Thermal decomposition of α-tetralyl hydroperoxide under non-isothermal conditions, without solvents

N. Shopova * and Sl. Ivanov

Institute of Organic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bontchev str., bl.9, 1113 Sofia (Bulgaria)

Abstract

The thermal decomposition of α-tetralyl hydroperoxide (THPO) has been investigated under a variety of conditions: in dynamic (argon and air) atmosphere, static air and self-generated atmosphere by employing DTA and TGA methods. The decomposition of THPO proceeds in two-stages during its thermochemical degradation under non-isothermal conditions in the temperature interval from room temperature to 500°C. It has been shown that the formation of associates resulting from the proton donor–acceptor interactions affects the initial temperature of hydroperoxide decomposition. Free-radical-induced decomposition proceeds in self-generated atmosphere at 165°C. 2,6-Di-*tert*-butyl-4-methyl phenol at some concentrations and phenyl-α-naphthylamine inhibit the induced radical decomposition. The products from the THPO decomposition are identical with those obtained during its decomposition in various solvents.

The DTA and TGA methods show promise as useful techniques for the investigation of free-radical induced decomposition of hydroperoxides.

INTRODUCTION

The thermal decompositions of hydroperoxides have been studied in a gas or a liquid phase and in the presence of various organic solvents [1–4]. Generally it has been established that the solvents take part in the reactions of thermal decomposition.

It is known that the processes of hydroperoxide decompositions in solvents are usually complicated by that of the so called free radical "induced" decomposition [5, 6]. The occurrence of this side reaction is characterized by the following basic features:

(a) the production of an S-shaped curve for hydroperoxide decomposition with coordinates $[ROOH]–f(\tau)$ which is indicative of the autocatalytic character of the process;

(b) effect of inhibitors — acceptors of free radicals;

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* Corresponding author.

(c) identification of products which are characteristic for the reactions of free radical induced hydroperoxide decomposition.

The conventional experimental methods for studying the induced decomposition are connected with loss of time and reagents. The mechanism of this reaction for primary and secondary hydroperoxides differs from that of tertiary hydroperoxides. This is due to the presence of active hydrogen atoms at the α-position in the primary and secondary hydroperoxides; these are absent in the tertiary hydroperoxides.

Some data on the thermal decomposition of cumyl hydroperoxide without solvents, in argon atmosphere and the effect of inhibitors are presented in refs. 7 and 8.

Tetralyl hydroperoxide is the primary product of tetralin auto-oxidation and it takes part in the degenerating branching step and to a lesser extent in the termination step. The study of its decomposition under non-isothermal conditions, without solvent could provide useful information concerning the mechanism of hydrocarbon oxidation.

The aim of the present work is to study the thermal decomposition of tetralyl hydroperoxide under non-isothermal conditions without solvent, and to follow the effect of various atmospheres.

EXPERIMENTAL PART

Tetralyl hydroperoxide was prepared by air oxidation of tetralin [9] and used after threefold recrystallization from petroleum ether (b.p. 30–50°C). Its purity was checked by the melting point, +54.6°C, and also by DTA analysis (Table 1).

2,6-Di-*tert*-butyl-4-methyl phenol was purified following the procedure described in ref. 10. Phenyl-α-naphthylamine was recrystallized three times from alcohol and dried to a constant weight.

Bis(α-tetralyl)peroxide was prepared from α-tetralyl hydroperoxide by the method of Triebs and Pellman [11].

α-Tetralon, α-tetralol (Aldrich) and 1,2-dihydro-naphthalene (Merk) were used as references, without further purification.

The thermal analyses were carried on a Q-1500 (MOM, Hungary) derivatograph under the following conditions: sample mass, 82 mg; balance sensitivity, ±1 mg; reference, α-Al$_2$O$_3$; heating rate 2.5°C min^{-1}; Pt crucible with diameter of 7 mm. The DTA experiments were conducted in the temperature region from ambient to 500°C under, (a) dynamic air and argon atmosphere (flow rate 17 l h^{-1}), (b) static air atmosphere, (c) self-generated atmosphere.

The decomposition experiments were carried out in ampoules, at a heating rate of 2.5°C min^{-1} up to 165 and 200°C.

The decomposition products were identified by HPLC using a Perkin-Elmer chromatograph with Diod Acay detector employing a Perkin-Elmer C 18.5 μm column (150 mm × 4 mm internal diameter). The eluting solvent

TABLE 1

Thermal decomposition data for α-tetralyl hydroperoxide (THPO) in various atmospheres

No.	Experi-mental atmosphere	Stage	Temperature interval of decompo-sition/°C	Mass loss/ %	$T_{W,max}/$ °C [a]	Thermal effect/°C		Residue/% at 500°C
						Endo	Exo	
1	THPO Ar, dynamic	1	85 [b]–138	18.6	135	50 [c]	135	
		2	138 –300	69.8	173	–	150	3.5
2	THPO air, dynamic	1	75 [b]–155	70.5	150	54 [c]	150	
		2	160 –250	21.5	170	–	155	2.0
3	THPO air, static	1	100 [b]–145	22.5	140	54 [c]	140	
		2	145 –280	71.3	160	–	155	2.5
4	THPO self-generated	1	105 [b]–165	28.0	165	54 [c]	165	
		2	165 –250	42.7	–	–	–	23.0

[a] DTG peaks. [b] Initial decomposition temperature. [c] DTA peaks corresponding to melting points of THPO.

was a mixture of acetonitrile and water at a flow rate of $1\ ml\ min^{-1}$. The detection was carried out at a wavelength of 250 nm.

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

RESULTS AND DISCUSSION

The absorption bands in the region $3452–3300\ cm^{-1}$ on the IR spectrum of THPO in a KBr pellet indicate the formation of molecular associates resulting from proton donor–acceptor interactions. Reasonably, one can expect that their decomposition might affect the thermal destruction of THPO.

The derivatograms in Fig. 1(a–d) show that under non-isothermal conditions THPO decomposition proceeds as a two-stage thermochemical process. The relatively low initial temperature of THPO decomposition in dynamic argon and air atmosphere (in Ar, 85°C; in air, 75°C; Table 1, Nos. 1 and 2) could be explained by the increase in vaporization from one side and by the operation of thermo-destructive processes under the action of air, from the other.

We have observed an increase in the initial temperature of decomposition during the thermal decomposition of THPO in static air atmosphere and self-generated atmosphere (Table 1, Nos. 3 and 4). In general, these differences can be attributed to the decrease in vaporization. However, other factors that affect the thermochemical stability of THPO should be
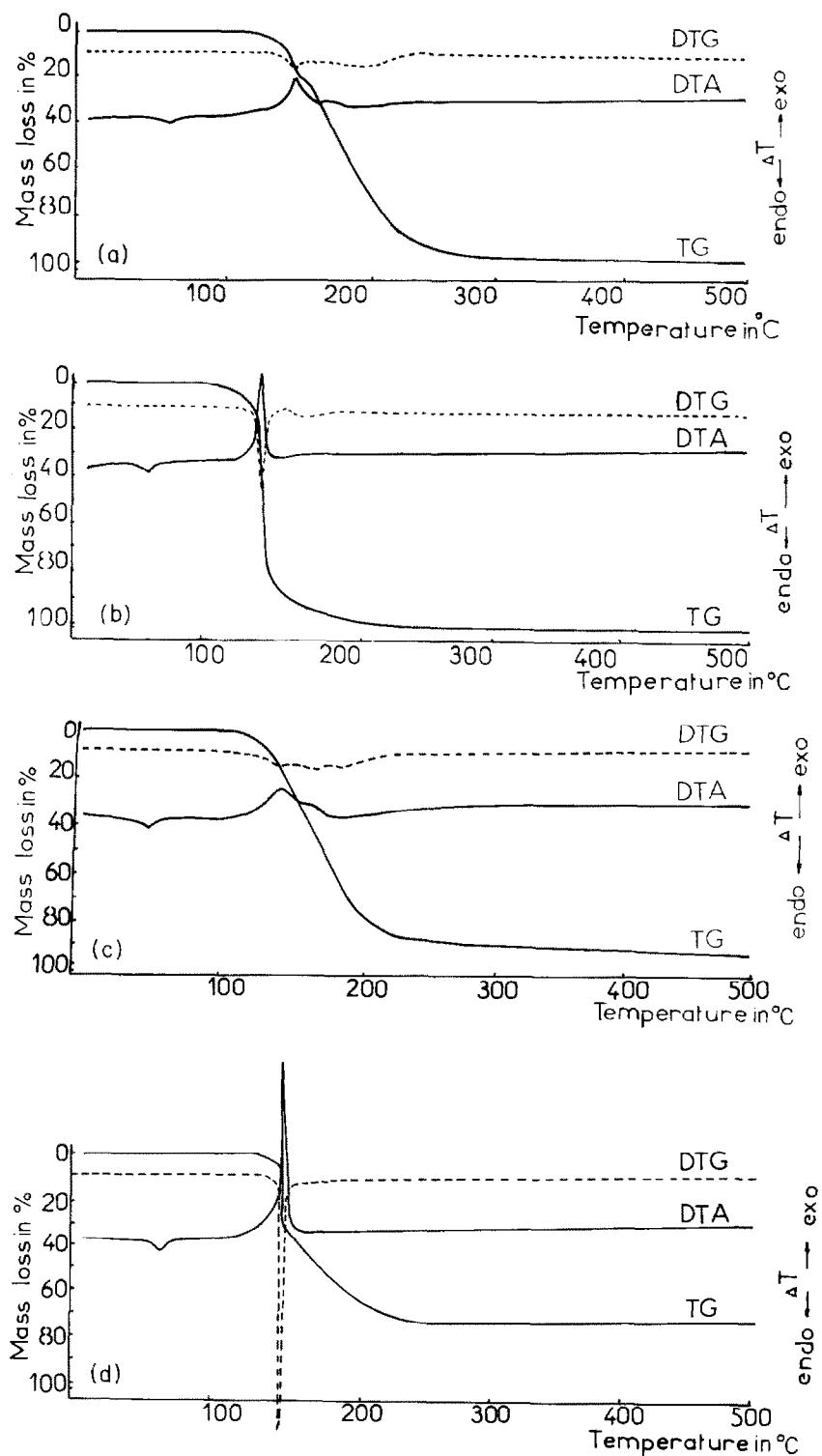
Fig. 1. TGA–DTA curves of α-tetralyl hydroperoxide: (a) in dynamic argon atmosphere; (b) in dynamic air atmosphere; (c) in static air atmosphere; (d) in self-generated atmosphere.

taken into consideration. It is known that hydroperoxides diluted in solvents [12] form both intermolecular self-associates as linear dimers, cyclic dimers and $n$mers with participation of cyclic dimers, and intramolecular associates as a result of the associative interactions between the OH group of the hydroperoxide and the π-electrons of the aromatic ring (OH $\cdots$ π).

Considering that under the experimental conditions of this work THPO is in a molten state above its melting point (according to the DTA analysis, Table 1), one can also expect associative interactions to proceed.

The OH $\cdots$ π centre distance is 3.783 Å, calculated after full optimization of molecular geometry [13]. This result suggests the formation of intramolecular associates [14]. The IR spectrum of THPO at a concentration of 4.69×10^{-3} mol l^{-1} in CHCl$_3$ shows an absorbance at 3552 cm^{-1}, which is ascribed to the OH stretching vibrations and which is shifted to the higher frequency of 3527 cm^{-1}. These data support the formation of hydrogen bond OH $\cdots$ π electrons of the aromatic ring. The low value of the enthalpy of the intramolecular hydrogen bond of THPO, $+0.9 \pm 0.1$ kcal mol^{-1} [15] allows us to assume that such associates cannot be regarded as an energetic barrier for the non-isothermal decomposition of THPO. However, the existence of an intramolecular hydrogen bond OH $\cdots$ π centre can decrease the concentration of intermolecular associates for a certain period of time.

We have registered the formation of intermolecular associates in the IR spectrum of a more concentrated solution of THPO (6.82×10^{-1} mol^{-1}) in CHCl$_3$ (Fig. 2). The absorption maximum at 3429 cm^{-1} is characteristic of the effect of associated OH groups and, similarly to other hydroperoxides [16], it can be ascribed to the vibrations of the OH bond in dimers, (HROOH)$_2$. This maximum increases with the increase in THPO concentration (Fig. 2, curves a and b). It has been found that the dimeric form of the hydroperoxide is the most stable associate regarding its thermal stability [17]. Generally, it can be assumed that the formation of associates could retard the homolytic decomposition of the hydroperoxide and
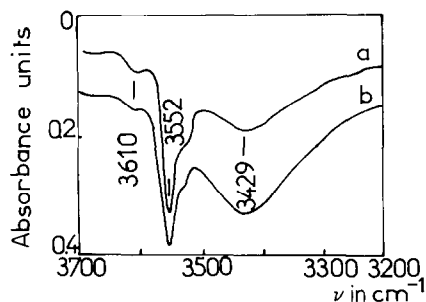

Fig. 2. IR spectra of α-tetralyl hydroperoxide in the range 3700–3200 cm^{-1}: curve a, THPO in CHCl$_3$ (6.82×10^{-1} mol l^{-1}); curve b, THPO in CHCl$_3$ (1.15 mol l^{-1}).

influence the initial temperature of its decomposition (Table 1, Nos. 3 and 4).

The variations in the character of the process of thermal destruction of THPO under different experimental conditions are presented in Table 1 and Fig. 1. The hydroperoxide decomposition in Ar atmosphere, during the first stage proceeds as an exothermal process with a maximum at 135°C. The absence of rapid degradation results in more stable products being obtained, whose degradation occurs during the second stage (see Fig. 1(a)). We have observed an absence of rapid degradation of THPO in static air atmosphere (Fig. 1(c)). The increase in the mass losses (22.5%) and the shift of the maximum rate of degradation to the higher temperatures during the first stage may be due to the effect of oxygen on the thermochemical destruction (Table 1, compare Nos. 1 and 3) and to the decrease in vaporization.

We have observed significant changes in the decomposition of hydroperoxide during the first stage when performing the DTA experiments in dynamic air atmosphere (Table 1, No. 2; Fig. 1(b)) and in self-generated atmosphere (Table 1, No. 4, Fig. 1(d)). A rapid exothermal reaction has been registered in both cases.

The TGA data in Fig. 1(b) and Table 1, No. 2 show that the mass losses

TABLE 2

Thermal decomposition of α-tetralyl hydroperoxide (THPO) in the presence of 2,6-di-*tert*-butyl-4-methyl phenol (AH) and phenyl-α-naphthlyamine (BH) [a]

No.	System	Stage	Temperature interval of decomposition/°C	Mass loss/ %	$T_{W,max}$/ °C [b]	Thermal effect/°C	
						Endo	Exo
1	THPO + AH [c]	1	90–160	19.5	155	45	155
	1 mol:1 mol	2	160–290	67.4	215	–	–
2	THPO + AH	1	95–160	15.3	155	50	155
	1 mol:0.7 mol	2	160–310	74.5	225	–	–
3	THPO + AH	1	95–160	12.3	150	47	150
	1 mol:0.25 mol	2	160–270	73.3	230	–	–
4	THPO + AH	1	118–160	8.0	155	50	155
	1 mol:0.1 mol	2	160–310	71.8	240	–	–
5	THPO + BH	1	105–165	11.4	150	47	150
	1 mol:0.5 mol	2	165–310	66.0	215	–	–

[a] Self-generated atmosphere. [b] DTG peak. [c] The concentration of the acceptor of free radicals is calculated as the amount of decomposed hydroperoxide during the induced decomposition at 165°C.

are 70.5% during the first stage of hydroperoxide decomposition. The exclusively fast decomposition of THPO (Fig. 1(b)) and the relatively low exothermal peak with temperature maximum at 155°C are associated with intensive vaporization and thermo-oxidative radical destruction under the influence of the dynamic air atmosphere.

We have observed that after minimizing the effect of the atmosphere, THPO decomposition in self-generated atmosphere (Fig. 1(d)) proceeds similarly to that in dynamic air atmosphere (Fig. 1(c)). However, it has been found that only 28% of THPO was decomposed during the first stage (Table 1, No. 4). A high exothermic peak with temperature maximum at 165°C has been obtained due to rapid radical decomposition (Fig. 1(d)). The TGA data show that $\partial G/\partial \tau \to \infty$ at 165°C. The results suggest that the thermal decomposition of THPO during the temperature interval 105–165°C proceeds both as thermal homolysis and free-radical-induced decomposition.

In order to check whether the effect observed by us is due to the free-radical-induced decomposition of the hydroperoxide we have studied the influence of typical scavengers of free tetralyl peroxy radicals: 2,6-di-*tert*-butyl-4-methyl phenol and phenyl-α-naphthylamine. It is well known that the hindered phenol 2,6-di-*tert*-4-methyl phenol (AH) inhibits the oxidation of hydrocarbons by replacing the chain propagation step by the reactions

$$RO_2^{\cdot} + AH \to ROOH + A^{\cdot}$$

$$RO_2^{\cdot} + A^{\cdot} \to ROOA$$
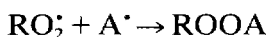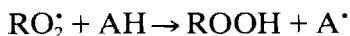
The TGA data of the THPO decomposition in the presence of acceptors show a similar two-stage decomposition (Table 2). During the first stage the maximum degradation rate shifts to lower temperatures (Table 1, No. 4 and Table 2, Nos. 1–5) and the amount of the decomposed product decreases markedly. The effect of the acceptors of free radicals is demonstrated most distinctly by the DTA data during the first stage (Fig. 3). The height of the exothermal peak which corresponds to the thermal effect of interaction between THPO and the scavenges of free radical decreases significantly compared to that of the neat THPO (compare Figs. 1(d) and 3). The thermal reaction between THPO and the acceptor of free radical results molecular products being obtained that decompose at higher temperatures during the second stage (Table 2). These data suggest that free radical induced decomposition of THPO proceeds in self-generated atmosphere at 165°C (Fig. 1(d)). In the presence of acceptors of free radicals this process is replaced by purely thermochemical destruction.

The relationship between the area of the exothermic peak that reflects the enthalpy changes of the interaction of THPO with 2,6-di-*tert*-butyl-4-methyl phenol and its concentration (Fig. 4) shows that the acceptor loses
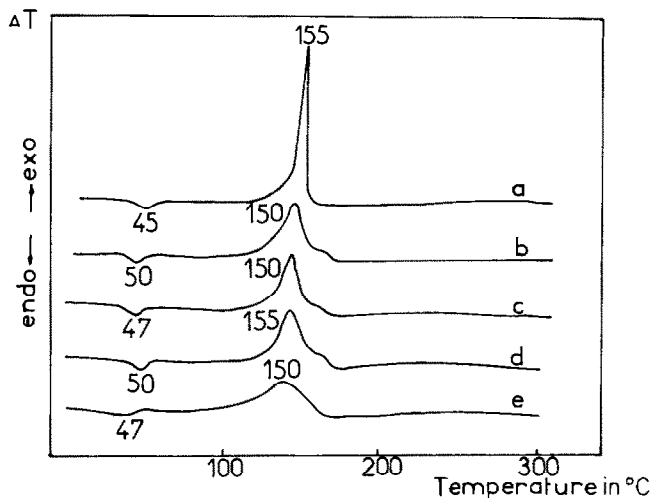
Fig. 3. DTA curves of α-tetralyl hydroperoxide + 2,6-di-*tert*-butyl-4-methyl phenol in concentration: curve a, 1 mol:1 mol; curve b, 1 mol:0.7 mol; curve c, 1 mol:0.25 mol; curve d, 1 mol:0.1 mol. Curve e, α-tetralyl hydroperoxide + phenyl-α-naphthylamine, 1 mol:0.5 mol.

its inhibitory properties at some concentrations. As is seen, this dependence is complex and differs essentially from the usual relationship characterizing the inhibitory ability of the acceptors of free radicals. At this stage of our research we cannot explain its character and in order to make this clear, further research is necessary.

The reactions responsible for the generation of free radicals from THPO are the thermal homolysis and the bimolecular hydroperoxide decomposition
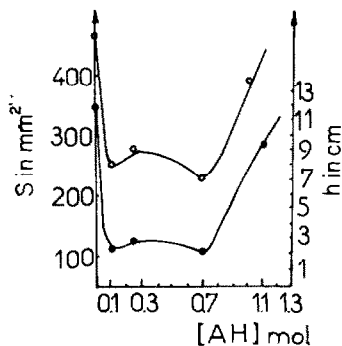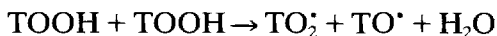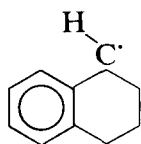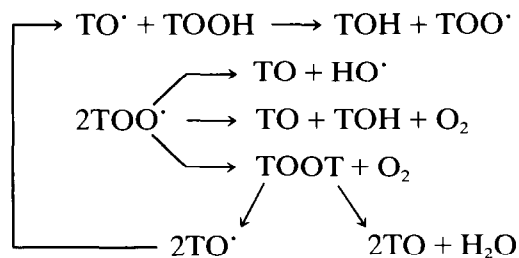
$$TOOH \rightarrow TO^{\cdot} + {}^{\cdot}OH$$
$$TOOH + TOOH \rightarrow TO_2^{\cdot} + TO^{\cdot} + H_2O$$

Fig. 4. System α-tetralyl hydroperoxide + 2,6-di-*tert*-butyl-4-methyl phenol. Area of exo peak (S, $\bigcirc$) and the height of exo peak (h, $\bullet$) versus concentration of acceptor (AH).

where T is

The HPLC data of the THPO decomposition products at 165°C prove the presence of α-tetralon, traces of α-tetralol, and of bis(α-tetralyl)peroxide (TOOT). The induced decomposition of THPO can be demonstrated by the equations

$$
\begin{array}{l}
\longrightarrow \text{TO}^{\cdot} + \text{TOOH} \longrightarrow \text{TOH} + \text{TOO}^{\cdot} \\[4pt]
\qquad\qquad \nearrow \text{TO} + \text{HO}^{\cdot} \\[2pt]
2\text{TOO}^{\cdot} \longrightarrow \text{TO} + \text{TOH} + \text{O}_2 \\[2pt]
\qquad\qquad \searrow \text{TOOT} + \text{O}_2 \\[2pt]
\qquad\qquad\quad \swarrow \qquad \searrow \\[2pt]
\text{2TO}^{\cdot} \qquad\quad \text{2TO} + \text{H}_2\text{O}
\end{array}
$$

We have identified a peak of 1,2-dihydronaphthalene on the HP liquid chromatogram of the THPO decomposition products at 200°C

$$\text{TOH} \xrightarrow{\;-\text{H}_2\text{O}\;} \text{1,2-dihydronaphthalene}$$
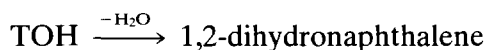
These data can be regarded as an additional argument for the process of free-radical-induced decomposition of THPO in self-generated atmosphere.

The significant amount of residue from the THPO decomposition at 500°C (Table 1, No. 4) points to the presence of products arising from the decomposition of 1,2-dihydronaphthalene [18].

CONCLUSIONS

A two-stage decomposition of α-tetralyl hydroperoxide has been established during its thermochemical degradation under nonisothermal conditions without solvents in the temperature interval from room temperature to 500°C.

It has been found that free-radical induced decomposition of α-tetralyl hydroperoxide proceeds in self-generated atmosphere; the products from the THPO decomposition are identical with those obtained during its decomposition in various solvents.

The TGA and DTA methods can be successfully used for the investigation of the induced decomposition of hydroperoxides.

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