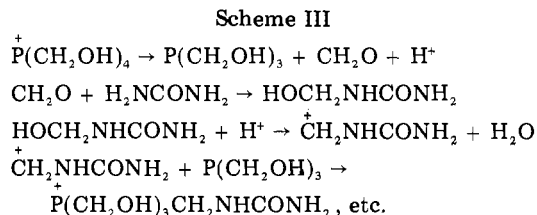
The action of phosphorus compounds appears to result from the formation of phosphoric and polyphosphoric acids during the combustion process. These acids are nonvolatile at the temperature of burning cellulose fibers around 420 °C[29] and can act as dehydration catalysts. The dehydration is assumed to occur via a carbonium ion mechanism, involving either general acid catalysis or, alternatively, phosphorylation of cellulosic hydroxyl groups, probably at the C-6 atoms of the glucose units.

The efficiency of phosphorus compounds is often dramatically increased in the presence of certain types of nitrogen compounds, such as ammonia, urea, guanidine, or dicyandiamide.[30] A combination of a phosphorus-based flame retardant with any of these nitrogen compounds leads to a further increase in char formation and to greater phosphorus retention in the char. Interestingly, some of the nitrogen is likewise retained, while in the absence of a phosphorus compound, the nitrogen is quantitatively volatilized. These results suggest that during combustion interactions between phosphorus and nitrogen are taking place which must involve the formation of heat-stable phosphorus–nitrogen bonds. Products formed at combustion temperatures may include phosphoramidates containing P–NH$_2$ groups that are presumably even better dehydration catalysts than P–OH compounds. The effect of nitrogen compounds on the flame-retardant activity of phosphorus compounds, therefore, represents a true case of synergism.

If the cellulose is in the form of a textile material, the flame retardant must be durably fixed to or within the fiber in order to withstand repeated laundering; at the same time, it is mandatory that the physical appearance and properties of the flame-retarded material remain acceptable. One way of achieving a permanent flame-retardant treatment is by polymerization of the flame retardant inside the cellulose fiber to form a highly cross-linked, water-insoluble polymer network. To be effective, this flame-retardant resin should contain high amounts of both phosphorus and nitrogen to utilize the synergistic effect of the latter.

A widely used, durable treatment of this type consists of a polymer formed by the reaction of a tetrakis(hydroxymethyl)phosphonium salt with a polyfunctional amine or amide, such as ammonia or urea.[31-33] In the case of urea, the flame-retardant polymer is formed by polycondensation involving the hydroxymethyl groups of the phosphonium salt and the amide groups of urea, as shown in Scheme III.[34]

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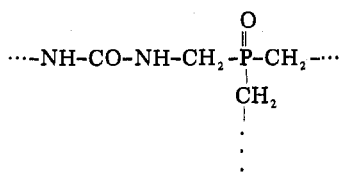(30) G. C. Tesoro and C. Meiser, Jr., *Textile Res.*, **40**, 430 (1970).
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In the technical application, the polymer is formed by padding an aqueous solution containing the phosphonium salt and urea onto the fabric which is then heat-cured. The durability of the treatment is enhanced by post-oxidation with hydrogen peroxide to form the more stable phosphine oxide structure; this oxidized polymer may be represented by VII.

$$\overset{\displaystyle O}{\underset{\displaystyle \underset{\cdot\,\cdot\,\cdot}{\overset{|}{CH_2}}}{\cdots\text{-}NH\text{-}CO\text{-}NH\text{-}CH_2\text{-}\overset{\|}{\underset{|}{P}}\text{-}CH_2\text{-}\cdots}}$$

VII

The cross-linked polymer is chemically inert and therefore not capable of interacting with the cellulose fiber. However, it has been shown that at temperatures above 240 °C the polymer is thermally degraded to water-soluble products, among which phosphoric acids and phosphoramidates have been isolated. In the case of the tetrakis(hydroxymethyl)phosphonium salt/urea system, therefore, the effective flame-retardant moieties are not present initially but are generated only in the course of the thermal degradation of the flame-retardant polymer.[35]

Conclusions

Highly effective phosphorus-based flame retardants for a variety of polymeric materials have been developed. As the use of synthetic polymer materials continues to increase while, at the same time, the general public is becoming more aware of the inherent flammability hazards of these materials, the need for even better flame retardants will remain strong. Not only will future flame retardants be required to reduce the hazards of flaming combustion, but at the same time, their effect on the generation of smoke and toxic gases in fire situations will become increasingly important. Similarly, the effects of flame retardants on health and environment is coming under close scrutiny. From what we know today, these additional demands are likely to increase further the importance of phosphorus derivatives vs. systems based on other elements.

Laser-Induced Vibrational Energy Transfer Kinetics: Methyl and Methyl-d_3 Halides

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Lasers came to the foreground early in their chemical careers in the study of energy-transfer processes at all levels of excitation. The flow of energy in nonreactive as well as reactive systems has great significance in both fundamental and practical forms. Relaxation processes, those by which an induced nonequilibrium distribution of populations decays back to normal statistical conditions, have been studied by a variety of techniques, including shock tubes, ultrasonic dispersion, excitation with conventional radiation sources, temperature and pressure jump, and, most recently, the use of lasers as tools for creating the initial nonequilibrium situation. These studies may yield a good deal of information concerning intermolecular potentials, but perhaps their greater impact will be in providing a general picture of

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pathways by which molecular energy flows.

Lasers have singular advantages over most excitation methods in that they make possible excitation of a specific energy level (by their nearly monochromatic nature) and, in addition, induce a significant excess population in that level (by their intensity). Having a system "prepared" in a specific state allows one to extract much more detailed information concerning relaxation rates and pathways than would otherwise be possible.

Let us refer specifically to the situation of molecular vibrational energy transfer. The classical ultrasonic dispersion technique has been used to measure overall relaxation rates for many species. Only recently, and by use of rather complicated deconvolution techniques, has any effort been made to deduce rate constants for specific pathways, e.g., from one excited vibrational level to another within the same species. Laser excitation provides direct access to such information. The procedure, which will be discussed in some detail below, involves direct placement of an excess few percent of the molecules in a sample into a specific vibrational level. Subsequently, one follows the time evolution of fluorescence emission from as many other vibrational levels as possible. Clearly, the access to detailed information concerning the collisional relaxation mechanisms is greatly enhanced.