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The Effect of 1- and 2-(1-Hydroperoxy-1-methylethyl)naphthalenes on the Liquid-Phase Oxidation of Alkylaromatic Hydrocarbons

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Abstract:

The properties of 1- and 2-(1-hydroperoxy-1-methylethyl)naphthalenes as initiators were studied in the liquid-phase free-radical oxidation of hydrocarbons with oxygen. 2-(1-Hydroperoxy-1-methylethyl)naphthalene was found to initiate the reaction, whereas unexpectedly, 1-(1-hydroperoxy-1-methylethyl)naphthalene was found to inhibit the reaction. The products of decomposition of the studied hydroperoxides were found to exhibit essential differences. Thermal decomposition of 1-(1-hydroperoxy-1-methylethyl)naphthalene was found to yield hydroxyaromatic compounds active as oxidation inhibitors. This fact explains the oft-reported lack of reaction in long-term oxidation of 1-isopropylnaphthalene and its disfavourable effect on the oxidation of 2-isopropylnaphthalene.

Introduction

2-(1-Hydroperoxy-1-methylethyl)naphthalene (HP-2) is an intermediate product forming while 2-naphthol is being synthesized from 2-isopropylnaphthalene (2IPN)[1−6] by a method analogous to that used to make phenol from cumene. This method is environmentally friendly and offers the advantages of consuming less energy and producing acetone as coproduct in comparison to the conventional fusion process.

The 2IPN used in this synthesis as a raw material is contaminated with 1-isopropylnaphthalene (1IPN),[7,8] which is difficult to remove because the two isomers are close-boilers. 1IPN has been found to affect adversely the oxidation of 2IPN. The 1IPN present in the raw material gives rise to a reduced reaction rate, lower yield, and poorer selectivity in the preparation of HP-2.[9,10] The reasons underlying the disadvantageous effect of 1IPN on the oxidation of 2IPN have not been elucidated so far.

The reported data on oxidation of 1IPN are controversial. Some investigators claim that 1IPN fails to undergo oxidation,[10,11] whereas others maintain that it is oxidized but at a lower rate, some 5−10 times lower than that of oxidation of 2IPN.[9,12] When 2IPN contaminated with the 1-isomer was used as a raw material, oxidation was found to yield the product which, in addition to major amounts of HP-2, contained minor amounts of 1-(1-hydroperoxy-1-methylethyl)naphthalene (HP-1).[9]

The course of free-radical chain oxidation of hydrocarbons is well-known to be affected by the resulting hydroperoxides. Thermal decomposition of hydroperoxides into free radicals causes the process to become frequently autocatalytic in nature and induces hydroperoxides to become initiators.

This study is intended to investigate the effect of HP-2 and HP-1 on the free-radical chain oxidation of hydrocarbons. The initiating properties of the two isomers were investigated. The model reaction studied was the free-radical chain oxidation of cumene in which HP-1 and HP-2 were used as initiators.

Results and Discussion

In view of the conflicting data concerning the oxidation of 1IPN, the kinetics of oxidation of this compound was examined. Table 1 lists the rates of oxidation (r_{ox}) of 1IPN and, for purposes of comparison, of 2IPN and cumene, each determined at a well-defined initiator concentration (c_i). The oxidizability ($k_p/k_t^{1/2}$) of the hydrocarbons investigated was evaluated from the well-known kinetic eq 1 describing the rate of free-radical and chain reactions.[13]

$$r_{ox} = r_i^{1/2}\frac{k_p}{k_t^{1/2}}c_{RH} \tag{1}$$

where r_{ox} = the oxidation rate, r_i = the initiation rate, $k_p/k_t^{1/2}$ = the oxidizability of hydrocarbons, and c_{RH} = the concentration of hydrocarbons.

The obtained results reaffirmed the reported data which maintained that 1IPN undergoes a free-radical oxidation except that the reaction rate is much lower (10−12 times) than that of 2IPN.[9,12]

Long-duration (8 h, 110 °C) trials to oxidize 1IPN with oxygen were a complete failure. Despite the large amount of the initiator (ACHN) dosed in several portions, the reaction was promptly inhibited. The product of the reaction was

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Table 1. **Kinetic data on oxidation of 1IPN, 2IPN, and cumene with oxygen**[a]

RH	c_{RH} [mol/dm^3]	temp [°C]	initiator	$c_i \times 10^3$ [mol/dm^3]	$r_i \times 10^7$ [b] [mol/dm^3·s]	$r_{ox} \times 10^5$ [mol/dm^3·s]	$k_p/k_t^{1/2} \times 10^2$ [(dm^3/mol·s)$^{1/2}$]
2IPN	5.457	75	AIBN	3.654	3.16	1.44	0.47
1IPN	5.813	75	AIBN	3.654	3.16	0.13	0.04
cumene	6.770	75	AIBN	3.654	3.16	2.47	0.65
2IPN	5.457	100	ACHN	12.282	13.88	7.13	1.11
1IPN	5.813	100	ACHN	12.282	13.88	0.75	0.11
cumene	6.540	100	ACHN	12.282	13.88	10.48	1.36
2IPN	5.457	110	ACHN	12.282	48.27	16.78	1.40
1IPN	5.813	110	ACHN	12.282	48.27	1.66	0.13
cumene	6.470	110	ACHN	12.282	48.27	24.45	1.72

[a] $p = 760$ mmHg. ACHN = 1,1′-azobis(cyclohexanecarbonitryle). [b] Evaluated as $r_i = 2ek_dc_i$ where: e = initiation effectiveness coefficient, which for AIBN and ACHN is 0.6,[14] k_d = decomposition rate constants, which for AIBN and ACHN are 1.6×10^{15} exp(30 800/RT) and 5.24×10^{16} exp(34 500/RT), respectively,[15,16] c_i = concentration of initiator.

Table 2. **Kinetic data on oxidation of cumene with oxygen in the presence of HP-1 and HP-2**[a]

c_{cumene}	HP-2	HP-2	HP-2	HP-1	HP-1
[mol/dm^3]	c_{HP-2} [mol/dm^3]	$r_{ox} \times 10^5$ [mol/(dm^3·s)]	$r_i \times 10^6$ [b] [mol/(dm^3·s)]	c_{HP-1} [mol/dm^3]	$r_{ox} \times 10^5$ [mol/(dm^3·s)]
6.47	0.00	0.00	–	–	–
6.34	0.10	3.61	0.11	0.10	0.00
6.21	0.20	6.42	0.36	–	–
6.07	0.30	9.00	0.74	0.30	0.00
5.94	0.40	11.21	1.20	–	–
5.81	0.50	13.05	1.70	–	–
5.67	0.60	14.83	2.31	0.60	0.00
5.54	0.70	16.25	2.94	–	–
5.41	0.80	18.00	3.74	–	–

[a] Temp = 110 °C, $p = 760$ mmHg. [b] r_i calculated from eq 1 by taking 1.72×10^{-2} [(dm^3/mol·s)$^{1/2}$] for $k_p/k_t^{1/2}$ in the oxidation of cumene at 110 °C.[17]

found to contain HP-1, but its concentration was too low (0.5%) to enable the compound to be isolated in a pure form. However, HP-1 used for the studies was prepared in another way as described in the Experimental Section.

Table 2 summarizes the results of experimental studies in which the initiating properties of HP-1 and HP-2 were checked in the model free-radical chain oxidation of cumene.

The studies showed HP-2 to be the initiator of the oxidation of cumene. The results of cumene oxidation experiments carried out in the presence of HP-1 were unexpected and surprising. In this case no oxidation of cumene took place, which shows HP-1 not to be an initiator of the reaction.

To establish the effect of HP-1 on the free-radical oxidation of hydrocarbons, the kinetics of oxidation of cumene was studied in the presence of ACHN as an azo-initiatior and in the presence of HP-1. Results are presented in Figure 1. This study showed **HP-1 to act as an inhibitor or an inhibitor precursor** in the free-radical chain oxidation process. Even minor amounts of the compound resulted in inhibition of the process.

These properties of HP-1, clearly nontypical of hydroperoxides, caused us to treat the results obtained with considerable caution. The HP-1 used in the present study was suspected to contain some small, undetectable amounts of 1-naphthol that caused the inhibition. To check for this possibility, comparative oxidation trials were conducted with cumene in the presence of ACHN and 1-naphthol and in the presence of ACHN and HP-1. Results are presented in Figure 2.

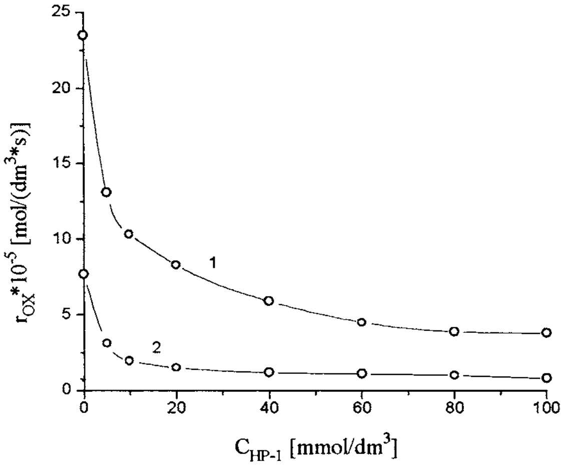


Figure 1. **Influence of the amount of HP-1 on the oxidation rate of cumene (2 cm^3) with oxygen (110 °C, 760 mmHg) in the presence of ACHN (curve 1, 18.44 mmol/dm^3, curve 2, 1.84 mmol/dm^3).**

Curve 1 shows the course of oxidation of cumene in the presence of ACHN. If additionally 1-naphthol is present as inhibitor (curves 2, 3), an induction period is observed to occur, in which the inhibitor becomes deactivated, whereupon the reaction continues to proceed as if no naphthol had been added. In the presence of HP-1 (curves 4, 5) the oxidation of cumene followed an entirely different course. In this case, the oxidation was preceded by no induction period, but it

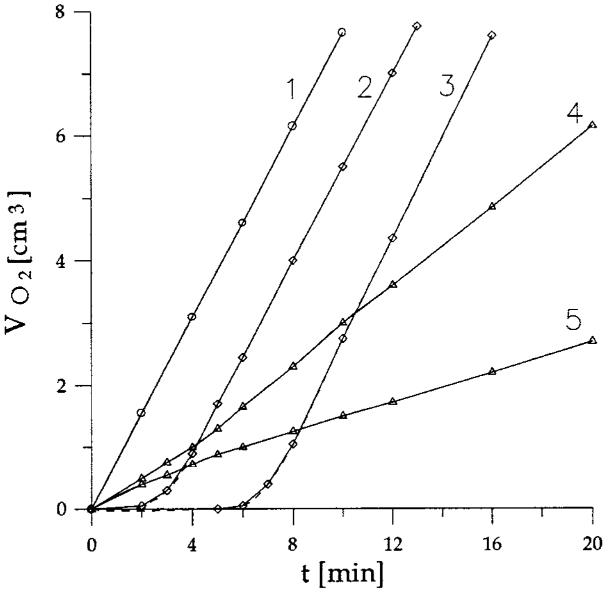


Figure 2. **Oxidation of cumene (2 cm^3) with oxygen in the presence of ACHN (curves 1−5, 18.44 mmol/dm^3) and 1-naphthol (curves 2 and 3, 0.62 and 1.94 mmol/dm^3, respectively) or HP-1 (curves 4 and 5, 10 and 100 mmol/dm^{3,} respectively) (110 °C, 760 mmHg).**

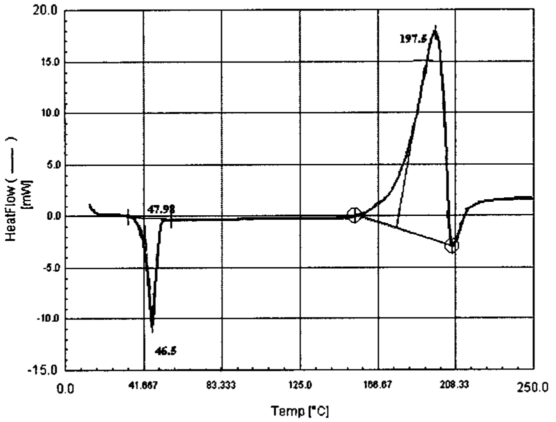


Figure 3. **The DSC thermogram of hydroperoxide HP-1 (heating rate, 10 °C/min).**

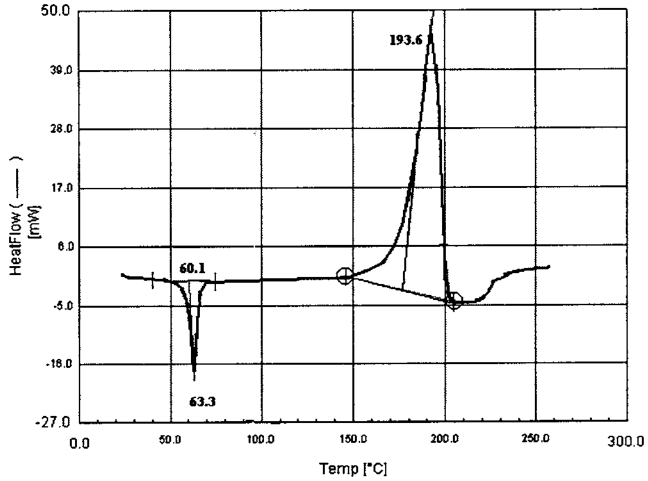


Figure 4. **The DSC thermogram of hydroperoxide HP-2 (heating rate, 10 °C/min).**

Scheme 1. **Typical reactions of 1−methyl-1-naphthylethyloxy radical**

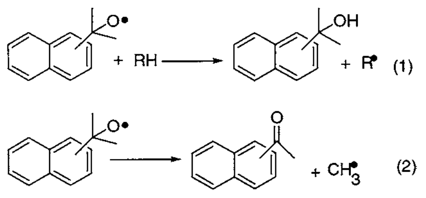


Table 3. **Selectivity of formation of a suitable alcohol and ketone in the thermal decomposition of HP-1 and HP-2 in cumene (0.1 mol/dm^3) at 120 °C**

hydroperoxide	time [h]	conversion of HP [%mol]	selectivity of alcohol [% mol]	selectivity of ketone [% mol]
HP-1	30	38	44	6
HP-2	30	65	78	22

occurred at a slower rate. This fact can speak in favour of a continuous formation of the inhibitor as a result of decomposition of HP-1.

To explain the dissimilar initiating properties of HP-1 and HP-2, a study was made to establish their thermal stabilities and to compare the chemical composition of the products of their thermal decompositions.

Differential scanning calorimetry (DSC) thermograms showed the thermal stabilities to be similar. The temperatures of maximum rates of thermal decomposition ($T_{\max}$) of the HP-1 and HP-2, read from the thermograms (Figures 3 and 4), are close to each other, 197.5 and 193.6 °C, respectively These hydroperoxides are more stable than is cumene hydroperoxide whose $T_{\max}$, determined under identical conditions, is 176 °C.

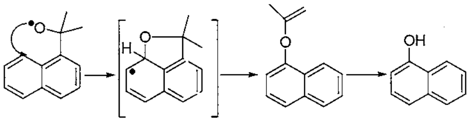
The products forming as a result of thermal decomposition can affect the course of the free-radical oxidation process. Thermal decomposition of hydroperoxides is well-known to yield alkoxy radicals, which are being further transformed to yield stable products, viz., corresponding alcohols and ketones (Scheme 1).

Table 3 gives the quantities of 2-(1-naphthyl)-2-propanol or 2-(2-naphthyl)-2-propanol and 1- or 2-acetylnaphthtalene in the products of thermal decomposition of HP-1 and HP-2.

The products of decomposition of the hydroperoxides examined were found to exhibit essential differences. It is surprising that the reaction of thermal decomposition of HP-1 produced ketone and alcohol with much lower selectivity than did the reaction of HP-2 run under identical conditions. This fact suggests that the 1-methyl-1-(1-naphthyl)ethyloxy radical, formed as a result of thermal decomposition of HP-1, also entered into reactions other than the well-known reactions: β-scission and hydrogen abstraction.

The products of decomposition of HP-1 were dark in colour; they contained some tarry substances. On the other hand, the products of decomposition of HP-2 were colourless. TLC analysis of the products of decomposition of HP-1 revealed the presence of unidentified substances which changed colour in the presence of the developer of hydroxyaromatic compounds. One of these substances is acidic in nature and can be removed from the decomposition products by extraction with aqueous 5% NaOH.

Scheme 2. **Proposed working hypothesis of the mechanism of 1-propenyloxynaphthalene and 1-naphthol formation**



These results together with preliminary IR, ^{1}H NMR spectra, and GC−MS analysis showed that 1-naphthol and 1-propenyloxynaphthalene could be the products of HP-1 thermal decomposition. No such compounds were found to occur in the products of decomposition of HP-2.

Intensive investigations were carried out to solve the mechanism of 1-propenyloxynaphthalene and 1-naphthol formation in the studied process. We believe that the different behavior of the 1-methyl-1-(1-naphthyl)ethyloxy radical is likely to have been essentially caused by the presence of carbon and hydrogen atoms at the *peri* position in relation to the substituent at the 1-position. On the basis of the obtained results we propose the possible working hypothesis presented in Scheme 2, but further evidence for it is necessary.

To elucidate the hypothesis further studies are planned (including theoretical calculations). The results and possible evidence of the proposed mechanism will be presented in the next contribution.

Conclusions

The initiating properties of hydroperoxides HP-1 and HP-2 were studied in a model process of free-radical chain oxidation of cumene with oxygen. The latter hydroperoxide was found to act as an initiator, whereas the former acted as a precursor of the inhibitor of oxidation processes of this type. This fact explains the oft-reported lack of reaction in long-duration oxidation of 1IPN and its disfavorable effect on the oxidation of 2IPN.

Experimental Section

General. The **DSC** analysis was performed at heating rates of 10.0 °C/min by using a Reometric Scientific DSC2-plus apparatus. The **HPLC** analysis was performed by using an Alliance Waters 2690 apparatus (Waters, Millipore, U.S.A.) consisting of a Waters 996 photodiode array detector (cartridge column Nova-Pak Silica 60 Å 4 μm (150 mm × 3.9 mm), with (99:1 v/v) *n*-hexane/2-propanol as mobile phase).[18] The **TLC** analysis of the products of decomposition of HP-1 and HP-2 was carried out by using Merck's aluminium plates coated with silica gel 60 F254 and CCl_4/C_6H_6/$CHCl_3$/MeOH (10/5/5/1.2) as the developing system; hydroxyaromatic compound was developed by using a 4% $FeCl_2$ solution in 0.5 mol/dm^3 HCl (R_f of the unknown substance, alcohols, and ketones were 0.34, 0.46, and 0.60, respectively).

1-Isopropylnaphthalene (**1IPN)** was prepared from 1-bromonaphthalene.[12]

2-Isopropylnaphthalene (**2IPN**) was obtained from a commercial product by crystallization.[7]

Cumene was obtained from a commercial product by refining with concentrated sulphuric acid and distillation from sodium; bp 152−152.5 °C; n_D^{20} 1.4916.

1-(1-Hydroperoxy-1-methylethyl)naphthalenes (**HP-1**) was prepared from 2-(1-naphthalenyl)-2-propanol; mp 42−44 °C.[19]

2-(1-Hydroperoxy-1-methylethyl)naphthalenes (**HP-2**) was isolated from the product of oxidation of 2IPN with sodium salt as an intermediate product[20] and then crystallized from *n*-hexane; mp 61−63 °C.

2-(1-Naphthalenyl)-2-propanol was prepared from 1-bromonaphthalene.[20]

2-(2-Naphthalenyl)-2-propanol was prepared from 2-acetylnaphthalene.[21]

1-Acetylnaphthalene, AIBN, and ACHN were purchased from Aldrich.

Determination of the Oxidizability of 1IPN and 2IPN. The kinetic data on the oxidation of 1IPN, 2IPN, and cumene in the presence of AIBN and ACHN were established by measuring the initial oxidation rates (r_{ox}) in the gasometric apparatus described elsewhere.[22] The r_{ox} data obtained were used to evaluate the oxidizabilities of studied hydrocarbons ($k_p/\sqrt{k_t}$, Table 1). The oxidizability was calculated from eq 1.

Determination of the Initiating Properties of HP-1 and HP-2. The initiating properties of hydroperoxides HP-1 and HP-2 were checked in the model free-radical chain oxidation process of cumene. The measurements of initial rates of cumene oxidation (r_{ox}), in the presence of the studied hydroperoxides (Table 2) and ACHN with HP-1 or 1-naphthol (Figures 1 and 2), were also carried out in the mentioned gasometric apparatus.[22]

Studies on Thermal Decomposition of HP-1 and HP-2. The hydroperoxides were thermally decomposed in closed glass test tubes. Each test tube was filled with about 1 cm^3 of a solution of hydroperoxide in cumene (0.1 mol/dm^3), flushed with oxygen, closed, and immersed in an oil bath at 120 °C. The concentration of the hydroperoxide, alcohol, and ketone in the decomposition product was analyzed by HPLC.[18]

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