

# Reactions of cumyloxy radicals in *n*-heptane at 50°C

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On the basis of the obtained data about decomposition products of cumyl hydroperoxide catalyzed by cobalt(II) cations in *n*-heptane at 50°C, the mechanism of the formation and the decay of cumyloxy radicals in saturated hydrocarbon are discussed and the value of their relative transfer reactivity is derived.

The production of cumyloxy radicals is usually achieved by thermal decomposition of cumyl peroxide. However, the reactions of cumyloxy radicals originating from this source could be quantitatively followed only under limited temperature conditions. Cumyl peroxide is practically utterly stable up to 100°C; therefore the experimental interval is always above this temperature.

It is evident from the works dealing with this problem [1–5] that cumyloxy radical is a very efficient hydrogen acceptor at higher temperatures and therefore also a suitable initiator of hydrocarbon polymer transformations. Since the temperature affects not only the rate but also the nature of the transformation reaction, the possibility of cumyloxy radical generation at lower temperature was examined, namely by decomposition of cumyl hydroperoxide catalyzed by cobalt(II) cations. *n*-Heptane was used as a model of the saturated hydrocarbon chain and the yield and transfer reactivity of cumyloxy radicals as well as the mechanism of their formation in this solvent at 50°C were discussed.

## Experimental

Cumyl hydroperoxide was isolated from a technical product in the form of sodium salt, treated with acetic acid, and the liberated hydroperoxide was distilled off at 65°C/0.2 torr. The product obtained in this way contained 99.1% of pure compound.

The second component of the redox system, cobalt(II) naphthenate, was a commercial product containing 10.9% of cobalt. The used *n*-heptane was of anal. grade.

Cumyl peroxide (Perkadox SB) used for polyethylene crosslinking was purified by twofold recrystallization from supercooled ethanol and the used polymer was a commercial type of the low-density polyethylene Bralen KB 2-11.

When preparing samples, the solutions of cumyl hydroperoxide in *n*-heptane were rinsed with purified nitrogen and their concentrations were determined iodometrically. After cooling the solutions below –50°C, a certain volume of cobalt(II) naphthenate of a known concentration in *n*-heptane, rinsed with nitrogen as well, was added. These solutions containing both components of the redox system of a required concentration ( $5 \times 10^{-3}$  moles of cobalt(II) naphthenate per 1 mole of cumyl hydroperoxide) were sealed in glass test tubes in nitrogen atmosphere and heated in a thermostat at 50°C for 4 hours.

The content of the remaining cumyl hydroperoxide and of the decomposition products (dialkyl peroxides, cumyl alcohol, and acetophenone) were determined after the decomposition was complete.

Cumyl hydroperoxide was determined iodometrically (0.01 N sodium thiosulfate) in glacial acetic acid in the presence of potassium iodide at laboratory temperature. This method enabled the quantitative analysis of hydroperoxide in the presence of dialkyl peroxides. The loss of cumyl hydroperoxide was in each case more than 96% at the end of the decomposition reaction.

The formed dialkyl peroxides were determined similarly as cumyl hydroperoxide but quantitative reaction was achieved in acetic acid and water in the presence of sodium iodide at boiling [6]. The determined amounts of dialkyl peroxides in dependence on the initial cumyl hydroperoxide concentrations are given in Table 1.

Table 1

The content of active oxygen [O—O] in the formed dialkyl peroxides after decomposition of cumyl hydroperoxide

[CHP] mol l <sup>-1</sup>	[O—O]	
	mol l <sup>-1</sup>	mol (mol CHP) <sup>-1</sup>
0.047	0.00230	0.049
0.063	0.00290	0.046
0.092	0.00377	0.041
0.109	0.00523	0.048
0.125	0.00612	0.049

Table 2

Cumyl alcohol (CA) and acetophenone (APh) formed on decomposition of cumyl hydroperoxide (CHP)

[CHP] mol l <sup>-1</sup>	[CA] mol l <sup>-1</sup>	[Aph] mol l <sup>-1</sup>
0.0277	0.0267	0.0018
0.0416	0.0390	0.0027
0.0555	0.0528	0.0037
0.0694	0.0630	0.0045
0.0804	0.0718	0.0050
0.0833	0.0750	0.0052
0.0971	0.0853	0.0062
0.1072	0.0940	0.0070
0.1110	0.1066	0.0072
0.1249	0.1162	0.0087

Cumyl alcohol and acetophenone formed during cumyl hydroperoxide decomposition were determined in separate samples by gas—liquid chromatography as described earlier [4]. Considering that these compounds were determined at higher temperatures

(150–200°C), the samples were heated before analysis at 155°C for 5 hours to attain quantitative decomposition of the formed dialkyl peroxides. The obtained results are summarized in Table 2.

Table 3

The gel content (g) of polyethylene cross-linked with 2 weight % of cumyl peroxide (8 hours at 145°C) in the presence of cobalt(II) naphthenate (Cat)

Cat [wt %]	g [wt %]
0.00	88.3
0.02	88.5
0.04	89.4
0.08	88.7
0.15	89.6
0.30	89.9
0.50	88.4
0.75	89.2
1.00	88.7

The effect of cobalt(II) naphthenate on the crosslinking of polyethylene initiated by cumyloxy radicals (generated by thermal decomposition of cumyl peroxide) was studied with samples prepared and heated according to [5]. The degree of polyethylene crosslinking was determined from the gel content estimated after 20 hours extraction in boiling benzene in the presence of an antioxidant (2,6-di-*tert*-butyl-4-cresol). The results are presented in Table 3.

### Discussion

As evident from Table 2, cumyl alcohol and acetophenone represented the main part of the decomposition products of cumyl hydroperoxide when the reaction was catalyzed by cobalt(II) cations. Moreover, the sum of their molar content (Fig. 1) gave the mean

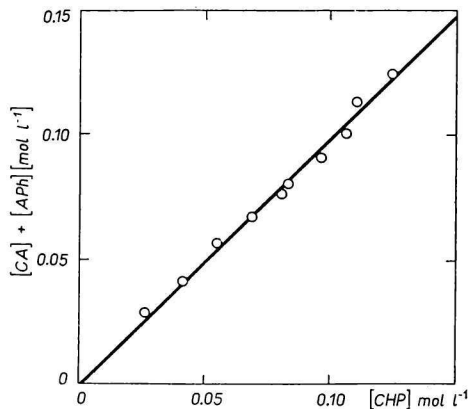
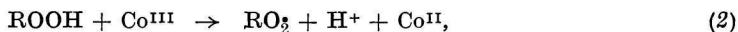


Fig. 1. The sum of cumyl alcohol and acetophenone moles (according to Table 2) vs. cumyl hydroperoxide concentration.

value of the hydroperoxide conversion to these products which was equal to the degree of hydroperoxide decomposition. However, this accordance does not mean that both compounds were primary decomposition products of cumyl hydroperoxide only, because beside them, dialkyl peroxides of not exactly identified structures were found among the decomposition products. They could be formed by mutual reaction of two peroxy radicals (formation of cumyl peroxide) as well as by recombination of peroxy radicals with the radicals of the medium (formation of cumyl heptyl peroxide) [7]. However, supposing that exclusively cumyl peroxide represents these dialkyl peroxides, maximum 5 mole % of cumyl alcohol (see Table 1) would be formed additionally under the decomposition conditions (one mole of this peroxide produces approximately one mole of cumyl alcohol [5]). Thus the content of cumyl alcohol primarily originating from cumyl hydroperoxide would be still at least 90 mole %.

Since the initiation process of such a redox decomposition of cumyl hydroperoxide (ROOH) is represented by simultaneous reactions [8]

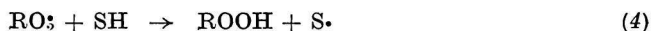


where cumyloxy ( $\text{RO}\cdot$ ) and cumylperoxy ( $\text{RO}_2\cdot$ ) radicals are formed in equimolar ratio, the found amount of cumyl alcohol (exceeding 50% molar content of the starting peroxide) points to the fact that its source was not only the transfer reaction of  $\text{RO}\cdot$  with *n*-heptane (SH)



but also the simultaneously formed  $\text{RO}_2\cdot$ .

The cumyl alcohol (ROH) production from cumylperoxy radical could then proceed by an analogical transfer with the medium [9]



which, regenerating the original hydroperoxide makes possible the subsequent reactions (1) and (3). Cumyl alcohol could arise from cumylperoxy radicals also in the case of their limited dehydrogenation capacity as a result of their mutual interaction [10]



where primarily cumyloxy radicals are formed.

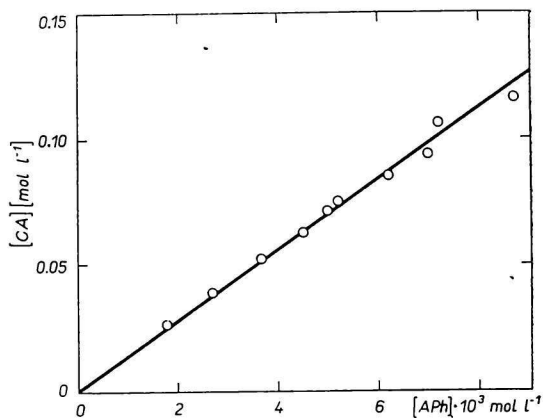
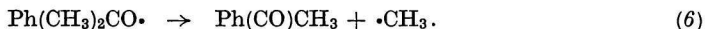


Fig. 2. The relation between the formed cumyl alcohol and acetophenone according to Table 2.

The minimal efficiency of cumyloxy radical production in the course of the discussed cumyl hydroperoxide decomposition was 90% and the simultaneously formed acetophenone was a product of cumyloxy radical fragmentation according to the known facts [1]



Moreover, it is interesting that the ratio of cumyl alcohol and acetophenone was in the overall concentration range of hydroperoxide constant (Fig. 2), similarly as in the case of thermal decomposition of cumyl peroxide [4]. Since this ratio remains over entire range of the followed peroxide concentration practically constant, no quantitative conclusions can be made on the occurrence of the substitution reaction of cumyloxy radical with the hydrogen atom of the hydroperoxide group and therefore this process will not be considered any more.

The effect of cobalt(II) naphthenate on the crosslinking of polyethylene initiated by cumyloxy radicals was examined with the purpose to judge the eventual redox reaction of cumyloxy radicals with cobalt(II) cation. The course of polyethylene crosslinking (Table 3), where the effect of cobalt(II) naphthenate practically did not occur, proved that in this process the formed cumyloxy radicals were not deactivated even by the eventual reaction



resulting in cumyloxy anions which could also form cumyl alcohol with the present protons. Thus the components present in the redox system (cumyl hydroperoxide and  $\text{Co}^{\text{II}}$ ) did not affect the deactivation processes of cumyloxy radicals so that these decayed mainly by transfer reaction with the medium and simultaneous fragmentation.

The derived conclusions are proved also by the value of cumyl alcohol and acetophenone ratio ( $14.2 \pm 0.5$ ) resulting from the line slope in Fig. 2. This ratio falls fairly well into

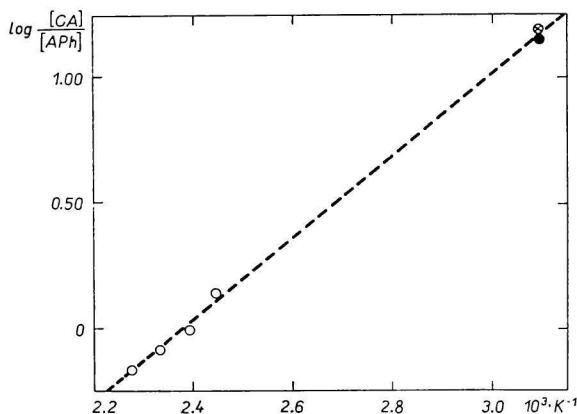


Fig. 3. Logarithm of cumyl alcohol and acetophenone ratio vs. reciprocal absolute temperature including the experimental value from this work (●), its correlated expression (⊙), as well as the appropriate data from the literature [5] (○).

the extrapolated line obtained from the Arrhenius dependence of similar experimental values (Fig. 3) determined during thermal decomposition of cumyl peroxide in *n*-heptane in the range of higher temperatures [5]. The eventual increase of this ratio owing to the above-discussed effect of dialkyl peroxides (to 15.5 maximum) is insignificant in this

respect and does not affect the total tendency of the illustrated dependence. The ratio of cumyl alcohol and acetophenone gives at the same time also the numerical value of the relative reactivity of cumyloxy radical towards *n*-heptane at 50°C.

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