## RADICAL PRODUCTS OF THE THERMAL DECOMPOSITION OF IONOL HYDROPEROXIDE

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It has been shown that the thermal decomposition of 4-hydroperoxy-4-methyl-2, 6-ditert-butylcyclohexadien-2, 5-one is accompanied by the rupture of the C—O bond in the COOH group, with the formation of 2, 6-ditert-butyl-4-methylphenoxyl radicals. On the basis of the electronic paramagnetic resonance spectra, it has been found that transfer of hydrogen occurs from the diphenylamine molecule and those of sterically hindered phenols to the radicals of 2, 6-ditert-butyl-4-methylphenoxyl radicals formed by the decomposition of the hydroperoxide.

The autooxidation of 2, 4, 6-trialkyl-substituted phenols by molecular oxygen leads to the formation of the corresponding hydroperoxides [1, 2]. Thus, when oxygen was passed through an alkaline solution of 2, 6-ditert-butyl-4methylphenol (ionol) (I), 4-hydroperoxy-4-methyl-2, 6-ditert-butylcyclohexadien-2, 5-one (II) was obtained in good yield [1, 2]. On decomposition of (II) in alkaline solution in an inert atmosphere, the principal product obtained was the original substance (I) [2], together with 4-oxy-4-methyl-2, 6-ditert-butylcyclohexadien-2, 5-one (III) [3]:



The mechanism of the conversion (II) into (I) and into (III) has not previously been considered.

In the present work we have investigated the thermal decomposition of (II) at the melting point.

The hydroperoxide (II) was obtained by the autooxidation of (I) in a solution of alkali in 90% ethyl alcohol at 40°C.



Fig. 1. EPR spectrum of radicals formed on decomposition of the hydroperoxide(II). Elementary analysis of the product formed gave, %: C 71.85; H 9.64. Calculated for  $C_{15}H_{24}O_3$  (II), %: C 71.43; H 9.52. Reaction with potassium iodide in acetic acid confirmed the presence of the peroxide group in (II). The infrared spectrum was also investigated using an 0.05 M solution of (II) in carbon tetrachloride; the following characteristic bands were observed: 1658-1676 cm<sup>-1</sup>, a doublet of the valence vibrations of the C=O group in 2, 5-cyclodienones [4, 5]; 3550 cm<sup>-1</sup>, the vibration band of the OH group in the hydroperoxide group OOH [6]; 2870, 2965 cm<sup>-1</sup>, the bands for the vibrations of the methyl group; 880 cm<sup>-1</sup>, the bands for the valence vibrations of the peroxide bond in the group GOOH [7]. In the infrared spectrum of (II) the band at 3650 cm<sup>-1</sup> corresponding to the non-associated hydroxyl group is absent, though it is present in the original compound (I) which indicates that complete conversion of (I) into (II) has occurred.

The thermal decomposition of molten (II) was carried out directly in the resonator of the EPR spectrometer with high-frequency

modulations. Heating of the samples was carried out by passing heated air through the resonator, the temperature of the air being maintained by means of an electronic thermoregulator.

Melting of (II) was observed at 113°C, and this was accompanied by the production of an EPR signal with wellresolved hyperfine structure (Fig. 2, without the central triplet). It consists of a quadruplet (1:3:3:1,  $a_1 = 11$  G) of triplets (1:2:1,  $a_2 = 1.7$  G). After a few minutes heating, a new triplet of structure (1:2:1,  $a_2 = 1.7$  G) was formed in the center of the EPR signal (see Fig. 1). The intensity of the new triplet signal increased rapidly with time, with



Fig. 2. Change in the concentration of primary radicals (I) and secondary radicals (II) with time.

simultaneous reduction in the intensity of the component of the initial quadruplet of triplets. The change in intensity of the initial and secondary EPR signals with time is shown in Fig. 2.

We have also investigated the infrared spectrum of the products of decomposition of (II). Unlike the spectrum of the initial hydroperoxide, the bands at 3550 and 880 cm<sup>-1</sup> corresponding to the hydroperoxide group are absent, while a band at 3650 cm<sup>-1</sup> appears, corresponding to the valence vibrations of unbonded hydroxyl, which is characteristic of sterically hindered phenols.

From the results obtained, it is possible to arrive at the following mechanism for the thermal decomposition of (II). Having regard to the general assumption that the thermal decomposition of hydroperoxides takes place according to the scheme  $ROOH \rightarrow RO \cdot + \cdot OH$  given in [8], the first stage of the decomposition of (II) would be represented in the following way:



The subsequent disproportionation of the radical (IV) should lead to the formation of the phenoxyl radical (V), in a way similar to that observed earlier [4]:



But the EPR signals observed by us, which develop during the fusion of (II) cannot be attributed either to the radical (IV), or to the radical (V), formed according to schemes (1) and (2).

The parameters of the EPR spectrum shown in Fig. 1 (number of lines, ratio of intensities and hyperfine interaction constants), correspond completely to 2, 6-ditert-butyl-4-methylphenoxyl radical (VI) [9].

In the case of radical (IV), however, the hyperfine interaction constants should be different from those of radical (VI), because of the inclusion in the conjugated system of one further oxygen atom. This phenomenon has been observed earlier [10].

The EPR spectrum (see Fig. 1) cannot be explained by the presence in the melt of radical (V), for which the EPR spectrum have been obtained [11, 12] and found to consist of 9 components with constants  $a_{\text{Hpara}} = 1.6 \text{ G}$ ;  $a_{\text{Hmeta}} = 1 \text{ G}$ .

Starting from these data, we may probably assume that the first product of the decomposition of the hydroperoxide (II) is the phenoxyl radical (VI), formed through the removal of the hydroperoxy radical from (II):



A similar unusual route for the thermal decomposition of organic peroxide compounds without rupture of the O-O bond has been observed earlier in an investigation of the mechanism of the decomposition of peroxides based on steri-



Fig. 3. EPR spectrum of the diphenylazote radical.

cally hindered phenols. Thus, it has been shown that, on heating 4-tert-butylperoxy-4-methyl-2, 6-ditert-butylcyclohexadian-2, 5-one, the C—O group of the C—O—-C—tBu bond is the one which undergoes disruption [13].

In a similar way, the thermal decomposition of bis-(1-phenyl-3, 5-ditert-butyl-2, 5-cyclohexadien-4-one)-peroxide (VII) also occurs through the homolytic rupture of the C—O bond, and leads to the formation of 2, 6-ditert-butyl-4-phenylphenoxyl radicals [14].

The appearance of a new triplet signal in the center of the quadruplet signal (see Fig. 1) may be explained by the isomerization of the phenoxyl radical (VI) into the oxybenzyl radical. This isomerization, with the transfer of hydrogen from the para-methyl group to the oxygen of the phenoxyl radical has earlier been shown by ourselves using isotopic labelling with deuterium [9]. The appearance of new radicals leading to the formation of the end products of the reaction finds expression in the EPR spectrum (see Fig. 1). The radicals formed during the thermal decomposition of organic perox-

ides are excellent initiators for polymerization processes [8]. We have shown earlier [15] that the thermal decomposition of bis-(1, 3, 5-tritert-butyl-2, 5-cyclohexadien-4-one)-peroxide is accompanied by the disruption of the peroxide bond, O-O and gives radicals which initiate the polymerization of methyl methacrylate. In contrast to this, the decomposition of the hydroperoxide (II) does not cause the polymerization of methyl methacrylate or vinyl acetate. This fact is in agreement with the observation in [14] that the products of the decomposition of the peroxide (VII) do not initiate the polymerization of acrylonitrile, since in this case also the disruption occurs without the rupture of the peroxide bond.

From what has been said, it can be seen that peroxide compounds formed from sterically hindered phenols may be decomposed thermally in two ways: either with the rupture of the peroxide bond or of the C—O bond in the group C-O-O-R.

In our previous work [9] it was shown that phenoxyl radicals formed during the decomposition of dimeric peroxides of substituted cyclodienone are able to split off hydrogen from the molecule of sterically hindered phenols according to the scheme

$$RO \cdot + R'OH \rightarrow ROH + R'O \cdot$$

In establishing that the thermal decomposition of (II) leads to the formation of the phenoxyl radical (VI), we have investigated the ability of this radical to split off a hydrogen atom from the N—H and O—H bonds of amines and phenols. We added a concentrated solution of diphenylamine (DPA) in xylene to a specimen of the substance (II) undergoing decomposition. After some minutes, the EPR spectrum of the mixture so prepared (Fig. 3) shows the production of a signal of triplet structure (1:1:1,  $a_4 = 10$  G), corresponding to the diphenylazote radical formed by reaction (4).



This EPR signal may possibly correspond to the location of signals corresponding to the radicals  $Ph_2N$  · and  $Ph_2NO$  ·, since the radical  $Ph_2NO$  · may be formed by the oxidation of the diphenylazote radical, which is formed first.

As an indication whether the phenoxyl radicals remove hydrogen from the DPA molecules, we added concentrated DPA solution to the decomposing (II) at the moment when the maximum concentration of (VI) radicals would be attained. A rapid reduction in the concentration of the phenoxyl radical (VI) was then observed, and signals corresponding to the radical (VIII) were observed in the EPR spectrum.

The phenoxyl radical (VI) is able to remove a hydrogen atom also from the hydroxyl group of the sterically hindered phenols. We have investigated this reaction using phenols of the structure



where R = H (IX), and Ph (X). The reaction was carried out under the same conditions as described above for DPA. In the presence of phenol (IX) the EPR spectrum obtained consisted of a triplet (1: 2: 1,  $a_5 = 9.8$  G) of triplets (1: 2: 1,  $a_6 =$ = 1.7 G). This spectrum belongs to the phenoxyl radical formed after the removal of hydrogen from the hydroxyl group of (IX), and corresponds to the interaction of an unpaired electron with two hydrogen atoms of the bridge methylene group, and weaker interaction with two hydrogen atoms in the metaposition of one of the rings. When the thermal decomposition of (II) is carried out in the presence of phenol (X), the EPR signal obtained corresponds to the phenoxyl radical of the oxidized form of (X). It consists of a doublet (1: 1,  $a_7 = 9$  G) of triplets (1: 2: 1,  $a_8 = 1.7$  G). This spectrum is due to the interaction of an unpaired electron with a hydrogen atom of the bridge group, and two hydrogen atoms in the meta-position of one of the rings. These facts indicate that the reaction which occurs is:



## REFERENCES

1. H. R. Gersmann and A. F. Bickel, J. Chem. Soc., 2711, 1959.

2. H. R. Gersmann and A. F. Bickel, J. Chem. Soc., 2359, 1962.

3. I. I. Conradi and G. A. Mc Laren, J. Am. Chem. Soc., 82, 4745, 1960.

4. V. D. Pokhodenko, L. N. Ganyuk, and A. I. Brodskii, DAN SSSR, 149, 321, 1963.

5. G. D. Cook, D. A. Kuhn, and P. Fianu, J. Am. Chem. Soc., 78, 2002, 1956.

6. A. V. Karyakin, Dissertation, MGU, Moscow 1958; M. A. Kovner, A. V. Karyakin, and A. P. Efimov, Opt. i spektr., 8, 128, 1960.

7. A. V. Karyakin, V. A. Nikitin, and K. I. Ivanov, ZhFKh, 27, 1856, 1953.

8. A. V. Tobolsky and R. B. Mesrobian, Organic Peroxydes, N. J., 1954.

9. A. I. Brodskii, V. D. Pokhodenko, and L. N. Ganyuk, Rozniki Chemii, 38, 105, 1964.

10. A. L. Buchachenko, Stable Radicals [in Russian], Izd-vo AN SSSR, p. 89, 1963.

11. K. Scheffler, Z. Analyt, Chem., 181, 456, 1961.

12. E. Müller, K. Ley, W. Scheffler, and K. Mayer, Chem Ber., 91, 2682, 1958.

13. J. M. Turner, J. Phys. Chem. 65, 2114, 1961.

14. E. R. Altwicker, C. D. Cook, and N. D. Gilmor, Tetr. Lettr., 721, 1963.

15. V. D. Pokhodenko, Dissertation, Kiev, 1953.

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