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Abstract

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RADICALS–PRODUCTS OF THE THERMAL DECOMPOSITION OF A SUBSTITUTED CYCLOHEXADIENONE PEROXIDE

At present, the homolytic mechanism of decomposition of organic peroxides of the type ROOR (1) is generally accepted; it is confirmed by the initiation of autoxidation and polymerization in the presence of decomposing peroxide, by the slowing of the peroxide decomposition rate in the presence of inhibitors of free-radical reactions, etc. However, direct observation of free radicals during the thermal decomposition of organic peroxides has hitherto not been possible, since these radicals are insufficiently stable for their registration by e.p.r. spectra and other methods. It could be expected that ROOR molecules, upon rupture of the peroxide bond O–O, would give more stable radicals if R represents shielded phenoxyls with bulky substituents containing a tertiary carbon in the ortho positions, since it is known that oxidation of the corresponding phenols gives fairly stable radicals.

We synthesized bis-(1,3,5-tri-tert-butyl-cyclohexadien-(2,5)-one-(4))-peroxide (I), as described in (2). On oxidation of a solution of 2,4,6-tri-tert-butylphenol in benzene by means of PbO_2 or $K_3Fe(CN)_6$, a blue phenoxyl radical is formed. On passing oxygen through, the color changes to yellow. After removal of part of the solvent, a yellow crystalline precipitate separates, with m.p. 149°.

In the infrared spectrum of a solution of (I) in CCl_4, the 3650 cm^{-1} band of the hydroxyl group of shielded phenols is absent, and there is a doublet band at 1650, 1667 cm^{-1} of a carbonyl group conjugated with a system of double bonds, which indicates the quinonoid character of the isolated peroxide. On treatment of a solution of (I) with hydroiodic acid, rapid liberation of iodine is observed. These facts confirm structure (I).

(I)

When heated to 200°, peroxide (I) melted and bubbles of gas were evolved from the melt. A sample of the decomposed peroxide, placed in the resonator of an RE-1301 instrument, gave an intense signal consisting of three components with

Fig. 1. EPR spectra of radicals: a —from thermal decomposition of peroxide (I); b —from decomposition of peroxide (I) in the presence of ionol

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an intensity ratio of 1 : 2 : 1 and a splitting between the lines of 1.3 oersted (Fig. 1a).

Analyzing the products of decomposition of (I), Cook (2) and Müller (3) found that they consist mainly of 2,6-di-tert-butyl-4-tert-butyloxyphenol (V), 2,6-di-tert-butylbenzoquinone (III), and isobutylene (VI). To explain the formation of these products, Müller assumed that decomposition of peroxide (I) proceeds by an ionic mechanism, involving transfer of the tert-butyl residue of one part of the peroxide to the oxygen of the second half of the dimeric molecule. The data obtained by us indicate that decomposition

this peroxide proceeds by a homolytic mechanism, with the formation of a stable radical.

The decomposition mechanism of (I) may be represented as follows. First, homolytic cleavage of the relatively weak O—O bond occurs. The radical (II) formed in this process then disproportionates, with transfer of one tert-Bu group to the peroxide oxygen, giving substituted benzoquinone (III) and the phenoxyl radical (IV). The latter, abstracting hydrogen from a second tert-Bu radical, gives phenol (V) and isobutylene (VI), which were found in the decomposition products.

Fig. 1. EPR spectra of radicals: **a** —from thermal decomposition of peroxide (I); **b** —from decomposition of peroxide (I) in the presence of ionol.

$$\begin{aligned}\text{(II)} &\longrightarrow \text{(III)} + \text{(IV)} + \text{tert-Bu}\cdot \\ &\longrightarrow \text{(III)} + \text{(V)} + \mathrm{H_2C{=}C(CH_3)_2}\ \text{(VI)}\end{aligned}$$

$$\text{tert-Bu} = -\mathrm{C(CH_3)_3}$$

The EPR spectrum in Fig. 1a corresponds to radical (IV), with triplet splitting on two equivalent meta hydrogens of the nucleus. The splitting constant, 1.3 oersted, is close to that obtained (4) for (IV) formed upon oxidation of the corresponding phenol. In the infrared spectrum of the decomposed peroxide, in contrast to the spectrum of the initial compound (I), a band appears at 3650 $\mathrm{cm^{-1}}$, which confirms the presence of molecules of the hindered phenol in the decomposition products.

The radical (IV) formed during the decomposition of (I) is capable of radicalizing substances that give stable radicals:

$$\mathrm{RO}^{\cdot} + \mathrm{R'OH} \rightarrow \mathrm{ROH} + \mathrm{R'O}^{\cdot};$$

for example, 2,6-di-tert-butyl-4-methylphenol (ionol). A 1 : 1 mixture of the latter with peroxide (I), when heated to 200°, gave in the melt a complex spectrum consisting of 15 components (Fig. 1b). At its center are three lines in the ratio 1 : 2 : 1 ($a = 1.3$ oersted), whose intensity exceeds the remaining components of the signal by a factor of 10. They coincide with the spectrum in Fig. 1a and belong to radical (IV). The remaining 12 lines are grouped into a quadruplet of triplets ($a_{\text{quadrupl.}} = 12$ oersted, $a_{\text{tripl.}} = 1.7$ oersted). The intensity ratio of the lines in the quadruplet is 1 : 3 : 3 : 1, and in the triplet 1 : 2 : 1. This spectrum of 12 lines corresponds exactly to the spectrum of the phenoxyl radical of oxidized ionol ([5,6]).

The large difference observed in Fig. 1b in the intensities of the spectra of the two radicals indicates that only a smaller fraction of the radicals (IV) formed during the decomposition of (I) reacts with ionol. This may be caused by the considerable viscosity of the melt, which hinders diffusion of the radicals.

In the spectrum in Fig. 1b, the simultaneous presence of radicals of the oxidizing agent and of the oxidation product is of interest. The simultaneous fixation of these radicals confirms the radical nature of the interaction of peroxides with hindered phenols.

The EPR spectrum presented in Fig. 1b does not change over many hours. This is consistent with the previously observed fact that further transformations of the primary phenoxyl radical cease because of the addition to it of residues of the decomposed peroxide.

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