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Chemistry

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Abstract

Full Text

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APPLICATION OF E.P.R. TO THE STUDY OF THE OXIDATION OF AMINO-ALKYLPHENOLS BY BENZOYL PEROXIDE

(Presented by Academician B. A. Arbuzov, June 22, 1963)

One of the authors has shown the effectiveness of ortho-amino-para-alkylphenols when used as antioxidant additives in various kinds of fuels (1). The proposed mechanism of stabilization by inhibitors of this type is radical in character. It seemed to us of considerable interest to investigate the process of formation of free radicals during the oxidation of *o*-amino-*n*-alkylphenols, using the method of electron paramagnetic resonance (E.P.R.).

[Fig. 1. E.P.R. spectrum of oxidized o-amino-n-tert.-butylphenol]

Fig. 1. E.P.R. spectrum of oxidized *o*-amino-*n*-tert.-butylphenol

The generally accepted mechanism of the action of oxidation inhibitors In—H includes, in the first stage, removal of labile hydrogen with the formation of a stable radical [$\mathrm{In}^{\cdot}$] or of compounds that are incapable of continuing the chain oxidation reaction:

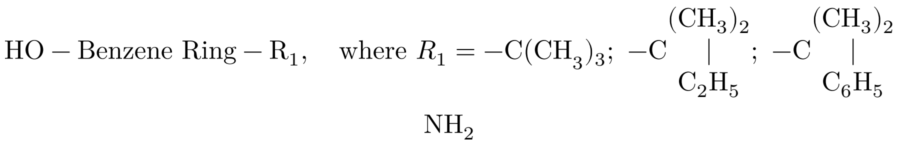
$$\mathrm{ROO}^{\cdot} + \mathrm{In{-}H} \rightarrow \mathrm{ROOH} + \mathrm{In}^{\cdot}$$

$$\mathrm{In}^{\cdot} + \mathrm{ROO}^{\cdot} \rightarrow \mathrm{ROOIn}$$

$$\mathrm{In}^{\cdot} + \mathrm{In}^{\cdot} \rightarrow \mathrm{In{-}In}$$

A number of works (2–7) have been devoted to elucidating the oxidation mechanism of the widely used inhibitor 2,6-di-tert.-butyl-4-methylphenol by means of the E.P.R. method. It was shown that a phenoxy radical is initially formed with abstraction of hydrogen from the hydroxyl group and subsequent formation of the final product, stilbenequinone.

In the present work, the results are presented of a study of the hyperfine structure of the E.P.R. spectra of certain derivatives of aminoalkylphenols. The inhibitors studied by us are characterized by the presence of hydroxyl and amino groups, each of which is capable of interrupting or retarding the chain oxidation reaction. We first studied compounds of series I.



$$\mathrm{HO-Benzene\ Ring-R_1},\quad \text{where } R_1 = -\mathrm{C(CH_3)_3};\ -\overset{(\mathrm{CH_3})_2}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\ ;\ -\overset{(\mathrm{CH_3})_2}{\underset{\mathrm{C_6H_5}}{\mathrm{C}}} \qquad \mathrm{NH_2}$$

(I)

The characteristics of these products are given in the work ([8]). Oxidation of benzene solutions of the compounds studied was carried out with benzoyl peroxide at

at room temperature. The concentration of radicals during the measurements did not exceed $1 \cdot 10^{-3}$ mole/liter. To exclude the possible influence of oxygen on the h.f.s. of the spectrum, a series of measurements was carried out on evacuated samples. The measurements were performed on a standard RE-1301 radiospectrometer with oscillating magnetic-field frequency $\nu_1 = 9320$ Mc/s and high-frequency modulation $\nu_2 = 975$ kc/s at room temperature.

In all cases the EPR spectra of the products listed consisted of more than 30 components with nine clearly distinguishable groups of lines (Fig. 1). Under the action of the oxidizing agent on aminoalkylphenols, the possibility is not excluded that, as was indicated, either the OH or the NH_2 is oxidized. The theoretically calculated spectra that we constructed on the assumption of oxidation of either the OH or the NH_2 group of I did not coincide with the experimentally obtained spectra. Apparently, the oxidation of I by benzoyl peroxide proceeds somewhat differently. The fact that the OH and NH_2 groups are in the ortho position to one another in the benzene ring will also play a considerable role in the formation of free radicals. In addition, during oxidation by benzoyl peroxide, addition products of the initial product and the peroxide radical may form ([9]). Thus, the formation of free radicals of different structure is possible, the spectra of which will be superimposed. All this considerably complicates the interpretation of the spectrum obtained upon oxidation of I. In order to exclude, during oxidation, the influence of the OH group, the methyl and ethyl ethers of *o*-amino-*p*-tert-butylphenol (II) were synthesized

$$\mathrm{R_2O}-[\text{Benzene ring with } \mathrm{R_1} \text{ and } \mathrm{NH_2}] \qquad (\mathrm{R_2} = -\mathrm{CH_3};\ -\mathrm{C_2H_5}). \qquad \text{(II)}$$

Fig. 2. EPR spectrum of the oxidized methyl ether of *o*-amino-*p*-tert-butylphenol:
a—experimental spectrum; *b*—theoretical spectrum.

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The oxidation conditions were the same as for I. The EPR spectrum consisted of four lines of hyperfine structure (Fig. 2a), and the substituents R_1 and R_2 did not affect the appearance of the spectrum. The EPR signal in evacuated samples did not change over several days. The observed EPR spectrum can be explained by the interaction of the unpaired electron with the nuclear spin of nitrogen $I_N = 1$ and of the proton $I_H = \frac{1}{2}$. To verify this assumption, theoretical spectra were calculated, in the construction of which possible interactions of the unpaired electron with the magnetic nuclei of the amino group and the ring were taken into account. The calculations were carried out on an M-3M electronic computer using a specially developed program (^{10}). To determine the constants a of the hyperfine interaction of the unpaired electron with the nuclei of nitrogen and hydrogen atoms, we constructed a spectrum of six lines of Gaussian form and analyzed the shape of the spectrum as a function of the widths of the individual components ΔH_n at half intensity. It turned out that the best agreement of the theoretical spectrum with the experimental one is obtained for the ratio $\Delta H_n/a = 1.03$, under the condition $a_N = a_H = a$ (Fig. 2b). This made it possible to determine $a_N = a_H = 3.5 \pm 0.2$ oersted and $\Delta H = 3.6 \pm 0.2$ oersted.

It may be considered that, in the first stage of oxidation of products I, abstraction of a hydrogen atom from the amino group occurs, with formation of free radicals

OR_2
[Benzene Ring with R_1]
$\dot{N}H$
(III)

The presence of appreciable spin density on the amino nitrogen may, as a result of the hyperconjugation effect, lead to interaction of the unpaired electron with the nucleus of the amino hydrogen. This origin of the observed EPR spectrum is confirmed by the data of work (^{11}), in which ion-radicals of semiquinones with amino groups were studied and hyperfine splittings from amino protons and nitrogen, comparable in magnitude, were obtained.

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1. F. N. Mazitova, Ya. M. Paushkin, *Khimiya i tekhnologiya topliv i masel*, No. 11, 10 (1958).
2. L. Cosgrove, W. A. Waters, *J. Chem. Soc.*, 1951, 1726.
3. A. F. Bickel, E. C. Kooyman, *J. Chem. Soc.*, 1953, 3211.
4. R. F. Moore, W. A. Waters, *J. Chem. Soc.*, 1954, 243.
5. C. D. Cook, B. E. Norcross, *J. Am. Chem. Soc.*, 81, 1176 (1959).
6. N. B. Neiman, A. L. Buchachenko, *Izv. AN SSSR*, No. 10, 1742 (1961).
7. A. I. Brodskii, V. P. Pokodenko, L. N. Ganyuk, *Zhurn. strukturnoi khim.*, 4, No. 2, 210 (1963).
8. F. N. Mazitova, Ya. M. Paushkin, *DAN*, 125, No. 5 (1959).
9. E. G. E. Hawkins, *Organic Peroxides*, London, 1961, p. 311.
10. M. A. Ikrina, A. V. Il' yasov et al., *DAN*, 147, No. 3 (1962).
11. J. Matsunaga, C. A. McDowell, *Canad. J. Chem.*, 38, 1167 (1960).

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