

ANALYSIS OF VARIOUS METAL OXIDE/ORGANOHALIDE-BASED FLAME RETARDANTS

Search for the retardation process

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The mechanism of evaporation of various metal oxides and the formation and evaporation of metal halides in the presence of chlorine-containing compounds have been studied by complex thermal analysis including atomic absorption measurement of the evolved species. The retardation process in the case of the $\text{MoO}_3 + \left\langle \begin{array}{l} \text{PVC or Cerechlor 70} \\ \text{halide donor} \end{array} \right\rangle$ and the $\text{ZnO} + \left\langle \begin{array}{l} \text{PVC or Cerechlor 70} \\ \text{halide donor} \end{array} \right\rangle$ system and that for $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ has been discussed.

It is well known that antimony trioxide (Sb_2O_3) is the most frequently used flame retardant additive for polymers due to its numerous advantageous properties. It is applied in the presence of halogen-containing compounds such as PVC or chlorinated paraffin where a pronounced synergetic effect develops. This effect is attributed to the formation of antimony trihalides (SbX_3 where $X = \text{Cl}$ or Br) [1, 2].

The mechanism of evaporation of Sb_2O_3 and that of the formation and evaporation of SbX_3 were studied at different Sb/X mole ratios by means of complex thermal analysis (TA) and flame atomic absorption technique (AT). With the aid of these methods the temperature of SbCl_3 formation and its evaporation could be detected [3].

Some attempts have been made recently to study the interaction of halogenated organic compounds with various metal oxides in order to replace Sb_2O_3 by other metal oxides.

Benbow and Cullis [4] divided the oxides into three groups: inert oxides, catalytic oxides and compounds that produce volatile metal halides. Oxides of Bi, Cd, Cu, Pb, Mo and Zn belong to the third group. It is assumed that of the oxides mentioned those of Bi, Zn and Mo may be suitable as flame retardants based on the low melting points of their chlorides.

Other authors [5, 6] have considered the applicability of hydrated aluminium oxide ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) as a flame retardant additive. It undergoes dehydration on heating which is an endothermic process, and the aluminium oxide left back forms, together with the charred residue of the polymer, an isolating layer which hinders the oxygen transport at the surface of the flammable material. In contrast to Sb_2O_3 , $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ is non-corrosive, harmless to health and compatible with materials usually present in flame retardant compositions. It is applied in a concentration of 10–20%, much higher than Sb_2O_3 .

Church and Moore [7] investigated molybdenum-based flame retardants applied with PVC and polyolefins, and stated that these compositions reduced the flammability to a small extent only, but smoke formation significantly, by 50–70% compared with non-treated samples.

Other authors [8] have found that the mechanism of the flame retardant action of MoO_3 is different from that of Sb_2O_3 .

It is possible to predict whether a metal oxide may be useful as replacement for Sb_2O_3 by heating it in an appropriate mixture with PVC or CP. The extent of volatilization of the metal oxide will depend both on its ability to react with the liberated hydrogen chloride and on the boiling point of the metal chloride formed.

The aim of this work was to follow the formation and vaporization of halides and to determine the possible similarity to the flame retardant action of Sb_2O_3 . Involatility in these experiments does not mean that the metal oxide is not capable of exerting any flame retardant action; rather, it indicates that the mechanism of such action is not similar that of Sb_2O_3 .

Experimental

Materials

Metal compounds: MoO_3 , ZnO , $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ used were of A.R. grade. Halogen compounds: Poly(vinylchloride) (PVC) (TVK, Hungary) and Cerechlor 70 (ICI) (chlorine content 70% w/w). (Both decompose quantitatively in the condensed phase to liberate HCl.)

Methods

Thermoanalytical measurements were carried out with a derivatograph. The sample mass in the measurements was 100 mg. The crucibles were made of oxide ceramics. A heating rate of 10 deg min⁻¹ was used.

In the combined furnace—flame atomic absorption method (AT) [9]—the dry aerosol formed from sample vapours in the furnace is transported into the flame for atomic absorption observation. In these measurements an acetylene-air mixture of nearly stoichiometric composition was used. For metal-specific studies a Pye—Unicam Model SP 90 A atomic absorption spectrophotometer was applied, with modified sample introduction.

Results and discussion

In Fig. 1 the thermoanalytical curves of MoO₃ are shown. The melting of the sample is indicated by a DTA peak at 800° in good agreement with literature data.

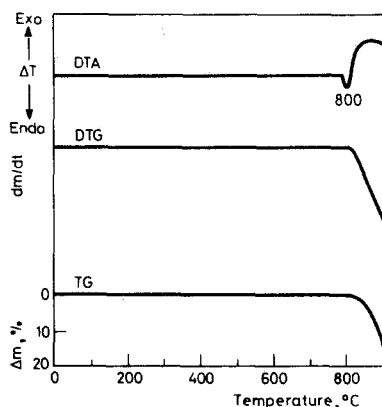


Fig. 1 TG, DTG and DTA curves of MoO₃ in air

When mixtures of MoO₃ with PVC or Cerechlor-70 with different mole ratios are heated, the following reaction may be assumed to take place between MoO₃ and the HCl released from the decomposed polymer:



Contrasting with the Sb₂O₃ → SbCl₃ transformation, this process is a redox reaction which accelerates the decomposition of the organic matrix. The decomposition of pure PVC is known to proceed with maximum rate at 290°,

resulting the release of the stoichiometric amount, 59% of HCl in an endothermic process.

In Fig. 2 the thermoanalytical curves of $\text{MoO}_3 + \text{PVC}$ mixture are shown. The decomposition of PVC proceeds in two distinct steps, with the first DTG peak appearing at 240° already. The weight loss calculated from the amount of PVC present considering the complete release of HCl (59%) is represented by the full line in the figure. However, the total weight loss is greater than that corresponding to the stoichiometric amount of HCl. As MoO_3 in itself undergoes no change in this temperature range, the additional weight loss should be ascribed to the release of the product of reaction of HCl with MoO_3 . TA and atomic absorption measurements (Fig. 3) prove the appearance of volatile molybdenum compounds in the gas phase. In addition to molybdenum pentachloride, the oxychlorides (MoOCl_3 , MoO_2Cl_2 and MoOCl_4) may also be assumed to form [10, 11]. The appearance of peaks on the AT curve in the range of $220\text{--}230^\circ$ and $290\text{--}310^\circ$ seem to justify this assumption (Fig. 3).

It is interesting to note that in N_2 atmosphere at higher temperatures the active carbon yielded by the decomposition of PVC (1a) and Cerechlor (2a) reduces MoO_3 to metallic Mo which is non-volatile in the temperature range studied. On the other

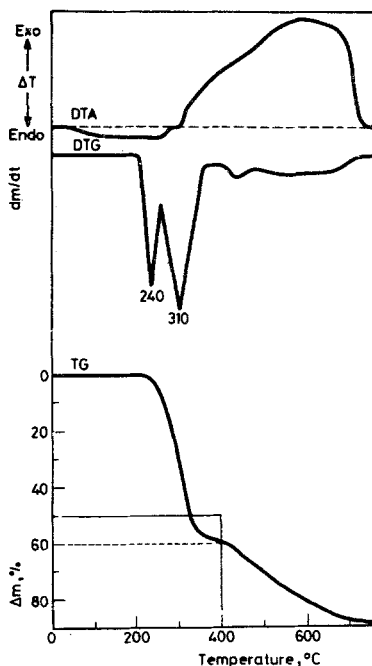


Fig. 2 TG, DTG and DTA curves of the mixture of $\text{MoO}_3 + \text{PVC}$ Mo/Cl = 1 : 5 in air

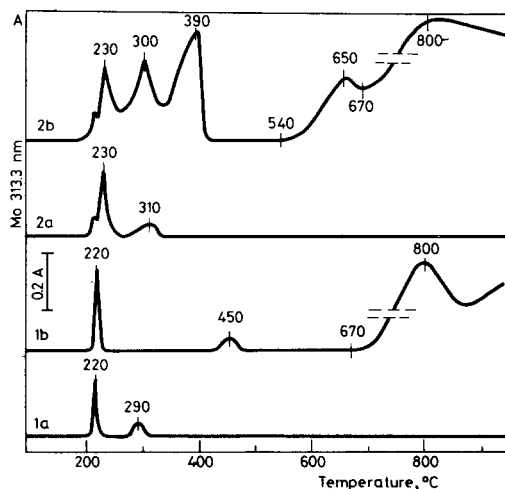


Fig. 3 AT curves of the mixture of $\text{MoO}_3 + \text{PVC}$ (1) and the mixture of $\text{MoO}_3 + \text{Cerechlor}$ (2); a: in nitrogen, b: in air

hand, in air curves 1b and 2b carbon is oxidized and the MoO_3 still present, as indicated by the melting point at 800° on the DTA curve, begins to evaporate, with maximum rate at 670° .

Zinc oxide undergoes no change up to 1000° as indicated by thermoanalytical curves.

The TA curves of a $\text{ZnO} + \text{PVC}$ mixture are presented in Fig. 4. The decomposition of PVC reaches its maximum rate at 270° , and at this temperature ZnCl_2 is formed. Presumably small amounts of ZnR_2 or Zn(OR)_2 are also produced, the alkyl groups R being provided by the decomposition of PVC. Evaporation of ZnCl_2 starts at 300° and it proceeds in a wide temperature range (Fig. 5).

The thermoanalytical curves of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ are shown in Fig. 6. The water is completely released up to 600° , indicated by a mass loss of 34.6%.

In some cases the positions and sequence of DTG and DTA peaks allow conclusions to be drawn concerning the crystalline structure of aluminium oxide hydrate [12]. In the present case the sample was found to contain hydrargillite as indicated by DTG and DTA peaks at 240° and 320° , and by the fact that 2.75 moles of water leave below 400° .

From the point of view of flame retardant action it seems to be advantageous that the water leaving up to 400° , with maximum rate around 320° , exerts a cooling effect in the temperature range where the degradation of most polymers proceeds. $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ used as a filler applied in amounts of 15 to 30% exerts a significant

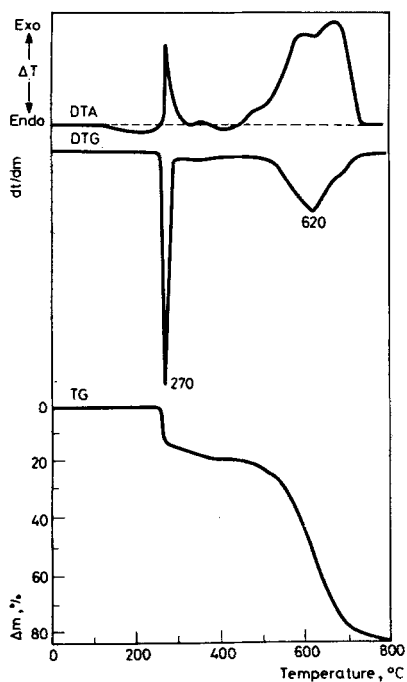


Fig. 4 TG, DTG and DTA curves of the mixture of ZnO+PVC Zn/Cl = 1:2 in air

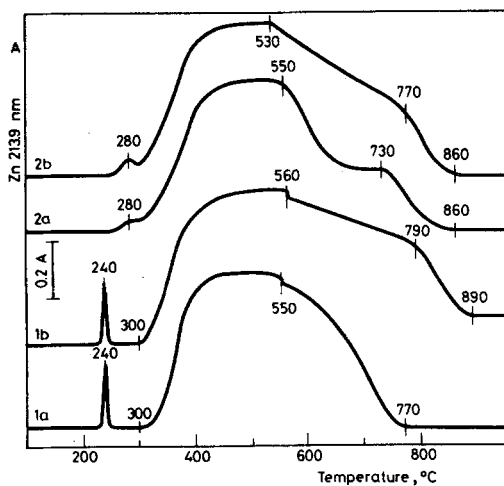


Fig. 5 AT curves of the mixture of ZnO+PVC (1) ZnO+Cerechlor (2); a: in nitrogen, b: in air

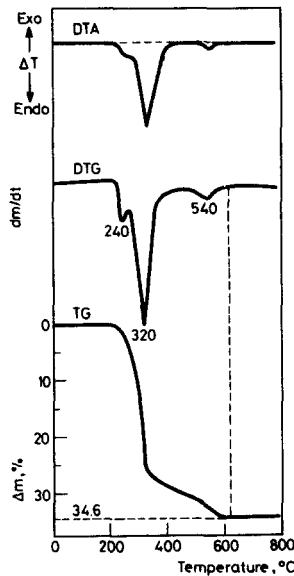


Fig. 6 TG, DTG and DTA curves of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

flame retardant effect. As shown thermoanalytical measurements, of aluminium oxide hydrates, hydrargillite is the modification best suited to flame retardant applications.

$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ was found not to react with either of the halogen donors studied.

Based on the results of measurements described we concluded that from the MoO_3 + halogen donor and ZnO + halogen donor mixtures volatile metal halides are released on heating, indicating that the mechanism of their flame retardant action is similar to that of Sb_2O_3 from which SbCl_3 is produced.

No volatile halide is released in the case of Al_2O_3 + halide donor systems under the conditions of the measurements.

Further investigations are in progress in order to decide whether or not Sb_2O_3 can partly or completely be replaced by the oxides studied.

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Zusammenfassung — Der Verdampfungsmechanismus verschiedener Metalloxide sowie Bildung und Verdampfen von Metallhalogeniden im Falle von chlorhaltigen Additiven wurde untersucht. Es wurden Messungen mittels komplexer Thermoanalyse einschließlich von Atomabsorptionsuntersuchungen der entweichenden Stoffe durchgeführt. Die Hemmungsprozesse von $\text{MoO}_3 + \text{Halogen}$, $\text{ZnO} + \text{Halogen}$ und $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ werden besprochen.

Резюме — Изучен механизм испарения различных оксидов металлов, а также образование и испарение галоидов металлов в случае хлорсодержащих добавок. Измерения проведены с помощью комплексного термического анализа, включая атомно-абсорбционный анализ выделяемых продуктов. Обсужден процесс замедления для составов $\text{MoO}_3 + \text{галоген}$, $\text{ZnO} + \text{галоген}$ и $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.