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# THERMAL DECOMPOSITION OF SPATIALLY HINDERED PHENOLS USING CHROMATOMASS-SPECTROMETRIC SYSTEM

*O. N. Nikulicheva*[1], *L. M. Pokrovskiy*[1], *A. P. Krysin*[1], *V. P. Fadeeva*[1] *and V. A. Logvinenko*[2]

[1]Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences, Novosibirsk
[2]Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, Novosibirsk 630090, Russia

## Abstract

The present paper deals with thermal decomposition of some spatially hindered phenols, which are in the industry as stabilizers in synthetic materials used. The investigated stabilizers are separated to two groups in respect to mechanism of decomposition (group I and II). This assumption was confirmed by chromatomass-spectrometric investigations. It allows a stabilizer for forming a plastic with variety properties to choose.

**Keywords:** chromatomass-spectrometry, compensation effect, kinetic parameters, spatially hindered phenols, thermal decomposition

## Introduction

The paper reports the study of thermal stability of spatially hindered phenols (SHP) which are used in the industry as stabilizers in synthetic materials and plastics. The thermal analysis was conducted by means of Derivatograph Q-1000-D (MOM, Hungary) in nitrogen atmosphere. Since the decomposition process takes place in the melt, it is possible to use an equation describing the kinetics of homogeneous processes to decide on a particular equation for kinetic parameter calculation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=Z\exp\left(-\frac{E}{RT}\right)(1-\alpha)^{\mathrm{n}}$$

where $t$ – time, $\alpha$ – conversion degree, $Z$ – preexponential factor, $E$ – activation energy, $n$ – reaction order, $R$ – gas constant and $T$ – temperature in K.

Kinetic parameters of SHP thermal decomposition were calculated with use of the original PC-program THERMOGRAF [1]. These kinetic parameters for the investigated substances are given in Table 1.

The non-isothermal kinetic parameters determined at different concentrations or temperatures often reveal a compensation effect (CE) [2, 3].

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# Experimental

The substances were linearly heated at rate of 1.25°C $\text{min}^{-1}$ to the temperature 10°C less than a maximum temperature of substance decomposition (according to the initial thermoanalytical studies of research compounds [4]). Further heating was interrupted and maintained under isothermal condition for half an hour. After fast lifting of heating furnace and cooling the condensed products of thermal decomposition were investigated on a spectrometer. The device was Gas-chromatography massspectrometer (GC-MS) on a quadrupole MS Hewlett Packard MSD 5971 coupled to a HP 5890/II GC fitted with an HP-5 (5%-diphenyl 95%-dimethylsiloxsane copolymer) fused silica column. Experimental conditions: carrier gas He at constant flow (1 $\text{cm}^3\text{min}^{-1}$), furnace temperature was programmed from 50 to 280°C (10°C $\text{min}^{-1}$), injector and detector (MSD) temperatures were 280°C and 170°C respectively. MSD was operated at 70 ev. Mass spectrometer Finnigan MAT-8200 with direct injection was used for study the high-boiling components. The recorded mass-spectra were compared with those of mass spectra libraries (our own, NIST 75K [5] and [6]).

# Results and discussion

The compensation effect ($\ln Z_i = aE_i + b$) observed indicates that investigated SHP were separated on two groups corresponding to two mechanism of decomposition (Fig. 1). The existence of CE for the reactions in the series of compounds can be explained [7] by the influence of steric factor and change the polarity of transition state at formation of activated complex, as intermediate product in reaction of thermal decomposition of complexly built organic compounds. To verify the correctness about two mechanism for the compounds studied the mass – spectrometry investigation of some initial and partially decomposed SHP were conducted.

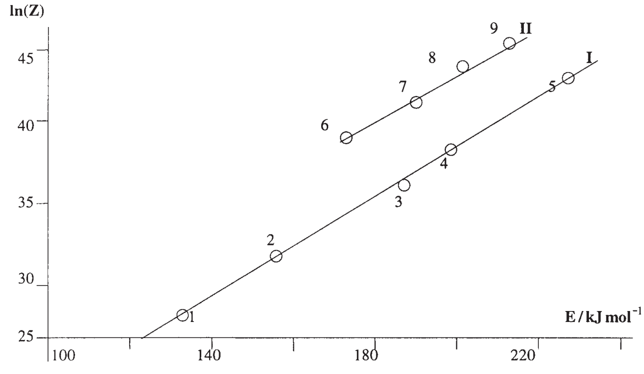
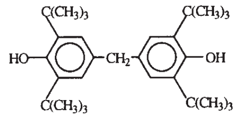
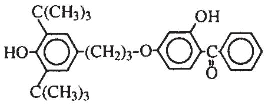
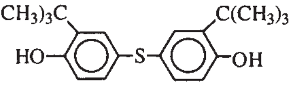
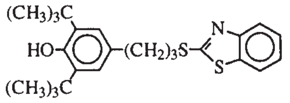
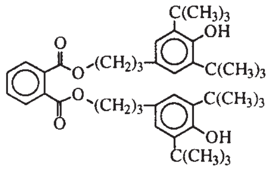
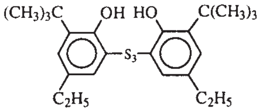
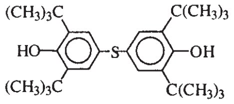
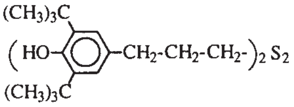
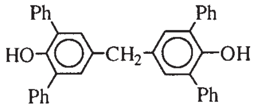


**Fig. 1** Compensation dependence for investigated compounds (the numbering corresponds to Table 1)

**Table 1** Kinetic parameters of SHP thermal decomposition

| N° | Compound | Formula | $E$/kJ mol$^{-1}$ | ln$Z$ |
|---|---|---|---|---|
| 1 | Di-(3,5-di-tert-butyl-4-hydroxyphenyl)-methane |  | 132.4 | 27.51 |
| 2 | 4-[3-(3,5-Di-tert-butyl-4-hydroxyphenyl)-propoxy]-2-hydroxybenzophenon (BENZONE-P) |  | 156.7 | 31.74 |
| 3 | Di-(3-tert-butyl-4-hydroxyphenyl)sulphide |  | 187.9 | 37.03 |
| 4 | 2-[(3,5-Di-tert-butyl-4-hydroxy phenyl)propyl-thio]benzothiazol |  | 195.0 | 37.97 |
| 5 | Di-[2-(3,5-di-tert-butyl-4-hydroxyphenyl)-ethyl]-phthalate (PHENOZAN 42) |  | 225.4 | 43.00 |
| 6 | Bis-(3-ethyl-5-tert-butyl-6-hydroxyphenyl)-trisulfide |  | 176.0 | 39.00 |
| 7 | Bis-(3,5-di-tert-butyl-4-hydroxyphenyl)-sulfide |  | 190.1 | 41.31 |
| 8 | Di-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propyl] disulfide (SO-4) |  | 203.8 | 43.38 |
| 9 | 4.4’-Bis-(3,5-diphenyl-4-hydroxyphenyl) methane |  | 214.8 | 45.24 |

The results of GC-MS study of Di-(3,5-di-tert-butyl-4-hydroxyphenyl)-methane (stabilizer MET) and bis-(3-ethyl-5-tert-butyl-6-hydroxyphenyl)-trisulfide (stabilizer S3) are given here as the most significant examples (Fig. 1, point 1 in line I and point 6 in line II ), they are accumulated in Tables 2 and 3.

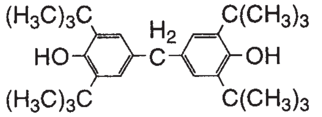
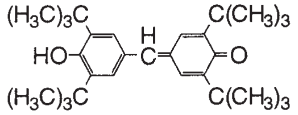
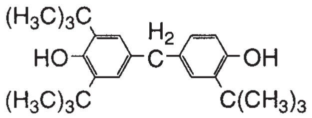
## Conclusions

This study of thermal decomposition products (both for the above mentioned stabilizers and others) provides the possibility to make the following conclusions:

– thermal decomposition of compounds, belonging to group I (Fig. 1), is connected originally with radical mechanism of cleavage/joining of tert-butyl groups. Further heating leads to more total destruction of molecule and formation of high molecular mass compounds, as the result of radicals association;

– thermal decomposition of SHP from group II (Fig. 1), is connected with breakage of C–S and S–S bonds, and the loss of sulfur atoms become prevailing. Such strong changes in molecular structure, as appear, lead to large changes of energy of activation and preexponential factor (Table 1).

**Table 2** The proposed structure of the products of thermal decomposition of stabilizer MET from data of GH-MS

| N° | % | MM | Formula | The note |
|---|---|---|---|---|
| 1 | 90.6 | 424 |  | The initial compound |
| 2 | 1.1 | 424 | Isomer of 1 | The spectra of compounds 1 and 2 coincide on masses, but are distinguished by intensity |
| 3 | 1.8 | 422 |  | The spectrum of compound 3 is close to spectrum of compound 1, but MM=422 |
| 4 | 6.2 | 368 |  | The spectrum of compound 4 like to spectrum of compound 1, but MM is 56 units less |
| 5 | 0.2 | 424 | Isomer of 1 | The spectrum of compound 1 is very close to spectrum of compound 1, but compound 5 leaves from column hardly later |

Mechanism of the first stage of thermal decomposition of substances from group I:

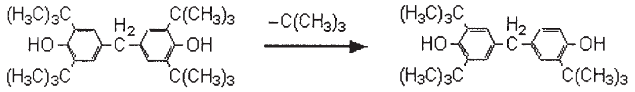
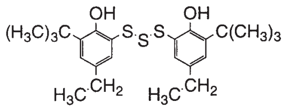
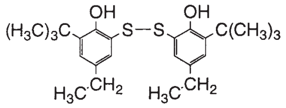
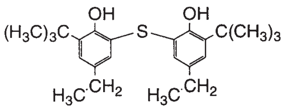
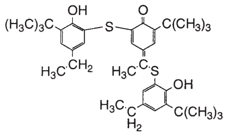
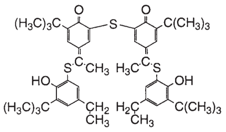
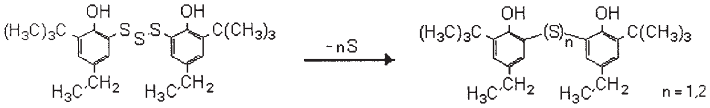


**Table 3** The proposed structure of the products of thermal decomposition for stabilizer S3 from data of GH-MS

| N° | MM | Formula | The note |
|---|---|---|---|
| 1 | 450 |  | The initial compound is practically absent |
| 2 | 418 |  | Is present, but in small quantity in comparison with compound 3.<br>2·177+2·32=418 |
| 3 | 386 |  | Identified mass: 2·177+32=386 |
| 4 | 592 |  | It is possible to assume, that this compound consists of already the identified masses:417+177–2=592 or 385+209–2=592 |
| 5 | 798 |  | 448+2(177–2)=798<br>384+2(177+32–2)=798 |

Mechanism of the first stage of thermal decomposition of substances from group II:



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