Teaching about Flame Retardants. A Joint Israeli–Dutch Project

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Man has always been fascinated by fire. For thousands of years the nature of fire was a great mystery. In fact, modern scientific chemistry began with the discovery of the role of oxygen in combustion processes by Antoine Lavoisier and some of his contemporaries in the late 18th century. When chemistry was introduced as a subject in secondary schools in the 19th century, combustion and the role of oxygen in it became a central topic in the curriculum in most countries.

When, more recently, it was expected that societal and environmental issues be included in the curriculum, topics such as fire prevention and fire fighting were often incorporated in a chapter on combustion. Thus, the three conditions for burning, namely fuel, oxygen, and heat (or, more precisely, a sufficiently high temperature), figure in some modern schoolbooks. These three factors are often visualized in a "fire triangle" (Fig. 1): if one factor is missing, combustion will not occur. In some textbooks fire precautions taken in the laboratory are explained in terms of flash points of combustible liquids and explosion limits of gas and air mixtures.

However, little or no attention is being paid in this context to the uses and the effects of flame retardants. Yet flame retardants are nowadays considered to be very important in the prevention and control of fires, and to this end are found in building materials, carpets, curtains, baby clothes, bedding, electrical appliances, computer cases, and numerous other products. They offer interesting chemistry, much of which is well within the scope of secondary education.

This article reports some ideas for teaching about flame retardants in precollege or slightly advanced chemistry courses. It is based on a joint project that involves curriculum development and teaching activities in Israel and in the Netherlands. As part of this project, the Science Teaching Department of the Weizmann Institute of Science in Israel published an industrial case study on the bromine industry for secondary schools (1). This case study is now an integral part of the curriculum for students in Israel who major in chemistry. The Dutch contribution to the project consists of a teaching unit on bromine industry topics. This unit was designed by the Centre for Science and Mathematics Education of Utrecht University and was taught in several schools in the Netherlands (2). Flame retardants play an important role in both units.
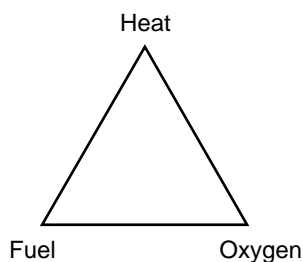
Combustion

Webster's dictionary (1995 edition) defines combustion as "any chemical process accompanied by the emission of heat and light, typically by combination with oxygen". Some materials ignite easily (e.g. cooking gas, gasoline, and paper), whereas others require a high temperature and a high oxygen concentration (e.g. Teflon and polyvinyl chloride). The flammability of a substance is often characterized by its ignition temperature (sometimes called autoignition temperature) and, in the case of a flammable liquid, also by its flash point. The ignition temperature is the lowest temperature at which combustion of the material will occur spontaneously under specified conditions. The flash point is the lowest temperature at which the vapor above a combustible liquid will ignite in air when exposed to a flame. The ignition temperature of ethanol, for instance, is 363 °C, while its flash point is 12 °C (3, 4).

The life cycle of a fire can be divided into four stages: ignition, propagation, steady combustion, and termination (Fig. 2). A single spark can often provide the energy required to start the combustion process. Once the material burns, energy is released and the fire spreads. The rate at which it spreads (the rate of flame propagation) depends on the kind of material burning and on the immediate environmental conditions. In the termination stage one or more of the factors essential to the combustion process are no longer present. This can occur naturally, e.g. when the supply of flammable material or oxygen is finished, or as a result of outside intervention.

Potential hazards of fires to humans include poisoning through inhalation of smoke or poisonous gases, tissue damage resulting from exposure to heat. and suffocation caused by reduced oxygen content in the air. Limited visibility through emission of thick smoke and soot may result in lengthening the exposure of victims trapped in a fire to these dangers.
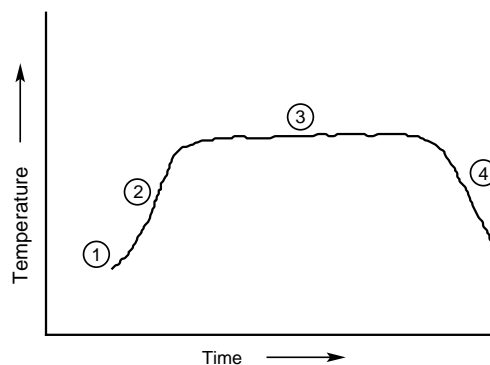

Figure 1. The Fire Triangle.

Figure 2. Stages in the life cycle of a fire: 1, initiation; 2, propagation; 3, steady combustion; 4, termination.

Flame Retardants

Residential fires annually kill between three and four thousand people and injure between 15 and 20 thousand more in the United States alone. Fires in the USA occur in almost half a million buildings each year, causing a property loss of seven billion dollars (*5*). These facts prove the need to look for ways not only to extinguish a blazing fire but also, when there is a fire source, to slow down or prevent the ignition and propagation steps. In response to this, the idea of retarding flames has been developed.

A flame retardant is a component of an otherwise combustible material that serves to slow down or to hinder the ignition or combustion of that material. The material does not become noncombustible, but the flame-retarding component is intended to prevent a small fire from rapidly developing into a major catastrophe (*6*). The main requirement for all flame retardants is to decrease the rate and intensity of combustion of the material and, as a consequence, to decrease the formation, in rate and in quantity, of dangerous substances such as carbon monoxide, soot, and others, including, in some cases, hydrogen cyanide. Even delaying the propagation of a fire a few minutes might save lives by giving people enough time to get out of the fire zone. Modern safety standards require self-extinguishing capability of a product when it is exposed to the most common sources of fire found in its normal surroundings. Two such sources are lit cigarettes smoldering in upholstered furniture and mattresses, and short circuits in electrical instruments. Figure 3 illustrates the effect of a typical flame retardant.

The term *flame retardant* is often used within the context of combustible synthetic or natural polymers; this usage will be followed in this article. A flame retardant in a polymer is either *additive* (i.e., an added component comparable to a plasticizer or a filler) or it is chemically incorporated into the polymer chains. In the latter case it is called a *reactive* flame retardant.

There are several ways in which flame retardants may work. As a rule a flame retardant interferes with one or more of the three factors essential to the combustion process. In practice, flame retardants are tailored to the specific properties of the flammable material and to the common causes of fire in the material's environment. The most important groups of chemicals used as flame retardants are (*7, 8*):

1. Organic halogen compounds, especially bromine and chlorine compounds, often in combination with antimony oxides (almost half the market volume in dollars);

2. Phosphorus compounds, such as phosphate esters (about 20%); and

3. Metal compounds such as alumina trihydrate, $Al_2O_3 \cdot 3H_2O$, and magnesium hydroxide, $Mg(OH)_2$ (another 20%).

Flame retardants are now the most used plastics additives. In fact, according to information provided by the Dead Sea Bromine Group they account for more than 35% of bromine consumption in the world, which is a 2.35 billion dollar market (1998). In this article we focus on some specific organic bromine compounds, as they are among the most important and interesting flame retardants.
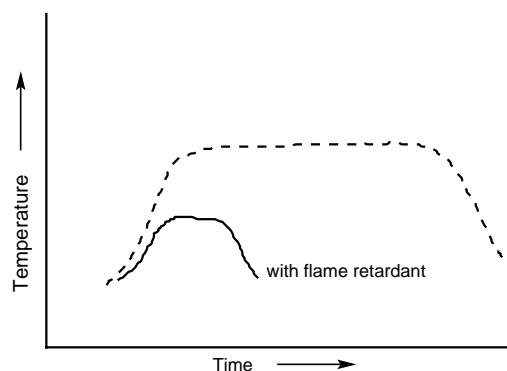

Figure 3. The effect of a flame retardant on a fire.

Demonstrations

Most students, when asked to name a substance that fulfills the definition of a flame retardant, come up with water because they know that wood, paper, and textile do not burn easily when wet. In practice, of course, water is used only on a temporary basis—for example, in case of a fire, to protect the adjoining premises. Further discussion with students can focus their attention on criteria for effective flame retardation in, say, a window curtain. In such a discussion, students can formulate very well some of the requirements that a suitable flame retardant should fulfill; for example, it should be a stable material that can be easily integrated into the cloth and that will retain its active properties until it is exposed to a fire. Obviously, the substance should not have a major effect on the characteristics of the cloth of the window curtain. Students find it much more difficult, however, either to suggest examples of suitable flame retarding substances or to think up a satisfactory explanation of flame retardation.

An indispensable part of a teaching unit on flame retardation is a demonstration of the striking difference between the combustion of polymer samples that are and are not protected by flame retardants (Fig. 4). A video film that shows clearly
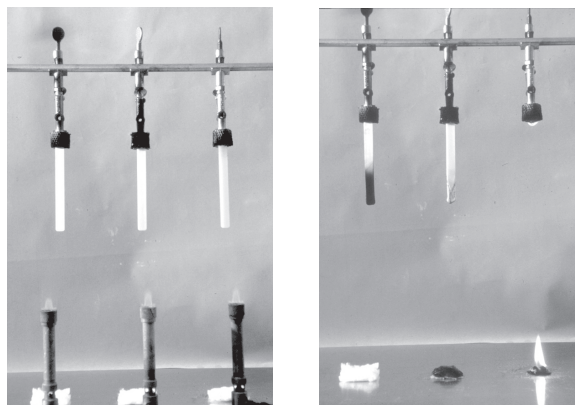

Figure 4. The effect of flame retardants on the combustion of plastic rods before ignition (left) and after burning (right). The left plastic rod has 24% flame retardant, the middle plastic rod has 3% flame retardant, and the right plastic rod has no flame retardant.

the effect of flame retardants on the combustion of various polymers was prepared by the Department of Science Education of the Weizmann Institute of Science. (An English version is in preparation.) Samples of flame-retarded plastic rods used in the video were donated by Bromine Compounds Ltd., which routinely prepares such samples for flammability and mechanical testing (9). It is, however, even more convincing to demonstrate the real thing by using small samples of textiles, some protected by flame retardants and some not protected, or small pieces of different pipes made from PVC and other plastics, to test for ease of combustion. Such samples are usually easy to obtain.

Other experiments with flame-retardant effects help to develop the theme further. For example, in a very simple demonstration a small, dry filter paper is covered partly with a very thin layer of dry powdered sodium bicarbonate, $NaHCO_3$, and ignited. The result is remarkable: only the part of the paper that is not covered will burn. Alternatively, a filter paper is soaked in a solution of sodium bicarbonate and then dried in an electric oven between 100 and 120 °C before ignition. The paper will burn a little or not at all. Similar demonstrations using mono-ammonium phosphate or ammonium bromide can also be performed. Such experiments will encourage students to become aware that flame retardation is an intriguing phenomenon and to search for possible explanations by exploring it in the laboratory.
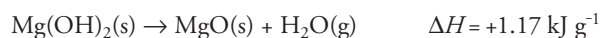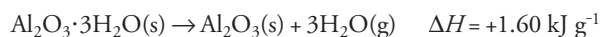
Retardation Mechanisms

Heating a sample of sodium bicarbonate in a dry test tube helps to reveal part of the mystery of flame retardation. Students will notice that water vapor condenses in the cooler part of the tube. By passing the gases through lime water, they will be able to find out that carbon dioxide is produced along with the water vapor:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Both gases are incombustible and, when given off by the decomposing powder on the ignited filter paper, will dilute the mixture of burning gases and oxygen and help to dispel the air that is necessary for the continuation of the burning process. In addition, the decomposition of sodium bicarbonate is an endothermic reaction (ΔH = +0.81 kJ g^{-1}) and causes a decrease in the temperature of the flame. (Reaction enthalpies are given per gram rather than per mole because the content of a flame retardant in a material is usually given as a mass percentage.) The combination of the two effects, involving two of the three factors of the fire triangle, prevents the paper from burning.

Sodium bicarbonate is not normally used as a flame retardant but it is used as a dry fire extinguishing powder. However, several substances in use as flame retardants (7), such as alumina trihydrate (decomposition temperature: 230 °C) and magnesium hydroxide (decomposition temperature: 320 °C) are based on the same principle, namely,

$$Al_2O_3 \cdot 3H_2O(s) \rightarrow Al_2O_3(s) + 3H_2O(g) \qquad \Delta H = +1.60 \text{ kJ g}^{-1}$$

$$Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(g) \qquad \Delta H = +1.17 \text{ kJ g}^{-1}$$

Other flame retardants, for example some phosphorus compounds, tend to form an almost incombustible glassy insulating layer that separates the solid polymer from the flame, thereby also creating a flame retarding effect.

At a slightly more advanced level, students will be able to understand the action of those flame retardants that interfere with the free radical mechanism of the combustion process. It is generally agreed that free radicals play an important role in the complex reaction mechanism of most combustions in the gaseous phase. When a polymer burns, radicals such as ·OH, ·H, ·R, ·O, and ·OR take part in chain reactions in each of the four stages of the combustion. The ·OH, ·H, and ·O radicals are especially reactive. Their formation is strongly endothermic, but when they react with each other or with other reactive radicals present in the gaseous phase, a large quantity of energy is released back into the flame. However, when they react with less reactive radicals or with molecules, there is a significant reduction in the net quantity of energy available for propagating the flame. Heavy atoms, such as halogens, act as "less reactive" radicals because they absorb a relatively large quantity of energy from the flame.

Students can figure out some reasons for the choice of the specific halogens to do this. Iodine compounds can be expected to be the most effective but they are not used in plastics because the C–I bonds are relatively weak, so the decomposition temperature is usually below the temperature of compounding or burning. Fluorocarbons are inherently incombustible but they do not impart flame-retardant properties to other compounds because in some cases the carbon–fluorine bond is too stable, while in others the highly reactive free fluorine atoms immediately form hydrogen fluoride molecules, which do not enter into the flame-quenching mechanism. Commercial halogen-containing flame retardants therefore include aliphatic, alicyclic, or aromatic compounds with either chlorine or bromine substituents (7).

Flame retardants containing bromine are usually more effective, on a molar basis, than those containing chlorine because bromine atoms are much heavier than chlorine atoms. Despite the high cost of bromine relative to chlorine, and despite a significant increase in the mass of the polymer caused by bromine compounds, brominated flame retardants are often preferred.

When brominated flame retardants absorb the required amount of energy, the C–Br bonds will break homolytically. The free bromine atoms formed by this process react with the hydrogen atoms of the polymer, forming hydrogen bromide molecules. These HBr molecules also play an important role in halting the chain reactions that take place during the burning process. They can, for instance, deactivate ·OH radicals as follows:

$$·OH + HBr \rightarrow H_2O + ·Br$$
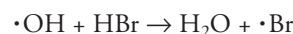
The newly formed free bromine atom regenerates HBr by capturing a free hydrogen atom present in the gaseous phase or by reacting with the polymer itself:

$$·H + ·Br \rightarrow HBr$$

$$RH + ·Br \rightarrow HBr + ·R$$
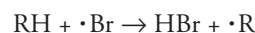
Several other reactions are possible. The main overall effect is that the heavy bromine atoms withdraw energy from the combustion-propagation mechanism.

Examples of Bromine Compounds Used as Flame Retardants

In order to meet both the desired flame retardancy and the desired mechanical properties of the product, most bromine-containing flame retardants are used as additives, usually not more than 30% of the mass of the final product. Some of these additive compounds also contain oxygen, phosphorus, or nitrogen. They are usually made from hydrocarbons and other organic compounds through multiple substitution or addition reactions involving elemental bromine. Substitution and addition reactions are included in most elementary organic chemistry courses, albeit normally with simpler hydrocarbon substrates.

Two examples of flame retardants are 1,2,5,6,9,10-hexa-bromocyclododecane (HBCD), produced from cyclododeca-1,5,9-triene and bromine:
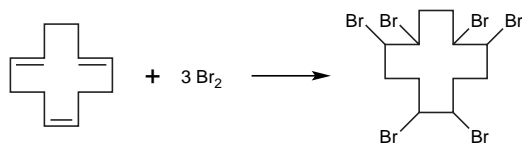
and tetrabromobisphenol-A (TBBA), produced from bisphenol-A and bromine:
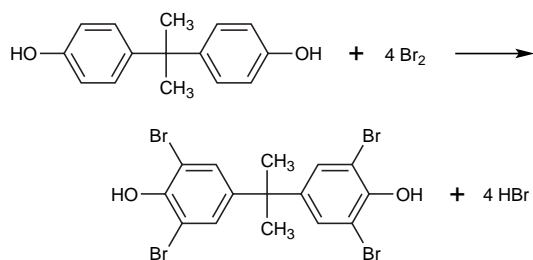
HBCD is an additive flame retardant, since it has no functional groups that can be chemically incorporated into the polymer chain. Reactive flame retardants are usually applied through copolymerization, one of the monomers being a suitable bromine or chlorine compound. TBBA is a reactive flame retardant, since it has two phenolic OH groups that can be incorporated into polymer chains. In fact, TBBA is used in the manufacture of some epoxy, phenolic, and polycarbonate resins. Tetrabromophthalic anhydride (TBPA) is often used in unsaturated polyesters.
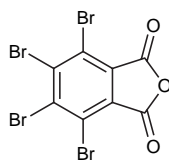
Tetrabromophthalic anhydride

Vinyl bromide is also used as a flame retardant monomer in some copolymerization reactions. Polyvinyl chloride (PVC) is a special case, since this polymer itself has flame-retarding properties.

Some flame retardants are either additive or reactive, according to their mode of application. For example, TBBA is also used as an additive in polystyrene and in some of its copolymers.

## Considerations for Choosing a Flame Retardant

The increase in public awareness to fire hazards and damage caused by fire has stimulated a strict application of standards and, as a result, a growing use of flame retardants in polymer products. Not all polybrominated organic compounds are suitable flame retardants for all applications. A substance must fulfill several requirements before it can be considered for application as a flame retardant in a specific polymer used for a specific purpose. The flame retardant is only one of many components, which, apart from the polymer itself, may include fillers, UV stabilizers, dyes, antioxidants, and antistatic additives. A flame retardant must be inexpensive, stable to heat and in some cases to light, and preferably colorless. It must not drastically change the physical and mechanical properties of the final product and it must be stable at temperatures at which the product is formed. To be effective, it should decompose around the same temperature at which the polymer itself begins to decompose, which is normally between 200 and 300 °C (*4, 7, 8*). If it is an additive flame retardant, it should blend easily with the polymer, which in practice requires it to have about the same viscosity in melt as the polymer.

Another requirement is that the flame retardant does not itself release toxic substances that might be dangerous either immediately or in the long run. The potential for release of toxic substances became an issue after the 1976 Seveso incident, when a mixture of chemicals including dioxin (2,3,7,8-tetra-chlorodibenzo-*p*-dioxin and some of its isomers), generally considered to be highly toxic, was released from an overheated vessel in the Icmesa plant in Lombardy, Italy, and settled on large areas of Seveso and other communities surrounding it. It is now known that dioxins can be formed when certain organic compounds that contain chlorine are burned. Bromine analogs of dioxin can be formed in fires involving certain brominated organic compounds. The dioxin formation problem must be taken into consideration not only in accidents involving fires but also when fire-protected household products are burned in a waste incinerator at temperatures that are too low.

In the last 20 years there has been much discussion about dioxins that are suspected to be toxic (*10, 11*). The U.S. Environmental Protection Agency (EPA) has issued a rule, 40 CFR/766, that requires producers to analyze eight listed brominated flame retardants for the presence of dioxins and furans in the material. In Germany, an ordinance was issued limiting the presence of dioxins and furans in flame retardants and in the flame-retarded polymeric matrix. From an educational point of view, the toxicity aspect of brominated flame retardants, precisely because of its serious nature, can be seen as an enrichment of the topic. Students can be introduced to a typical environmental and health dilemma: how, in the case of fires, to balance the risk of dioxin formation against the potential life-saving effects of flame retardants. In discussions of this problem, students are likely to suggest solutions, such as more fundamental research into the toxicity of dioxins, the development of flame retardants that produce nontoxic dioxins or no dioxins at all, or the introduction of recyclable flame retardants.

As environmental and health requirements have become more important, much research effort is indeed being invested

to develop safe flame retardants. Thus brominated trimethyl-phenylindane, which, owing to its molecular structure, does not form dioxins in a flame, was recently developed by the bromine industry to overcome this problem.

Phenylindane
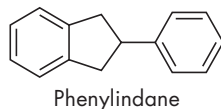
There is also a trend to develop flame retardants that can be recycled during recycling of the plastic product itself. Thus, two features of flame retardants have recently become essential for their production and use: the stability of the flame retardant during recycling and no production of dangerous derivatives when the flame retardant is exposed to a fire.

Results of the Project

The unit on flame retardants has been taught in Israeli secondary schools since 1990 as part of an industrial chemistry case study on the bromine industry (*11–13*). This unit takes about three to five lessons, depending on the students' background knowledge in polymer chemistry. Teachers who teach this case study participate in an in-service training course in which time is devoted to the subject of flame retardants and to ways for implementing the unit in class.

The case study deals with a variety of subjects such as bromine and its properties, occurrence of bromine in the world, extraction of bromine from the water of the Dead Sea, the production process, and past and present uses of bromine and its compounds. The use of flame retardants is just one of many applications of bromine compounds, and students found it to be very absorbing. Many reported that the study of flame retardants was one of the most interesting chapters in their chemistry studies. It is not only connected to other topics, such as polymers and combustion, but it is also relevant to everyday life. Because fire is a real danger in modern life, students are very much aware of the need to protect society. In this context fire protection applies to students personally in their homes, in public buildings, and even during their army service.

In the Netherlands, the Israeli teaching material was adapted to the locally prevailing syllabus and to the requirements of the school system. The Dutch version, which requires eight to ten lessons, offers students an opportunity to reexamine, in a new context, several topics taught earlier. It covers the discovery of bromine, its extraction from the Dead Sea, and the bromine industry, with special emphasis on flame retardants as an important modern application of bromine. Some aspects of flame retardants addressed by the unit are the industrial synthesis of a number of specific bromine compounds, the mechanisms of the flame-retardation process, and safety and environmental aspects of using (or not using) flame retardants. Some experiments on flame retardation were included in the unit. The Dutch students worked in small groups, aiming to answer questions and solve problems distributed throughout the text. They were asked to try to reach consensus within each group and hand in only those answers that were agreed upon by the group. This contributed to the intensity of group discussions and to the quality of the answers. Afterwards,

making use of data collected in the classroom, the material was revised. A translation in English of this second version, including a teacher's guide, is available on request.

In their comments, Dutch students indicated that the material, apart from being rather unorthodox, was interesting and instructive. Like their Israeli counterparts, they appreciated the link with everyday life situations and societal issues.

The project has shown that some important aspects of flame retardants can be taught on various levels in chemistry courses without demanding specific knowledge of complicated organic compounds, processes, or mechanisms. The chemistry of flame retardants can be integrated into a variety of contexts, such as combustion processes, organic chemistry, polymers, and chemical industry.

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