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Abstract

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REARRANGEMENT OF THE FREE RADICAL OF OXIDIZED IONOL

Oxidation of sterically hindered phenols with bulky substituents in the ortho and para positions gives long-lived radicals, which are especially stable if the substituents do not contain α-hydrogen (^{1}). These radicals then give, depending on the reaction conditions and the nature of the substituents, a variety of secondary products. Such reactions have in recent years been the subject of a number of investigations. In particular, the oxidation of 2,6-di-tert-butyl-4-methylphenol (ionol), used as an inhibitor of oxidation of polymeric materials, has been studied in detail.

As the primary product of ionol oxidation, a phenoxyl radical (I), formed by abstraction of hydrogen from the hydroxyl (^{2}), or a benzyl radical (II), formed by abstraction of methyl hydrogen (^{4,5,7}), has been proposed:

$$[\ \text{phenoxyl radical structures}\ ] \rightleftarrows [\ \text{phenoxyl radical structures}\ ] \longrightarrow \ \text{benzyl radical structure} \qquad (R = C($$

(I) (II)

The benzyl radical readily explains the formation of dimers (III) and (IV):

dimer structure stilbenequinone structure

(III) (IV)

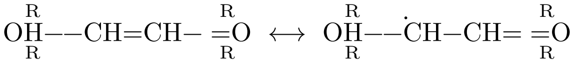
which were isolated (^{1,3,4,11}), but the phenoxyl radical was identified from infrared spectra (^{1,2,11,13}), EPR spectra, and addition reactions.

To reconcile these data, Cook (1) proposed that the primary phenoxyl radical (I) rearranges into the benzyl radical (II), which then dimerizes to 4,4-dioxydibenzyl (III) and is oxidized to stilbenequinone (IV). However, such a rearrangement had not been experimentally confirmed, and the question of the nature of the primary radical had not been finally clarified. For experimental confirmation of this rearrangement and further study of the mechanism of ionol oxidation, we used isotopic labeling with deuterium and separation of the products by paper chromatography, previously applied for this purpose by A. L. Buchachenko and M. B. Neiman (8). Infrared spectra were studied in CCl_4 solutions on a Zeiss UR-10 spectrometer. EPR spectra were observed on an RE-1301 instrument.

A solution of ionol in benzene was oxidized in air by means of PbO_2 at room temperature, after which it was filtered and chromatographed on paper with elution by 96% alcohol. As in (8), two spots were obtained—the upper yellow one (A) and the lower orange one (B). Before oxidation, ionol had in its spectrum a number of bands: an intense band at 3647 cm^{-1}, characteristic of phenolic hydroxyl free from hydrogen bonds (9); a band at 1565 cm^{-1}, also present in other phenoxyl radicals (13); a band at 2870 cm^{-1} of the CH_3 group; bands at 2962, 2915, 1160, 867, 835 cm^{-1} of 2,4,6-trisubstituted phenols; bands at 1434, 1395, 1364, 1235 cm^{-1} of tert-butyl, etc. (Fig. 1b). The solution of the yellow spot (A) had the same spectrum, but a new doublet appeared in it at 1655, 1642 cm^{-1} (Fig. 1a), characteristic of the $C = O$ bond in 2-

5-cyclodienones (2,11,13). The dry yellow spot and its solutions in benzene, toluene, CCl$_4$, or CS$_2$ gave no EPR signal.

A solution of the orange spot (B) gave a spectrum coinciding with the spectrum of unoxidized ionol and of the yellow spot (A), except for the following differences. The carbonyl doublet of yellow (A) disappeared completely and a new narrow intense band appeared at 1610 cm^{-1} (Fig. 1b), characteristic of a conjugated C $=$ C bond. Its identification is not entirely unambiguous. Some authors (15) assign it to a carbonyl bond strongly weakened by conjugation, and similarly explain the band near 1570 cm^{-1} (1). However, in various phenoxyl radicals the latter is observed as a doublet 1590/1573 (strong); 1507/1509 (medium) (1,13). In the spectrum of spot (B) we found no signs of the second component of this doublet, while the first is also present in unoxidized ionol. With the exception of these cases, in none of the numerous carbonyl compounds studied, and in particular quinones—diphenyl derivatives, was a valence frequency for C $=$ O observed below 1634 cm^{-1} (10). The dry orange spot (B) gave an intense EPR signal in the form of a 1:1 doublet with a splitting of 14.5 oersted between components, without hyperfine splitting, similar to that observed in (8). On wetting the spot or dissolving it in the solvents listed above, the signal disappeared. The spectral data and the doublet splitting of the EPR spectrum are consistent with the structure of a dimeric radical



$$\mathrm{O}\overset{R}{\underset{R}{\mathrm{H}}}\!-\!-\mathrm{CH{=}CH}-\overset{R}{\underset{R}{=}}\mathrm{O} \longleftrightarrow \mathrm{O}\overset{R}{\underset{R}{\mathrm{H}}}\!-\!-\dot{\mathrm{C}}\mathrm{H{-}CH}=\overset{R}{\underset{R}{=}}\mathrm{O} \qquad (V)$$

The doublet corresponds to splitting of the free-electron level on the meta-hydrogen*.

Earlier, in the EPR spectrum of an oxidized solution at strong dilution (^{14}) and on prolonged standing (^{6}), a doublet was also observed, but with components split into quintets, which can be attributed to additional coupling of the unpaired electron with the neighboring four hydrogens in the meta position and in the CH groups.

On standing, oxidized ionol gives an orange precipitate with the same infrared spectrum and doublet in the EPR spectrum (Fig. 2) as in the orange spot, but with a splitting of 16.4 oersted. The EPR signal did not change on further standing for 2 months in air. On cooling to the temperature of liquid air, both the precipitate and spot (B) give the same increase in splitting to 19.2 oersted.

To determine the nature of the primary radical and to confirm its rearrangement, the experiments described were repeated with ionol in which the hydroxyl hydrogen had been replaced by deuterium by repeated exchange with a mixture of alcohol and 99.8% D_2O. After exchange, the spectrum of unoxidized ionol had a characteristic OD band at 2692 cm^{-1}, close to the OH frequency of light ionol reduced by a factor of $\sqrt{2}$. Otherwise the spectrum did not differ from the latter (Fig. 1c). In the solution of the orange spot, after elution with dry ether, this frequency disappeared and an intense band of the OH group appeared at 3647 cm^{-1}. Since these operations were carried out in solvents containing no mobile protons, replacement of the OD group by OH during oxidation and dimerization can be explained only by rearrangement (I) → (II), in which D is first split off from the hydroxyl with formation of a phenoxyl radical, which then is converted into a benzyl radical with transfer of a hydrogen atom from methyl to oxygen. Dimerization of (II) gives (III), and upon further oxidation —the radical (V) and the final quinone (IV).

Bennett (^{7}) found that, on standing of a solution of oxidized ionol, the kinetics of disappearance of the EPR signal follows first order with respect to concentration of phenol. This makes it possible to assume that the rate of the overall oxidation reaction is controlled by the rearrangement stage, proceeding intramolecularly, and not by transfer of hydrogen from the methyl group of one radical to the oxygen of another.

Fig. 1. Infrared spectra in CCl_4 solutions in the region 1500-1700 cm^{-1}: *a* —yellow spot (A) of oxidized ionol; *b* —orange spot (B) of oxidized ionol; *c* —unoxidized ionol, 0.1 mol/liter.

* In (^{8}) the radical doublet in the dry orange spot was attributed to radical (VI) with hindered rotation of the CH_2 group.

Under mild oxidation of ionol by means of HgO in benzene, we observed the same changes in the EPR spectrum as those described by Beconsall (^{6}). At first a symmetrical quadruplet appears, with triplet splitting of its components, similar to that observed earlier (^{7}, ^{8}). Then a new triplet appears in the center, the intensity of which increases with a simultaneous decrease in the intensity of the initial quadruplet. Subsequently the triplet is transformed into a doublet with components split into quintets and, finally, into a broad doublet without hyperfine structure. We found the same transformations in 2,6-di-(1,1′-dimethylpropyl)-4-methylphenol. More detailed data on this phenol, which has not been studied previously, will be presented in a subsequent communication.

Fig. 2. EPR spectrum of the precipitate isolated from a solution of oxidized ionol.

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Note: Figure translations are in progress. See original paper for figures.