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ORIGINAL PAPER

Studies on the mechanism of decomposition of 1-methyl-1-(1-naphthyl)ethyl hydroperoxides to 2-(1-naphthyloxy)propenes

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Abstract Thermal decomposition of 1-methyl-1-(4-methyl-1-naphthyl)ethyl hydroperoxide under gas chromatography-mass spectroscopy (GC–MS) conditions gives 2-((4-methyl-1-naphthyl)oxy)propene as the main product (50.5%), without any detectable traces of the isomeric 2-((5-methyl-1-naphthyl)oxy)propene. This finding excludes the rearrangement pathway of 1-methyl-1-(1-naphthyl)ethyl hydroperoxides to the corresponding 2-(1-naphthyloxy) propenes, which involves formation of a naphthofuran derivative as an intermediate and transfer of the isopropenyloxy group to the 8 position. This result, as well as our previous density functional theory (DFT) calculations, points to the rearrangement pathway involving an oxirane-type intermediate as the most plausible pathway to 2-(1-naphthyloxy)propenes. This rearrangement is responsible for the unusual inhibition effects of 1-methyl-1-(1-naphthyl)ethyl hydroperoxide on the liquid-phase oxidation of isopropylarenes with oxygen.

Keywords Reaction mechanism · Oxidations · Peroxides · Thermal decomposition

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Introduction

Free-radical chain oxidation of isopropylarenes with oxygen is well known to be affected by the resulting hydroperoxides, which are primary oxidation products. Usually, as a result of thermal decomposition of hydroperoxides into free radicals, the process becomes autocatalytic in nature [1]. Recently, we have demonstrated that 1-methyl-1-(1-naphthyl)ethyl hydroperoxide (**1**) inhibits free-radical oxidation of isopropylarenes, e.g. oxidation of 1-isopropylnaphthalene, 2-isopropylnaphthalene or cumene, whereas 1-methyl-1-(2-naphthyl)ethyl hydroperoxide (**2**) actually acts as an initiator of these reactions [2]. The inhibition activity of hydroperoxide **1** creates a serious technical problem, since 2-isopropylnaphthalene, used in 2-naphthol production by means of a method analogous to phenol production, is contaminated by a small amount (5–10%) of 1-isopropylnaphthalene, which is difficult to remove. The 1-isopropylnaphthalene present in the raw material reduces the oxidation rate and results in lower yield and poorer selectivity in the production of hydroperoxide **2** [3–10].

Our comparative studies of the thermal decomposition of hydroperoxides **1** and **2** under GC–MS conditions revealed a considerable dissimilarity in the decomposition route of these two isomeric hydroperoxides [11]. The hydroperoxide **2** decomposition product was typical for decomposition of this kind of compound and contained 2-(2-naphthyl)-2-propanol (39%), 2-(2-naphthyl)propene (21%) and 2-acetylnaphthalene (40%), whereas the hydroperoxide **1** decomposition products contained 2-(1-naphthyl)-2-propanol (23.5%), 2-(1-naphthyl)propene (9.2%) and 1-acetylnaphthalene (19.7%), and, unexpectedly, 2-(1-naphthyloxy)propene (45.6%) as the main product [11]. Similar results were obtained when we compared the thermal decomposition under GC–MS conditions of 1-(2-anthryl)-1-methylethyl hydroperoxide and 1-(1-anthryl)-1-methylethyl hydroperoxide. In this case, the main product of decomposition of the latter compound was 2-(1-anthryloxy)propene (81.2%) [11]. To the best of our knowledge, 2-aryloxypropenes have thus far not been described as thermal decomposition products of 1-aryl-1-methylethyl hydroperoxides.

Assuming that the inhibition effect of hydroperoxide **1** is connected with its atypical thermal decomposition to 2-(1-naphthyloxy)propene, we considered three plausible pathways of the transformation of **1** to 2-(1-naphthyloxy)propene (Scheme 1, X = H) [2, 11, 12].

Pathways **A** and **B** start from the abstraction of a hydrogen from the *peri* position of the neighbouring ring. Pathway **C** consists of the intramolecular attack of the oxygen radical on the carbon atom at position 1 with formation of an epoxy-like product. In all of the considered reaction paths, intermolecular hydrogen abstraction by 1-methyl-1-(1-naphthyl)ethoxy radical or other radicals is necessary for the formation of 2-(1-naphthyloxy)propene (Scheme 1). We assume that this very reaction step is responsible for the inhibition effect of hydroperoxide **1** in the oxidation of isopropylarenes, as it terminates the free-radical chain [11].

The aim of our investigations described in this paper was to establish if the isopropenyloxy group in 2-(naphthyloxy)propenes remains at position 1, as would be expected for pathways **B** or **C**, or whether it migrates to position 8 of the naphthalene ring, according to pathway **A** (Scheme 1). This differentiation would allow us to exclude one or two of the three considered pathways of formation of 2-(1-naphthyloxy)propene. We tried to achieve this goal by marking the 4 position of 1-methyl-1-(1-naphthyl)ethyl hydroperoxide with a methyl group (Scheme 1, X = Me).

Results and discussion

As should be expected, the results of the thermal decomposition of 1-methyl-1-(4-methyl-1-naphthyl)ethyl hydroperoxide **3** under GC–MS conditions were similar to those obtained for hydroperoxide **1**. The main decomposition product of hydroperoxide **3** was the corresponding 2-(naphthyloxy)propene (50.5%) with molecular mass of 198, which could have the structure of 2-((4-methyl-1-naphthyl)oxy)propene **4** or the isomeric structure of 2-((5-methyl-1-naphthyl)oxy)propene (Table 1).

In order to determine the structure of the 2-(naphthyloxy)propene, we carried out the thermal decomposition of hydroperoxide **3** on a preparative scale in cumene at 120–140 °C (Table 1). As we expected because of the instability of 2-aryloxypropenes [11], the decomposition products contained much less 2-(naphthyloxy)propene (6.9%); nevertheless, we were able to isolate a pure sample of 2-(naphthyloxy)propene using preparative thin-layer chromatography (TLC). Its MS spectrum was identical to the MS spectrum of 2-(naphthyloxy)propene obtained by decomposition of hydroperoxide **3** under GC–MS conditions. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of the 2-(naphthyloxy)propene revealed that we obtained 2-((4-methyl-1-naphthyl)oxy)propene **4**, without any detectable traces of the isomeric 2-((5-methyl-1-naphthyl)oxy)propene. Crucial for this conclusion was the detailed analysis of the ^{1}H NMR spectrum of naphthyloxypropene **4** in the range of the naphthyl group (8.1–7.0 ppm). Apart from two multiplets at 8.04–7.97 ppm (2H) and 7.57–7.48 (2H), which were assigned to protons at positions 5, 6, 7 and 8, there were two doublets at 7.27 ppm (1H, $J = 7.2$ Hz) and 7.05 ppm (1H, $J = 7.5$ Hz), which clearly indicated protons at positions 2 and 3 in an AX spin system. Such a spin system of two coupled protons, isolated from coupling with other protons

Scheme 1

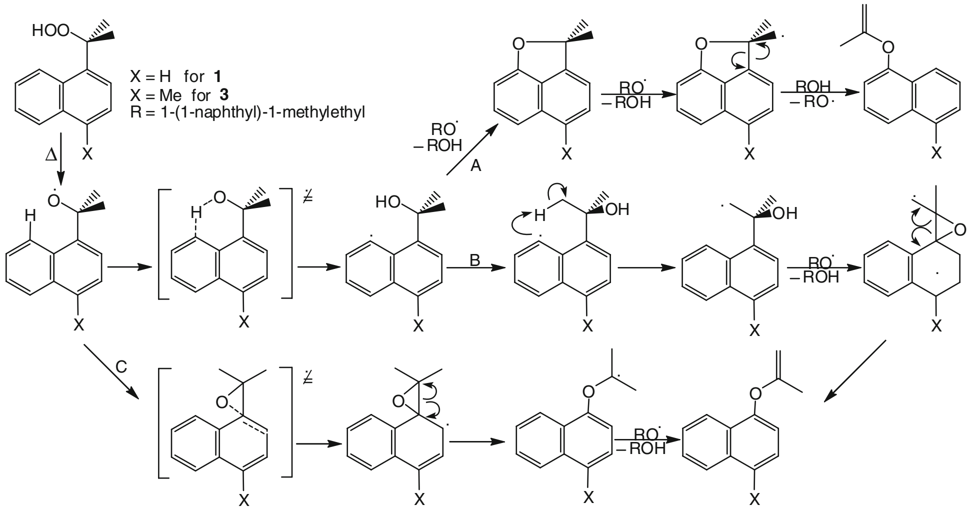
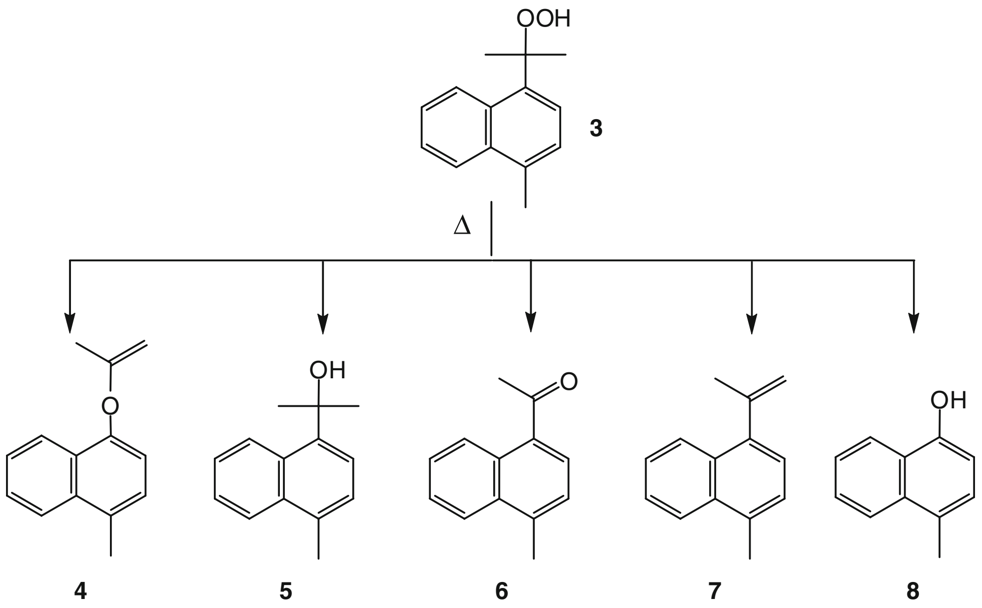


Table 1 Products of thermal decomposition of hydroperoxide **3** under GC–MS conditions and in cumene



Yield of decomposition products (%)					
	Aryloxypropene **4**	Alcohol **5**	Ketone **6**	Alkene **7**	Phenol **8**
GC–MS[a]	50.5	15.4	18.3	13.5	0.0
Cumene[b]	6.9	41.1	6.4	35.5	6.4

[a] Solution of **3** was introduced directly into the GC–MS apparatus

[b] Solution of **3** in cumene was decomposed and the obtained product was determined by GC–MS

of the naphthalene ring, is possible only in the case of naphthyloxypropene **4**.

Identification of naphthyloxypropene **4** as the main product of thermal decomposition of hydroperoxide **3** under GC–MS conditions means that decomposition pathway **A** (Scheme 1), involving formation of a naphthofuran derivative as an intermediate, can no longer be considered.

To determine the reasons for the differences in the chemical behaviour of hydroperoxides **1** and **2**, we carried out calculations of the possible rearrangement pathways of alkoxy radicals derived from **1** and **2** using first a simple semiempirical AM-1 method with MOPAC-7 (RHF for open shell system) [11, 13], and later, more advanced DFT computations with GAUSSIAN-98 using the unrestricted B3LYP hybrid functional with the 6-31G* base [12]. The AM-1 method pointed to paths **A** or **B** as more favourable ways of rearrangement of the alkoxy radical derived from hydroperoxide **1**, which eventually proved to be misleading [12]. On the other hand, DFT-level calculations showed that the rearrangement via the oxirane-type triangle intermediate (path **C**) was more favourable if compared with the abstraction of a hydrogen atom from the *peri* position and explained why 2-(naphthyloxy)propene is formed only by decomposition of hydroperoxide **1** [12]. The higher steric hindrance of the alkoxy radical derived from hydroperoxide **1** results in a higher energy for this radical and lowers the rearrangement barrier for this radical ($\Delta G = 40.2$ kJ/mol) if compared with the energy barrier for the radical derived from hydroperoxide **2** (56.1 kJ/mol) [12]. The results and conclusions of the DFT calculations are consistent with the results of experiments described in this paper and point to pathway **C** as the most plausible rearrangement of hydroperoxide **1** to 2-(1-naphthyloxy)propene.

Experimental

A GC–MS apparatus equipped with a Varian 3300 gas chromatograph (DB5 capillary column, 30 m, $\varphi = 0.25$ µm, helium 30 cm^3/min) conjugated with a SSQ 700 Mat Finnigan mass spectrometer with EI ionisation (70 eV) was used. High-resolution mass spectra (HRMS) were recorded on an AMD 604 spectrometer with EI ionisation. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Unity Inova-300 spectrometer using TMS as an internal standard. Elemental analyses were performed using a Perkin Elmer 2400 series II instrument, and the results agreed with calculated values. Melting points of synthesised compounds were determined in capillary tubes on an SMP 3 (Stuart Scientific) apparatus. Kieselgel 60 (Merck 0.063–0.200 mm) was used for column chromatography. TLC analyses were performed using Merck's plastic plates coated with silica gel 60 F254. Preparative TLC was performed using Merck's glass plates coated with silica gel 60 F254 (20 cm × 20 cm × 2 mm).

2-(4-Methyl-1-naphthyl)-2-propanol

To a stirred suspension of 1.76 g magnesium turnings (72.6 mmol) in 60 cm^3 dry THF was added a solution of 15 g 1-bromo-4-methylnaphthalene (67.9 mmol) in 21 cm^3 dry THF dropwise. An iodine crystal and methyl iodide were added to start the reaction. The reaction mixture was boiled under nitrogen for 3 h. After cooling to 0 °C, a solution of 5 cm^3 dry acetone (97.9 mmol) in 24 cm^3 THF was added. The stirring was continued for 1.5 h at 0–5 °C, and the reaction mixture was poured into 33 g ice with 57 cm^3 sulphuric acid (5%). The precipitated crystalline substance was filtered off, the organic and water layers were separated, and both were extracted with toluene. The combined toluene extracts were washed with an aqueous solution of Na_2CO_3 (10%) and then with water, and dried over $MgSO_4$, and the solvent was evaporated. A quantity of 10.4 g crude product was obtained and then crystallised from 50 cm^3 hexane to obtain 5.6 g pure product (28 mmol, 41% yield). m.p.: 83–84 °C (85–86 °C [14], 90 °C [15]); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.87$–8.85 (m, 1H, Ar), 8.05–8.01 (m, 1H, Ar), 7.53–7.44 (m, 3H, Ar), 7.24–7.22 (m, 1H, Ar), 2.67 (s, 3H, $–CH_3$), 1.99 (s, 1H, –OH), 1.84 (s, 6H, $C(CH_3)_2$) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 141.6$, 134.4, 133.8, 131.0, 127.8, 125.6, 125.1, 124.9, 122.4 (Ar), 74.0 ($\underline{C}(CH_3)_2$), 31.7 ($C(\underline{C}H_3)_2$), 19.6 ($–\underline{C}H_3$) ppm.

1-Methyl-1-(4-methyl-1-naphthyl)ethyl hydroperoxide (**3**, $C_{14}H_{16}O_2$)

To an intensively stirred mixture of 5.0 g 2-(4-methyl-1-naphthyl)-2-propanol (25 mmol) in 56 cm^3 toluene was added a solution of 0.034 cm^3 H_2SO_4 (96%, 0.6 mmol) in 10.9 cm^3 H_2O_2 (65%) at 60 °C. The reaction progress was monitored by TLC using a benzene/acetone 9:1 (v/v) mixture as the eluent and a saturated solution of NaI in acetic acid for developing hydroperoxide spots. After 3 h, the reaction mixture was cooled to room temperature, and the organic layer was separated and washed with water (3 × 15 cm^3), an aqueous solution of Na_2CO_3 (4%, 2 × 12 cm^3) and a saturated solution of $(NH_4)_2SO_4$ (10 cm^3), and then dried with $MgSO_4$. The obtained product (55.6 g) contained 6.3% hydroperoxide **3** (3.5 g, 16.2 mmol, 65% yield) based on iodometric analysis [16]. After evaporation of the solvent, the pure hydroperoxide (2.7 g, 12.5 mmol, oil) was isolated by column chromatography using benzene/acetone 20:1 (v/v) as the eluent (77% yield); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.71$–8.68 (m, 1H, Ar), 7.91–7.87 (m, 1H, Ar), 7.37–7.34 (m, 2H, Ar, –OOH), 7.24 (d, $J = 7.5$ Hz, 1H, Ar), 7.09 (d, $J = 7.4$ Hz, 1H, Ar), 2.52 (s, 3H, $–CH_3$), 1.67 (s, 6H, $C(CH_3)_2$) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 137.1$, 134.8, 133.6, 130.9, 126.1, 125.8, 125.7, 125.2, 125.0, 124.9 (Ar), 86.0 ($\underline{C}(CH_3)_2$), 26.9 ($C(\underline{C}H_3)_2$), 19.6 ($–\underline{C}H_3$) ppm. Elemental analysis was performed after additional purification by column chromatography (benzene/acetone 20:1 v/v).

Thermal decomposition of **3** in GC–MS

A solution of hydroperoxide **3** in $CHCl_3$ at a concentration of 0.001 mg/cm^3 was introduced into the GC injector at 60 °C, and the injector temperature was gradually increased at a rate of 25 °C/min up to 270 °C. Decomposition products were separated on a DB5 capillary column (30 m, $\varphi = 0.25$ µm, helium 30 cm^3/min).

Thermal decomposition of **3** in cumene

The hydroperoxide **3** was decomposed in a closed glass test tube. Each test tube was filled with about 1.5 cm^3 **3** (1.7 g, 7.8 mmol) dissolved in 16 cm^3 cumene (0.5 mol/dm^3), flushed with argon, closed, and immersed in an oil bath at 120 °C for 3 h and then at 140 °C for 4 h. The hydroperoxide was completely decomposed. Composition of the obtained products was determined by GC–MS analysis. The naphthyloxypropene **4** was isolated from the obtained product.

2-((4-Methyl-1-naphthyl)oxy)propene (**4**, $C_{14}H_{14}O$)

The product obtained by decomposition of hydroperoxide **3** in cumene was diluted with 5 cm^3 diethyl ether and extracted with an aqueous solution of NaOH (15 cm^3, 8%). The organic layer was washed with water (3 × 10 cm^3) and dried with $MgSO_4$. The solvents (diethyl ether and cumene) were evaporated, and **4** was isolated by preparative TLC using first benzene and then hexane as eluents. A quantity of 0.07 g pure **4** was isolated. Column chromatography was also used (hexane/acetone 9:1 v/v), but subsequent reactions occurred (e.g. hydrolysis to 1-naphthol), and **4** was not isolated. HRMS (EI): Found: 198.1048; $C_{14}H_{14}O$ requires: 198.1045; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.04$–7.97 (m, 2H, Ar), 7.57–7.48 (m, 2H, Ar), 7.27 (d, $J = 7.2$ Hz, 1H, Ar), 7.05 (d, $J = 7.5$ Hz, 1H, Ar), 4.10 (s, 1H, $C(CH_3)=C\underline{H}_2$), 3.81 (s, 1H, $C(CH_3)=C\underline{H}_2$), 2.67 (s, 3H, $Ar–CH_3$), 2.13 (s, 3H, $C(C\underline{H}_3)=CH_2$) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$):

$\delta = 160.1$ ($\underline{C}(CH_3)=CH_2$), 149.6, 133.7, 130.5, 127.2, 126.2, 126.1, 125.5, 124.4, 122.6, 116.2 (Ar), 88.7 ($C(\underline{C}H_3)=CH_2$), 20.0 ($Ar–\underline{C}H_3$), 19.1 ($C(CH_3)=\underline{C}H_2$) ppm; MS (EI): $m/z = 198$ (M^+, 63), 158 (100), 157 (42), 155 (37), 128 (52), 127 (23), 115 (21).

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