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# The thermal decomposition of α-tetralyl hydroperoxide under non-isothermal conditions, in the presence of tetralin

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## Abstract

The thermal decompositions of tetralin and of α- tetralyl hydroperoxide (THPO) in the presence of tetralin have been investigated in the temperature range 23–500°C by employing DTA and TGA. The thermochemical decomposition of tetralin is a one-stage process in the temperature range 65–180°C under non-isothermal conditions.

It was shown that tetralin retards the thermal decomposition of THPO due to the decrease of the steady-state concentration of tetralyl radicals and its participation in the radical decomposition. The formation and decomposition of the intermolecular (OH...π) associates between THPO and the tetralin molecule influence the hydroperoxide homolysis and the initial temperature of the decomposition. The presence of γ-*o*-hydroxyphenyl butyric acid, a natural inhibitor of the studied systems, was observed.

The presence of bitetralyl peroxide and bitetralyl ether in the reaction product at 160°C indicates that termination reactions take place with the dominating participation of tetralyl radicals. The presence of bitetralyl tetroxide indicates a probable gas-phase mechanism in non-isothermal conditions and decreased oxygen access.

*Keywords:* Bitetralyl ether; Bitetralyl peroxide; CI MS; γ-*o*-Hydroxyphenyl butyric acid; Tetralin; α-Tetralyl hydroperoxide; TG/DTA

## 1. Introduction

The influence of solvents on the thermal decomposition of hydroperoxides under isothermal conditions has been investigated in studies of unimolecular homolysis [1–4].

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Thomas and Hatl [5] noted that the thermal decomposition of hydroperoxides in solvents depends on the easy auto-oxidation of the solvents, and suggested that concerted C–H and O–O bond breaking might be responsible

$$R_1H + R_2OOH \rightarrow R_1^{\cdot} + R_2O^{\cdot} + H_2O \qquad (1)$$

This has been supported by measurements of the rates of free-radical production but it must be stressed that induced decomposition is also facilitated by auto-oxidizable solvents, probably through the formation of thermally labile mixed peroxides [1].

$$R_1O_2^{\cdot} + R_2^{\cdot} \rightarrow R_1OOR_2 \rightarrow R_1O^{\cdot} + R_2O^{\cdot} \qquad (2)$$

Clearly there are some marked differences in the thermal decomposition of hydroperoxides in the presence of various solvents.

The thermal decomposition of tetralin has been investigated, with the study of the separate steps of oxidation process, in oxygen and inert atmosphere and under isothermal conditions [6–8]. The reaction of auto-oxidation of pure tetralin at temperatures of 30°C and above shows a fairly pronounced autocatalysis. This is due to the thermal decomposition of tetralin hydroperoxide [8].

Russel [9] investigated peroxide-catalysed reactions and established that small amounts of tetralin reduce the rate of cumene oxidation in a cumene–tetralin system. The tetralyl-peroxy radicals terminate radical reactions more readily than cumyl-peroxy radicals because of their lower steady-state concentration.

It was established that the steady rate of thermally initiated oxidation of tetralin in the temperature range 69–120°C is considerably slower than the maximum rates of oxidation initiated chemically or by other means. The retardation effect is possibly due to the formation of self-inhibitors during the thermally initiated oxidation [10].

Our previous investigations [11] have shown that the thermal decomposition of α-tetralyl hydroperoxide (THPO), the primary product of tetralin auto-oxidation, proceeds in two stages. We observed a free-radical-induced decomposition at 165°C under non-isothermal conditions and decreased air access. The products of this reaction are α-tetralon, traces of α-tetralol and bis(α-tetralyl) peroxide. The data suggest that a gas phase decomposition could take place. The present investigation was promoted by this assumption and by the absence of literature data on the thermochemical decomposition of tetralin and systems of tetralin–α-tetralin hydroperoxide under non-isothermal conditions.

The purpose of this work was to study the thermal decomposition of α-tetralin hydroperoxide (THPO) in the presence of tetralin in the temperature range 23–500°C and to discuss the mechanism of the thermochemical decomposition and some competitive reactions

## 2. Experimental

Tetralin (Merck) was washed with concentrated sulphuric acid until the washing became colourless, and then washed repeatedly with distilled water and stored over anhydrous magnesium sulphate. Prior to use it was distilled under purified nitrogen and the fraction boiling at 46°C (1–3 mmHg) was collected [10]. The purified product was characterized by iodometric peroxide tests and GLC .

Tetralyl hydroperoxide was prepared by air oxidation of tetralin [11] and followed by three-fold recrystallization from petroleum ether (b.p. 30–50°C). Its purity was checked by melting point, 55.6°C.

The thermal analyses were carried on a Derivatograph Q-1500 (MOM, Hungary) under the following conditions: sample mass, 84 mg; balance sensitivity, ±1 mg; reference, $Al_2O_3$; heating rate, 2.5°C $min^{-1}$; Pt crucible, 7 mm diameter. The TG/DTA experiments were conducted in the temperature range from ambient to 500°C, in the self-generated atmosphere.

The IR analysis was performed on a Brucker IFS 113 V apparatus using the KBr technique.

The decomposition experiments were carried out in an ampoule, placed in a silicone bath and heated at a heating rate of 2.5°C $min^{-1}$ up to 160°C.

The CI MS measurements of the reaction mixture were conducted on a JEOL JMSD-300 double-focussing mass spectrometer. The reaction gas was isobutane, the emmission current 100μA.

## 3. Results and discussion

The TG/DTA tetralin data demonstrate that a one-stage process of thermochemical decomposition takes place in the temperature range 65–180°C (Fig. 1). The thermochemical changes are the result of evaporation and radical decomposition reactions. The tetralyl radicals can be formed in the absence of oxygen as well as through reaction with the air oxygen dissolved in the tetralin

$$2RH \rightarrow 2R^{\cdot} + H_2 \qquad (3)$$

$$2RH + O_2 \rightarrow 2R^{\cdot} + H_2O_2 \qquad (4)$$

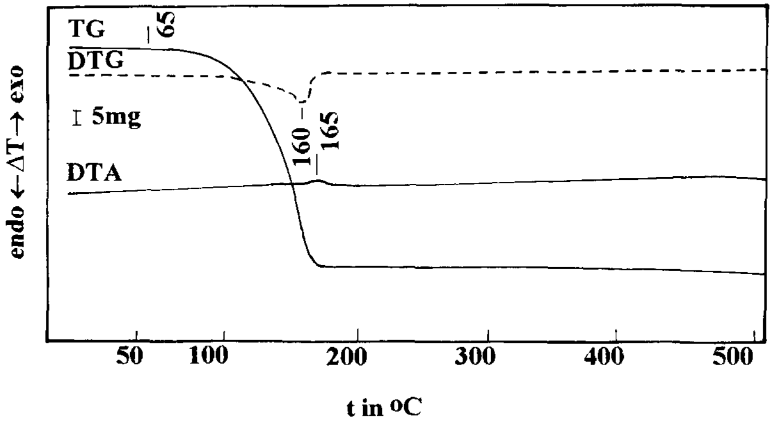


Fig. 1. Thermal decomposition of tetralin.

The presence of even a small amount of oxygen provokes the oxidation process resulting in the formation of tetralyl hydroperoxide

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \quad (5)$$

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \quad (6)$$

The insignificant exo peak at 165°C is probably due to THPO decomposition (Fig. 1).

Neither endothermic peaks registering evaporation nor radical-initiated reactions are observed: in these experimental conditions, relatively large radical concentrations are produced in a short time and the rate of the termination processes (reactions (7) and (8)) are very fast

$$2R^{\cdot} \rightarrow R\text{–}R \quad (7)$$

$$2RO_2^{\cdot} \rightarrow \text{molecular products} \quad (8)$$

It is reasonable to expect that the thermally unstable tetralin, even when added to THPO in very low concentrations, could influence the initial temperature ($T_i$) of THPO decomposition. However, the derivatograms register that the $T_i$ of systems 2 and 3 of THPO–tetralin (Table 1, Fig. 2b and c) are not significantly different from that of pure hydroperoxide. The intensity of the exo peak is decreased (Fig. 2b) and the temperature range of the exothermal reactions is shifted to a lower temperature (Fig. 2a–c).

The labile hydrogen atoms at the α-position in the tetralin molecule with a C–H bond energy of 343 kJ mol$^{-1}$ [12] determines the behaviour of tetralin in the studied systems as an inhibitor or accelerator of THPO decomposition.

Table 1
Thermochemical decomposition of α-tetralyl hydroperoxide and tetralin (THPO + T)

| No. | Products/mM | Stage | Temperature interval of decomposition/°C | Mass loss, % | $W_{max}$/°C[a] | Thermal effect/°C | |
|---|---|---|---|---|---|---|---|
| | | | | | | Endo | Exo |
| 1. | THPO | 1 | 105–165 | 38,0 | 165 | 56[b] | 165 |
| | 0.512 | 2 | 165–245 | 60.7 | | | |
| 2. | 0.49 THPO | 1 | 106–160 | 45,0 | 160 | 50[b] | 160 |
| | + T 0.027 | 2 | 160–230 | 50,0 | | | |
| 3. | 0.48 THPO | 1 | 107–155 | 46.3 | 155 | 45[b] | 155 |
| | + 0.042 T | 2 | 155–240 | 48.7 | | | |
| 4. | 0.50 THPO | 1 | 80–150 | 39.2 | 150 | 40[b] | 150 |
| | + 0.06 T | 2 | 150–235 | 58.8 | | | |
| 5. | 1 THPO | 1 | 70–140 | 25.0 | 140 | - | 140 |
| | + 1 T | 2 | 140–275 | 74.0 | | | |
| 6. | 0.16 THPO | 1 | 60–160 | 40.2 | 160 | - | 160 |
| | + 0.46 T | 2 | 160–240 | 51.7 | | | |
| 7. | 0.64 T | 1 | 65–180 | 97.6 | 160 | | 165 |

[a] DTG peak. [b] Melting point.

The reactions generating radicals from THPO in these experimental conditions are thermal homolysis and bimolecular hydroperoxide decomposition

$$\mathrm{ROOH \rightarrow RO^{\cdot} + OH^{\cdot}} \tag{9}$$

$$\mathrm{2ROOH \rightarrow RO^{\cdot} + H_2O + ROO^{\cdot}} \tag{10}$$

These reactions are preceded by decomposition of the associates produced by proton-acceptor interactions. Our earlier investigations [11] show that the decomposition of THPO intermolecular associates retards its homolytic decomposition and influences the initial temperature of decomposition $T_i$. It is known that hydroperoxides dissolved in aromatic solvents form the associates OH–$\pi$-centre of an aromatic ring [12]. The IR

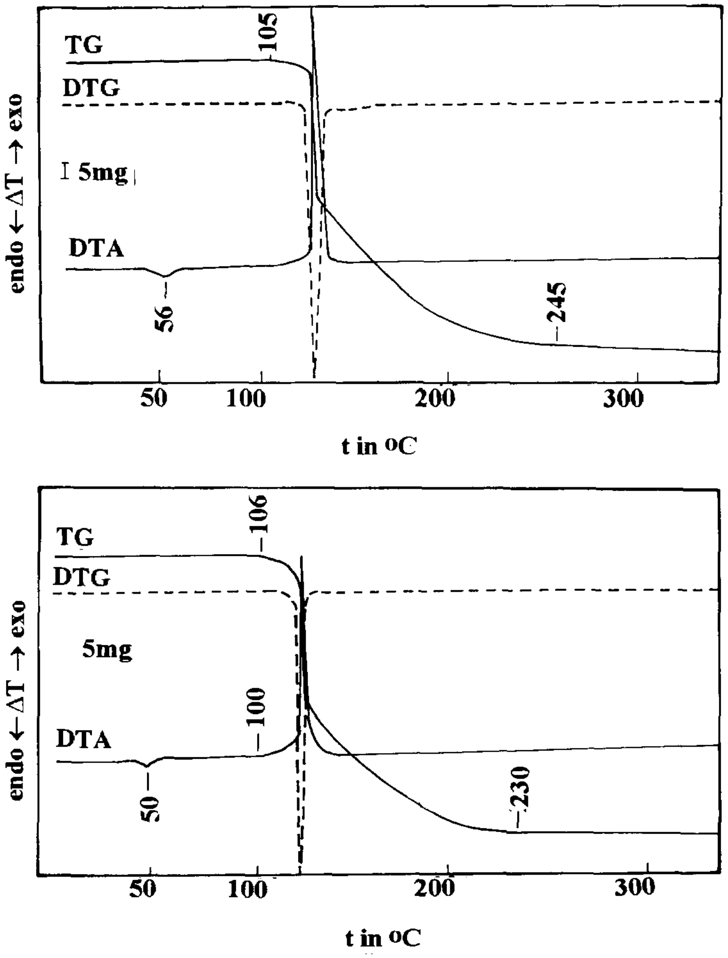


Fig. 2. TG/DTA data of $\alpha$-tetralyl hydroperoxide and tetralin: (a) $\alpha$-tetralyl hydroperoxide; (b) 0.49 mM THPO + 0.027 tetralin; (c) 0.48 THPO + 0.042 mM tetralin; (d) 0.50 mM THPO + 0.06 mM tetralin.

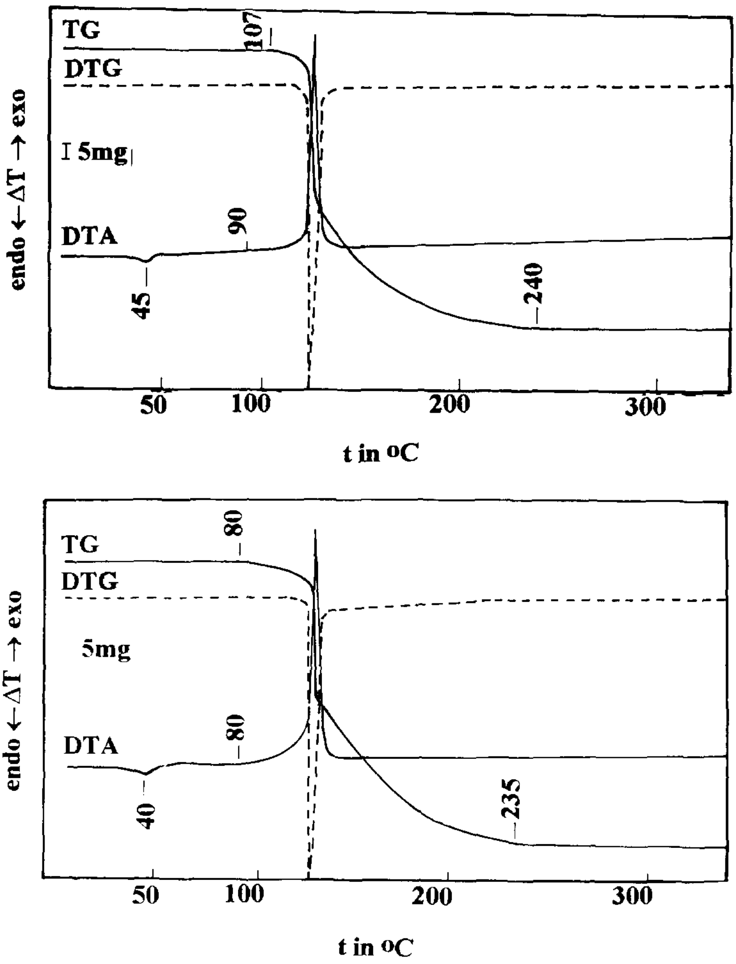


Fig. 2. *(Continued)*

spectrum of THPO shows an absorbance at 3552 cm$^{-1}$ which is ascribed to the OH stretching vibrations, but the absorbance at 3527 cm$^{-1}$ is indicative of the hydrogen bond OH–$\pi$-electrons of the THPO aromatic ring. The dimer maximum occurs at 3429 cm$^{-1}$.

Comparing these results with the IR spectrum of the system 0.48 mM THPO–0.042 mM tetralin, we note the appearance of an absorbance at 3552 cm$^{-1}$, ascribed to the monomeric species. The proof for the substitution of part of the THPO intermolecular associates, with THPO–tetralin (OH...$\pi$) associates, is the shift of the absorbance maximum from 3429 cm$^{-1}$ to 3464 cm$^{-1}$. The hydrogen bonds in these associates are weak and their concentration decreases with increasing temperature. Nevertheless, their decomposition is an energetic barrier for a certain period of time, thus retarding radical-generation reactions (9) and (10), affecting $T_i$. The insignificant changes in the $T_i$

values of systems 2 and 3 with 0.027 and 0.042 mM tetralin, could be due to the formation and decomposition of intermolecular associates between THPO and tetralin molecules. It is known that hydroperoxides diluted in aromatic solvents are thermally more stable than in aliphatic solvents [12]. On raising the concentration of tetralin in the systems, such effects are not observed because of the increase in the evaporation rate and the thermochemical decomposition. The decrease in the intensity of the exo peak in system 2 with 0.027 mM tetralin (Fig. 2b) is due to a decrease in the steady-state concentration of tetralyl radicals and to fast chain-termination reactions. As a result, stable molecular products are probably obtained at these temperatures. The retardation effect of the tetralin on the THPO decomposition is due not only to the formation of associates, but also to the participation of tetralin in competitive chain radical reactions.

However, tetralin also facilitates the bimolecular decomposition of the THPO and thus accelerates the thermochemical decomposition in the systems

$$2ROOH + RH \rightarrow 2RO^{\cdot} + R^{\cdot} + H_2O \qquad (11)$$

This reaction has a positive thermal effect and usually accompanies free-radical-induced decomposition which is why the intensities of the exo peaks in systems 3 and 4 with 0.042 and 0.060 mM tetralin increase in comparison with the system with a low concentration of tetralin (Fig. 2b,c,d).

The weight loss during the first stage of decomposition in the system with 0.06 mM tetralin is lower than in systems 2 and 3 (Table 1). It is probable that the tetralyl radicals formed terminate radical decomposition through reaction (7) and the following reactions

$$R^{\cdot} + ROO^{\cdot} \rightarrow ROOR \qquad (12)$$

$$R^{\cdot} + RO^{\cdot} \rightarrow ROR \qquad (13)$$

The shift of the temperature range of the exothermal reactions to lower temperatures with increasing tetralin concentration in the systems, could be the result of the lowering of the steady-state concentrations of the tetralyl and tetralylperoxy radicals responsible for the radical-terminating reactions.

The CI MS data of the decomposition products resulting from the reaction between 0.50 mM THPO and 0.06 mM tetralin at 160°C (Fig. 3) register the following ions: m/z (relative intensity, %), 181 (25) $(M+1)^+$ and 179 (27) $(M-1)^+$ which can be assigned to $\gamma$-*o*-hydroxyphenyl butyric acid; 195 (20) $(M+1)^+$ to $\beta$-*o*-carboxyphenyl propionic acid; 277 (10) $(M-1)^+$ to bis-tetralyl ether; 293 (20) $(M-1)^+$ to bis-tetralyl peroxide; 325 (10) $(M-1)^+$ to bis-tetralyl tetroxide. The peaks 163 (100) $(M-1)^+$, 147 (60) $(M+1-H_2O)^+$, 131 (60) $(M-1-O_2)^+$ indicate the presence of the $\alpha$-tetralyl hydroperoxide. In isobutane, the CI mass spectra of THPO showed the ions $(M+1-H_2O)^+$ and $(M-1-O_2)^+$. The same ions appear in the isobutane CI MS of cumyl hydroperoxide.

The presence of bitetralyl ether (m/z 277) as a reaction product shows that the terminating reaction (13) takes place. The peak at m/z 325, which is indicative of

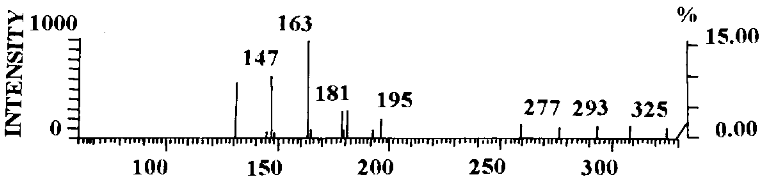


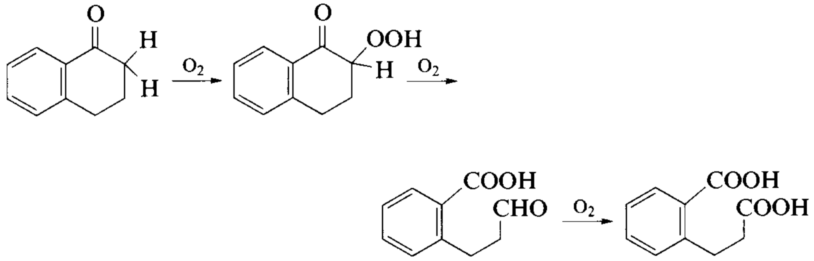
Fig. 3. Mass spectrum of the decomposition products from the system 0.50 THPO + 0.06 mM tetralin at 160°C.

bis-tetralyl tetroxide, suggests a free-radical mechanism

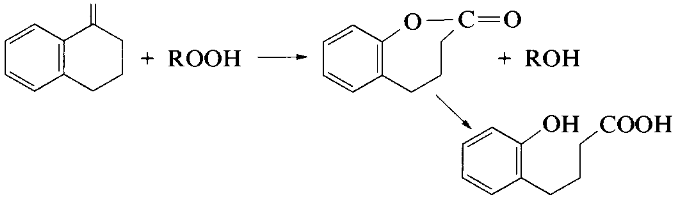
$$\begin{array}{l} 2C_{10}H_{11}O_2 \\ \quad\upharpoonleft\!\downharpoonright \\ C_{10}H_{11}OOOOC_{10}H_{11} \rightarrow \begin{array}{l} 2C_{10}H_{11}O + O_2 \\ (C_{10}H_{11})_2O_2 + O_2 \end{array} \end{array} \tag{14}$$

It is known that these reactions predominate in the gas phase. Under non-isothermal conditions and decreased air access in our experiments, reaction (14) becomes possible.

*β*-*o*-Carboxiphenyl propionic acid and *γ*-*o*- hydroxyphenyl butyric acid can be obtained by the following reactions



(15)



(16)

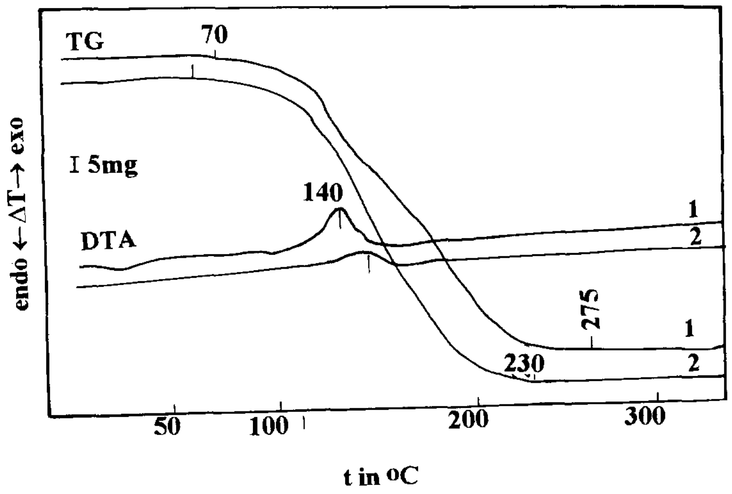


Fig. 4. TG/DTA data of the systems: (1) THPO/tetralin 1:1; (2) 0.16 mM THPO + 0.46mM tetralin.

A smooth 2-stage thermochemical decomposition is observed on the derivatograms of the system THPO–tetralin 1:1, in the temperature range 70–275°C (Fig. 4, curve 1). The lowered initial temperature indicates an evaporation process. Fast radical decomposition reactions are not observed. It is clear that the terminating reaction dominates, leading to the formation of thermally stable products. The self-inhibitor $\gamma$-*o*-hydroxyphenyl butyric acid determined by MS, 181 (25) $(M+1)^+$ and 179 (27) $(M-1)^+$ also has a retarding effect. Nearly all phenols act as inhibitors, both in the initial stage of the hydrocarbon auto-oxidation and in the degenerated branching reactions of the hydroperoxides obtained. Roberson and Waters have shown that $\gamma$-*o*-hydroxyphenyl butyric acid is an inhibitor of the auto-oxidation of tetralin even if added at the stage of rapid oxidation [14].

With the increase of the content of tetralin in the system to 70%, 0.046 mM, the intensity of the exo peak decreases significantly due to the increase in the intensity of evaporation (Fig. 4, curve 2). The decreased weight losses during the second stage indicate radical reactions taking place with a different mechanism; probably with this system the reactions proceed in the gas phase.

## 4. Conclusions

Tetralin retards the thermal decomposition of THPO in non-isothermal conditions due to the decrease in the steady-state concentration of tetralyl radicals and their participation in the radical decomposition.

The decomposition of the associates OH–$\pi$-electrons, resulting from proton-acceptor interactions, influences the homolytic decomposition and the initial temperature of the decomposition.

We observe the presence of $\gamma$-*o*-hydroxyphenyl butyric acid, a natural inhibitor of the studied systems.

The presence of bitetralyl peroxide and bitetralyl ether in the reaction product at 160°C, for the system 0.50 mM THPO–0.06 mM tetralin, indicates that terminating reactions take place, with the dominating participation of tetralyl radicals.

The presence of bitetralyl tetroxide indicates a probable gas-phase mechanism in non-isothermal conditions and the absence of oxygen.

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