

Note

FLAME COOLING ACTION OF HEX EJECTED FROM THE HET MOIETY

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The Diels–Alder adduct of hexachlorocyclopentadiene (HEX) and maleic anhydride, HET anhydride or chondric anhydride and its hydrolysis product, 1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid (HET acid) are widely used in the preparation of flame retardant polymers [1–3]. Chaigneau et al. [4] studied the degradation of HET anhydride at 1000°C whereas Weiner [5] examined its degradation in solution. But there is no reported work on the degradation of HEX and HET acid. Further, in previous papers [6,7] it was suspected that HEX ejected due to the action of heat from the HET moiety will act as a flame cooling agent due to the hindrance of oxygen diffusion into the flame zone because of its bulkiness. Subsequently the present work reports the results of flash pyrolysis studies up to 1600°C on HEX and HET anhydride and HET acid up to 800°C. The studies reveal that HEX can withstand very high temperatures, thus leading to flame cooling action under extreme temperature conditions.

EXPERIMENTAL

HEX was supplied by Ega-Chemie. Both HET anhydride and HET acid were supplied by Vianova (Austria) as gift samples. All the materials used in the present study were used without further purification. The materials were pyrolyzed using a Hewlett Packard Model 18580A pyrolyzer with a platinum ribbon probe and helium as carrier gas. HEX was pyrolyzed at 400, 800, 1200 and 1600°C. A ramp rate of 10°C ms⁻¹ was applied, the ribbon being kept for 10 s at the end temperature. The product separation was achieved in an OV17 column using a Hewlett Packard Model 5830A gas chromatograph, interfaced directly with the pyroprobe (interface temperature 200°C). Product identification was performed in a Balzers QMG 511 quadrupole mass spectrometer coupled to the gas chromatograph (GC/MS interface temperature 200°C) by means of a jet separator. The flame ionization detector (FID) response was calibrated by means of respective standards for quantitative analysis.

RESULTS AND DISCUSSION

Degradation of HEX

The flash pyrolysis of HEX showed that degradation did not occur up to 800°C. At 1200 and 1600°C small amounts (below 5%) of low molecular weight products were formed. These results reveal that up to 800°C HEX is highly stable, and at temperatures higher than 800°C it fragments to other chlorinated products but the % fragmentation is roughly 5%.

Degradation of HET anhydride

HET anhydride sublimes at 90–100°C at 0.5 Torr [8]. The main degradation path of HET anhydride is the well-known retro-Diels–Alder reaction to yield HEX and maleic anhydride. The products of degradation and the % decomposition of HET anhydride are listed in Table 1. On raising the pyrolysis temperature from 400 to 800°C, the % decomposed HET anhydride increased from 3.9 to 57.6%. At all the pyrolysis temperatures employed, HET anhydride was not eluted from the column. However, when an acetone solution of HET anhydride was injected into the column, this compound was found to be eluted under the conditions employed in this research; so the HET anhydride may not be evaporated from the ribbon under the conditions of flash pyrolysis. Further condensation on the lines of the interface seems improbable, since HET anhydride is eluted as a product of pyrolysis from HET acid (cf. the following section).

TABLE 1

Degradation of HET acid and HET anhydride in flash pyrolysis experiments

<i>T</i> (°C)	Total % decomposition	Amount of degradation products (moles) per mole of the substance pyrolyzed		
		HET anhydride	HEX	Maleic anhydride
<i>HET acid</i>				
400	21.1	21.8×10^{-2}		
600	18.7	9.85×10^{-2}	8.81×10^{-2}	8.96×10^{-2}
800	54.6	9.91×10^{-2}	38.28×10^{-2}	47.98×10^{-2}
<i>HET anhydride</i>				
400	3.9		3.29×10^{-2}	4.54×10^{-2}
600	17.0		19.03×10^{-2}	14.98×10^{-2}
800	57.7		53.7×10^{-2}	61.64×10^{-2}

Degradation of HET acid

Table 1 shows the results of degradation studies of HET acid. In contrast to HET anhydride, at 400°C HET acid undergoes mainly the dehydration process to yield the corresponding anhydride. When the pyrolysis temperature is increased the dehydration reaction decreases to 9.8% (at 600°C) in comparison with 21.1% (at 400°C), whereas the retro-Diels–Alder process is enhanced. At 800°C, the formation of HEX and maleic anhydride covers 43% of degradation while the amount of dehydration reaction remains approximately the same.

The viewpoint of whether HET acid decomposes simultaneously into HEX and maleic acid, the latter being dehydrated to maleic anhydride, or if HET acid in the primary degradation step suffers dehydration to yield HET anhydride which then splits into HEX and maleic anhydride, has been described in detail in connection with the studies on oligoesters of HET acid [9].

In previous papers [6,7] it was stated that HET acid-containing polymers are flame retardant due to the HEX ejection in a multistage process, which acts in a multi-dimensional way, e.g., as a flame poisoning agent and as a flame cooling agent, hindering the oxygen diffusion into the flame zone. From the experimental results presented here, it can be concluded that HEX can withstand very high temperatures, although it is conceded that the experimental conditions of flash pyrolysis cannot be compared directly to other types of pyrolysis experiments.

Nevertheless, there is a distinct possibility that the HEX molecule can penetrate a hot flame zone without degradation, so it can subsequently act as a flame cooling agent due to its bulkiness in the gas phase. Clearly, besides this path of action, it acts as a flame poisoning agent, owing to the chlorine transfer in the condensed phase, even at 350°C, as already proved in previous research [6,7,9].

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