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Thermal Decomposition of Tetrabromoethylcyclohexane

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Tetrabromoethylcyclohexane (TBECH), which serves as a fire retardant agent, was decomposed in defined and controlled conditions simulating some characteristic temperature and atmosphere conditions of fire development.

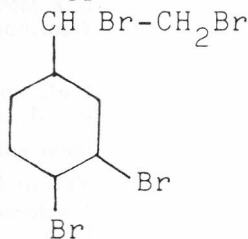
Under the experimental conditions TBECH converted into a large portion of gases, some volatile-condensable products and very little residue. The gases consisted mainly of HBr while light hydrocarbons, light bromine-containing hydrocarbons and CO₂ were in low concentrations.

Among the volatile-condensable products, twenty one components were identified by GC-MS. They were cyclohexadiene, aromatics predominated by benzene and styrene and bromine-containing aromatics, containing one or two bromine atoms. Among the bromine-containing aromatics, the monobromine ones made up a fair concentration, especially bromoethylbenzene.

As regards the yield of decomposition products, dehydrobromination highly predominated. High temperatures caused some additional fragmentation by cleavage of C—C bonds. Secondary reactions of decomposition fragments are also stated.

INTRODUCTION

Tetrabromoethylcyclohexane (TBECH) is a widely used fire retardance agent (FRA). It is added to polymer materials in order to inhibit the excited H* and OH* radicals,¹ responsible for fire spreading, which are evolved while organic matter is burning. TBECH is often used as FRA in expanded polystyrene foam (EPS) as it is intended for use in thermal and acoustic insulation in civil engineering or in other applications where a fire would be of great danger.



TBECH

It is known² that the presence of TBECH in EPS controls the quantity and type of volatile-condensable products and the quantity and type of light gases released during combustion.

In that study, the complexity of the mixture of volatile-condensable products and of the gases released did not allow a detailed insight into decomposition products released or caused by the presence of TBECH. In the investigation presented now, pure TBECH was submitted to investigation of its thermal decomposition. The main aim of this study was to find out what kind of decomposition products could be released and what HBr release efficiency could be expected during a fire. For this reason, TBECH was submitted to decomposition under controlled decomposition conditions representing some typical stages of fire development regarding the temperature and surrounding atmosphere.

EXPERIMENTAL

Thermal decomposition of TBECH was carried out in a flow-tube reactor permitting precise control of decomposition temperature and atmosphere. The outlet of the reactor was connected to a cooled absorber for quantitative collection of volatile-condensable products. The device is described in details elsewhere.²

Thermal decomposition parameters were as follows:

sample size: 1, 0.1 and 0.01 g of TBECH
 temperature: 823, 1023 and 1223 K
 atmosphere: air and N₂

Volatile-condensable products were absorbed either in cooled *n*-hexane at 253 K or in cooled styrene at 253 K.

In the same device, 2 g of EPS containing 2% TBECH was decomposed at 823 K in air. Volatile-condensable products were retained in *n*-hexane at 253 K.

In order to resolve and identify decomposition products absorbed in cooled solvent, they were analyzed by means of a high resolution gas chromatography-mass spectrometry coupled system (GC-MS). GC-MS equipment and experimental conditions were as follows:

Gas chromatograph	Varian 3700
Column	
Stationary phase	SE-54, 1.0 ⁰ %, low polar
Type	wall coated open tubular
Inner diameter	0.5 mm
Length	25 m
Resolution after Kaiser	26
Temperature	320 K (4 min) $\xrightarrow{4 \text{ K/min}}$ 400 K
Carrier gas	He
Pressure	0.18 MPa
Flow	2 mL/min
Sample size	
in <i>n</i> -hexane as solvent	2 μ L, splitless injection
in styrene as solvent	0.2 μ L, splitting injection
GC-MS coupling	open split
Mass spectrometer	Varian MAT 112 S
Scanning rate	1 s/decade
Interscan time	0.2 s
Resolution	1 : 500
Ionization	electron impact
Electron energy	70 eV
Emission current	0.7 mA
Ion source temperature	500 K
Ion source pressure	10 ⁻⁵ Pa

The percentage of the sample converted into volatile-condensable decomposition products was determined by gas chromatography of the mixture collected in *n*-hexane, using styrene as external standard. The concentration of each product in the mixture was determined by the normalization method. No correction factors were applied. The experimental conditions of the quantitative analysis were as described for gas chromatography in GC-MS. Flame ionization detection was applied. Quantitative analysis was performed for the products when 0.1 g of TBECH was decomposed.

Light decomposition products, which were not retained by cooled solvent, were investigated by means of mass spectrometry, using direct introduction of gas mixture into the ion source under conditions as above for mass spectrometer, except for the scanning rate and interscan time which were varied in order to get representative spectra.

Isomers which had similar mass spectra were distinguished by using reference compounds and by the difference in retention time, assuming that they corresponded to the differences in boiling points. In order to differentiate every single bromostyrene generated by decomposition among the isomers, GC relative retention times, $t_{R'}$, were expressed in relation to ethylbenzene at 335 K, in the way mentioned earlier.³

RESULTS AND DISCUSSION

TBECH was decomposed under non-flaming combustion. Regarding the decomposition temperature, the conditions simulated fire beginning, developed fire and mature fire. The surrounding atmosphere simulated either decomposition in air with full oxygen content or decomposition in the atmosphere as if all the oxygen were already consumed by thermooxidation processes during a fire.

TBECH converted into residue yielded less than 0.1%, volatile-condensable products retained in *n*-hexane between 5 and 7% and the gas fraction was 93 to 95% of the decomposition products. MS analysis of the gas fraction showed that it mainly comprised HBr, while low aliphatics, partly brominated, gave low intensities. Weak CO₂ spectrum was recognized when TBECH was decomposed in air.

















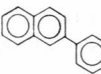



Components of the volatile-condensable fractions were identified and their relative concentration in the fraction were determined. The results are presented in Table I, where the components are listed in order of their GC retention times. (The component number is the same as the corresponding GC peak in Figure 1)

For some identified components the relative retention times, in relation to ethylbenzene at 335 K, are given.

The identified components (twenty one) together made up 91% (923 K, air) to 98% (823 K, N₂) of the respective volatile-condensable fractions.

Vinylcyclohexene, the precursor of TBECH, was not found among the identified components. Cyclohexadiene (1) appeared as the only identified alicyclic compound. All the other identified components belong either to aromatics or to the aromatics containing bromine. Benzene (2) and styrene (6) predominated among the aromatics. Styrene reflects complete dehydrobromination of TBECH:

TABLE I
Volatile-Condensable Products of Thermal Decomposition of TBECH

Peak No. (Fig. 1)	Decomposition product	Relative retention time *	Percentage in mixture of volatile-condensable products/conditions						Peak No.	Decomposition product	Relative retention time *	Percentage in mixture of volatile-condensable products/conditions					
			Air 823 K	Air 1023 K	Air 1223 K	N ₂ 823 K	N ₂ 1023 K	N ₂ 1223 K				Air 823 K	Air 1023 K	Air 1223 K	N ₂ 823 K	N ₂ 1023 K	N ₂ 1223 K
1			12.7	8.3	2.6	7.5	6.7	3.1	12		8.77	0.5	0.7	0.8	0.8	0.8	<
2			42.9	42.3	38.2	28.1	35.4	43.4	13			<0.1	0.1	0.5	<0.1	0.1	<
3			0.9	1.5	2.0	0.8	1.6	2.1	14		11.03	0.5	0.5	0.5	0.4	0.5	<
4			2.2	2.1	2.1	4.7	3.0	2.2	15			0.1	<0.1	<0.1	<0.1	<0.1	<
5			0.5	1.1	3.2	0.6	1.7	3.6	16		12.36	1.0	1.0	1.1	0.8	0.9	<
6			6.5	8.8	18.7	36.2	12.0	11.6	17	DIBROMDSTYRENE		0.2	0.3	0.2	<0.1	0.3	<
7			2.9	2.7	2.6	1.8	1.7	1.9	18			<0.1	<0.1	<0.1	<0.1	<0.1	<
8			<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	19			<0.1	0.1	0.1	<0.1	0.1	<
9			15.3	24.4	19.9	13.4	27.3	22.1	20			1.7	0.4	0.3	0.9	0.3	<
10		8.12	0.9	1.0	1.6	0.9	0.8	1.0	21			1.6	0.3	0.3	0.6	0.3	<
11		8.52	0.5	0.8	1.0	0.6	0.8	0.8									

* In relation to ethylbenzene at 335 K, isothermally

Its yield was strongly dependent on decomposition conditions.

Benzene (2) generation is a consequence of loss of the aliphatic chain in addition to HBr release from the cyclic part of TBECH. Being a compound of highly stable structure, it is an expected product of the thermal decomposition of organic matter.²⁻⁷ Toluene (3) and ethylbenzene (4) should be explained as products of hydrogenation in the aliphatic chain of the dehydrobrominated decomposition fragment. Xylene should be attributed either to secondary reactions between decomposition fragments or to rearrangement reactions.

Among the decomposition products, a number of compounds appeared which were found to contain a larger number of atoms than TBECH. These are naphthalene (13), bromomethylindene (18), phenyl naphthalenes (19, 20) and tetrahydropyrene (21). Their production could be attributed to secondary reactions of decomposition fragments which stabilized through cyclization into a condensed aromatic structure.

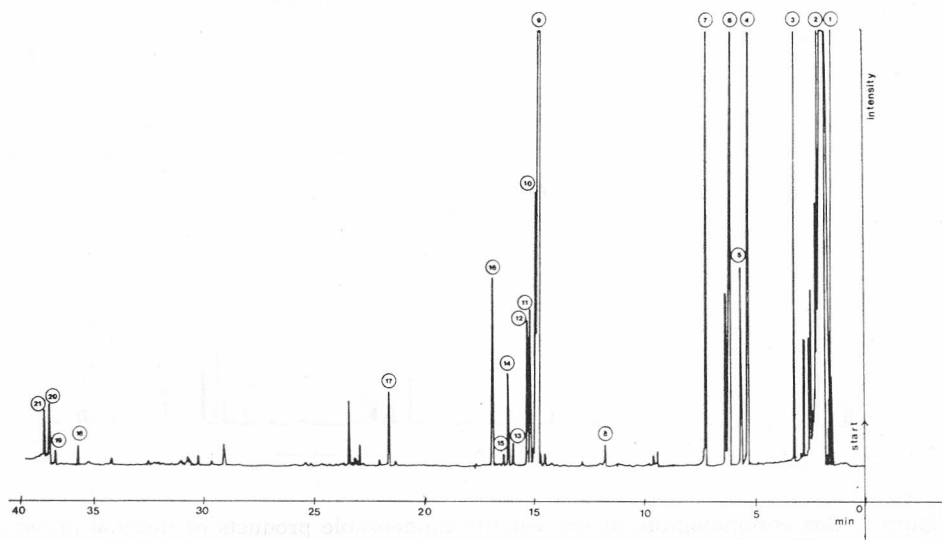
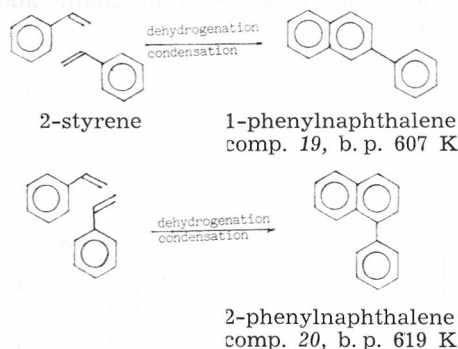


Figure 1. Gas chromatogram of the volatile-condensable products of thermal decomposition of TBECH produced at 823 K in air and collected in *n*-hexane (253 K).

Phenyl-naphthalenes resemble the condensation of two styrene molecules, followed by the loss of hydrogen:



These two isomers were assumed to be retained in the low polar GC column used according to their boiling points, and were differentiated by means of boiling points.

Bromomethylidene (18) was produced in a concentration as low as <0.1%. One of plausible ways of its generation could be the recombination of styrene and a bromine-containing small molecule (*e. g.* bromoacetylene).

This presumption was supported by a considerable increase in bromomethylidene concentration when the TBECH decomposition products were introduced into styrene as a cooled solvent (Figure 2). Bromomethylidene was found to be a recognizable component, in the mixture as complex as the mixture

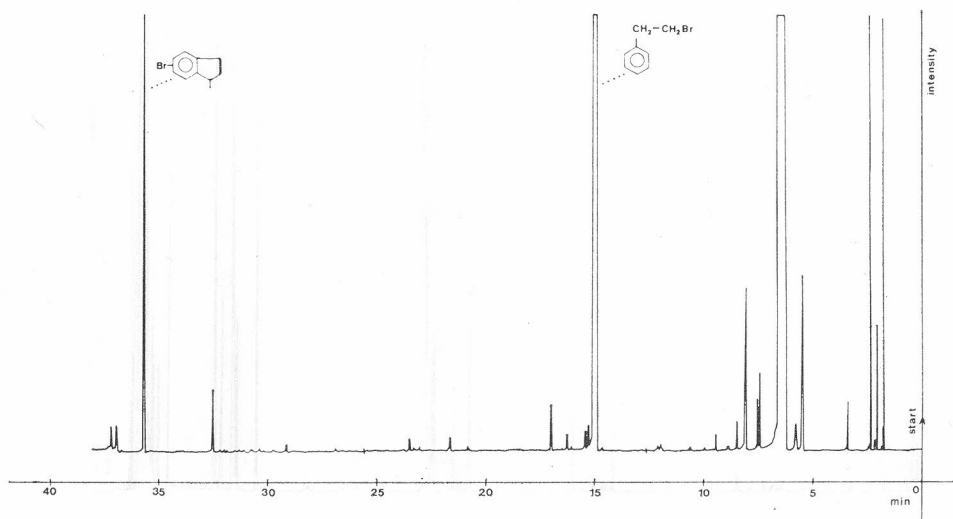


Figure 2. Gas chromatogram of the volatile-condensable products of thermal decomposition of TBECH produced at 823 K in air, and the products of the secondary reaction between styrene and the decomposition gases fraction collected/generated in styrene (253 K).

of volatile-condensable products released in the non-flaming combustion of EPS (Figure 3). This should be probably explained by the reaction of styrene largely due to depolymerization of polystyrene chain⁸ and bromine-containing product(s) from TBECH.

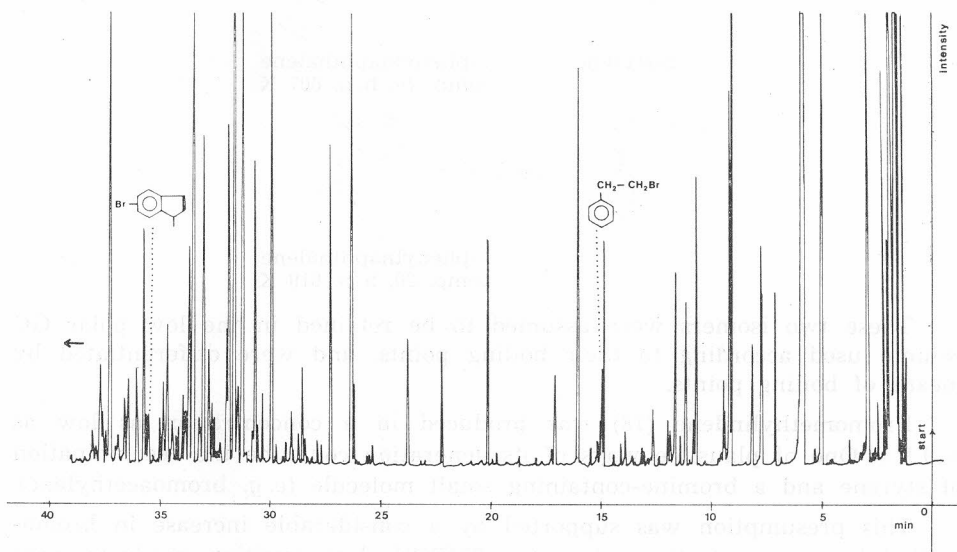
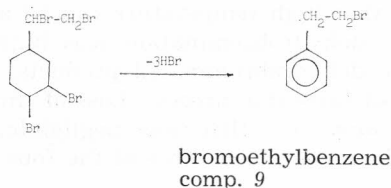


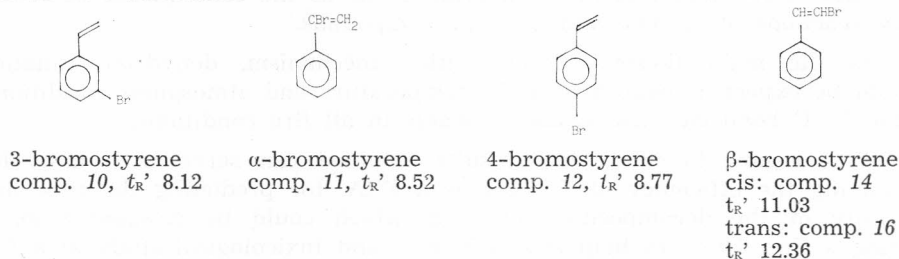
Figure 3. Gas chromatogram of the volatile-condensable products of thermal decomposition of EPS containing 2% of TBECH, produced at 823 K in air and collected in *n*-hexane (253 K).

A remarkable component of the volatile-condensable products of TBECH was bromoethylbenzene (9). Since the lowering of the sample size from 0.1 to 0.01 g (air, 1023 K) did not diminish the concentration ratio of bromoethylbenzene to styrene, it was presumed that bromoethylbenzene could be generated by primary decomposition reaction:



Also, this compound could be a secondary reaction product generated by the addition of HBr to styrene. This statement was supported by the remarkable increase of bromoethylbenzene content when the TBECH decomposition products, containing plenty of HBr, were introduced into styrene (Figure 2). Similarly, the relatively high concentration of bromoethylbenzene in the mixture of volatile-condensable products of EPS (Figure 3), containing TBECH only as an ingredient, could be explained by the reaction between HBr released from TBECH and styrene as the main decomposition product of polystyrene.⁸

There are five bromostyrene isomers among the identified volatile-condensable products which contain one bromine atom. They were distinguished by mass spectra, by their boiling points in relation to GC retention and by reference compounds (10, 12 and 16). As an additional way of distinction, their relative retention times in relation to ethylbenzene at 335 K were determined for the GC condition used. This data could be of help in further investigation. All of the identified bromostyrenes reminded us of the rest of the TBECH structure:



Two products containing two bromine per molecule were identified in low concentrations: dibromobenzene (15) and dibromostyrene (17). No compound containing three or four bromine atoms was found in the mixture of volatile-condensable products released from TBECH.

Among the components identified in the volatile-condensable fractions, common concentrations of the compound types were in a relation as
aromatics > monobromoaromatics \gg dibromoaromatics.

The volatile-condensable products containing bromine made up roughly 2% of all decomposition products and conserved a very low portion of the bromine contained in TBECH.

As one quarter of the TBECH molecular weight (mol. wt. 428) belongs to the hydrocarbon part and three quarters are made up of four bromine atoms, it means that roughly 20% of the hydrocarbon part of the molecule was converted into the light fraction not collected in the cooled *n*-hexane (5 to 7% of TBECH converted into volatile-condensable products).

In spite of the fact that high temperature caused a number of concurrent decomposition reactions, dehydrobromination was highly predominant. Comparing the yields of the dehydrobrominated products, the complete dehydrobromination was the most favorable process. Loss of three HBr was drastically lower and the loss of only two HBr was negligible. There was no single component identified which contained three of the four bromine atoms present in TBECH.

CONCLUSION

TBECH readily decomposes under the conditions which characterize the main stages of fire development. HBr is the largest decomposition product, extensively released under all fire temperatures and atmosphere conditions. As HBr inhibits fire spreading, TBECH should be expected to act as an efficient FRA from the very beginning of the fire and that its efficiency will not depend on the fire stage.

In addition to HBr, a variety of compounds could be released from TBECH in relatively low concentration during a fire. Among the light products there could be aliphatic hydrocarbons, a low portion of them containing one bromine and a little CO₂ (when decomposed in air). Among the heavier products which are volatile, cyclohexadiene, aromatic hydrocarbons and aromatics containing one and, to a much lesser extent, two bromine atoms, could be present.

If TBECH were incorporated in EPS, an increase in the bromoethylbenzene and bromomethylindene yield could occur as the consequence of secondary reactions of styrene and bromine compounds.

As the main thermal decomposition mechanism, dehydrobromination should be expected regardless of the temperature and atmosphere conditions. Some C—C bond cleavage is also probable in all fire conditions.

With regard to safety, the results obtained can serve as a basis for predicting the efficiency of TBECH as a FRA, for predicting the type and quantity of the decomposition products which could be released from it during a fire. This can help environmental and toxicological study of a fire when a polymer material containing TBECH as FRA is involved.

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SAŽETAK**Termička dekompozicija tetrabromoetilcikloheksana***A. Alajbeg*

Tetrabromoetilcikloheksan (TBECH), koji služi kao usporivač gorenja, razgrađen je pod definiranim i kontroliranim uvjetima koji simuliraju nekoliko stanja temperature i atmosfere karakterističnih za razvoj požara.

Kod svih iskušanih eksperimentalnih uvjeta termičke razgradnje TBECH je velikim dijelom prešao u plinove, dao nešto hlapivih produkata koji na sobnoj temperaturi kondenziraju te vrlo mali ostatak. Plinoviti se dio, uglavnom, sastoji od HBr, dok su laki ugljikovodici, laki bromirani ugljikovodici i CO₂ bili slabo zastupljeni.

S pomoću vezanog sustava GC-MS identificiran je 21 produkt: to su hlapivi spojevi koji pri sobnoj temperaturi kondenziraju. Među njima su cikloheksadien, aromati te aromatski spojevi koji sadrže jedan ili dva atoma broma. Bolje su zastupljeni oni s jednim atomom broma, osobito bromoetilbenzen.

Prema iscrpku produkata razgradnje, glavni proces termičke razgradnje jest dehidrobromiranje. Visoke temperature uzrokuju dodatnu fragmentaciju pucanjem veza C—C. Utvrđene su i sekundarne reakcije razgradnih fragmenata.