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Abstract

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STUDY OF THE OXIDATION OF THE METHYL ETHER OF *o*-AMINO-*p*-tert-BUTYLPHENOL BY THE E.P.R. METHOD

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It was reported in work ([1]) that, in studying by the method of electron paramagnetic resonance (e.p.r.) the oxidation products of the methyl ether of *o*-amino-*p*-tert-butylphenol (MEABP) with benzoyl peroxide (BP), spectra of hyperfine structure (h.f.s.) were obtained; from their analysis it followed that, in the first stage of oxidation of MEABP, a hydrogen atom is abstracted from the amino group with formation of a free radical.

The changes occurring with time in the h.f.s. spectrum showed that the oxidation process proceeds further, and moreover in several stages, and depends on the ratio between MEABP and the oxidizing agent (BP).

For a detailed study of the oxidation products and of the process of oxidation of the initial MEABP by benzoyl peroxide, we carried out experiments with a consecutively increasing amount of oxidizing agent. The various stages of oxidation, accompanied by formation of free radicals, were recorded from changes in the h.f.s. spectra. Oxidation of MEABP was carried out in evacuated ampoules in a solution of dry benzene. The e.p.r. measurements were performed on an RE-1301 radiospectrometer at room temperature ($\nu = 9320$ MHz).

For the experiments, the initial products MEABP and BP were taken in the following molar ratios: $1 : 1/8$; $1 : 1/2$; $1 : 1$.

In the case of a clearly insufficient amount of oxidizing agent ($1 : 1/8$), a spectrum is obtained (Fig. 1a) consisting of 4 lines, which is described in work ([1]). When the initial products were taken in the ratio $1 : 1/2$, a singlet with line width δH between inflection points of ~ 4 oersted initially appears (Fig. 1b), which after several minutes gradually changes into a pronounced triplet (Fig. 1c). The time of transition from singlet to triplet is considerably accelerated by heating the solution. Finally, at a ratio of the initial products of $1 : 1$, after 20 h a spectrum consisting of 5 h.f.s. components is observed (Fig. 1d). The spectrum does not change over five days upon storage at a temperature of $\sim 22°$.

Fig. 1. E.p.r. spectra of a benzene solution of MEABP oxidized with BP at various molar ratios of MEABP and BP:
a–$1 : 1/8$; *b*, *c*–$1 : 1/2$; *d*–$1 : 1$ (in an evacuated sample); *e*–$1 : 1$ in air.

Fig. 1

Figure 1: Fig. 1

On the basis of analysis of the EPR spectra obtained in studying oxidation with different quantitative ratios between MEABP and PB, the following stages of oxidation may be proposed, which proceed with the formation of free radicals. With a deficiency of PB (1/8 mole), it is possible to fix the initial stage of oxidation of MEABP. The spectrum obtained, as indicated in (1), corresponds to possible structural formula I, formed by abstraction of a hydrogen atom from the amino group; the contribution to the HFS is due mainly to the nucleus of the nitrogen of the amino group and the hydrogen of the amino group ($a_N = a_H = 3.5 \pm 0.2$ Oe).

(structure I) $\qquad R_1 = -C(CH_3)_3, \quad R_2 = -CH_3.$

(I)

If a larger amount of PB (1/2 mole) is taken, the process of further oxidation of I takes place. In a number of works (2-4) it has been shown that, at high concentrations of PB when it is used as an oxidizing agent, products of addition of the peroxide to the oxidized substance may be formed. It is possible that the process of oxidation of I proceeds with abstraction of a second hydrogen atom from nitrogen and addition of a peroxide residue to the oxidized product, with formation of radicals II.

The singlet observed in this case (Fig. 1b) with $\delta H = 4.1 \pm 0.2$ Oe can be explained as the beginning of the oxidation of I into II. This process lasts several minutes, after which the singlet changes into a triplet. The triplet obtained, with an HFS constant $a'_N = 14.5 \pm 0.2$ Oe and $\delta H = 2.4 \pm 0.2$ Oe, is probably due to the nucleus of the N^{14} nitrogen atom (nuclear spin $I = 1$), which may correspond to the following possible structures:

(structures II)

(II)

An excess of oxidizing agent (1 mole) continues the oxidation process of II, at the same time stimulating pairing of molecules with the formation of radicals of structure III. Taking steric factors into account, we give only the most probable structures.

(structures III)

(III)

The spectra of these radicals (Fig. 1e) consist of five lines with an intensity ratio of $1 : 2 : 3 : 2 : 1$, which can be explained by interaction of the unpaired electron with two nitrogen atoms (5). Analysis of this experimental spectrum, carried out similarly to that in work (1), made it possible to determine the isotropic coupling constants for the nitrogen atoms: $A_1 = 6.1 \pm 0.4$ Oe and $A_2 = 5.5 \pm 0.4$ Oe. The resulting ratio of the constants, 0.98, indicates an almost equally probable interaction of the unpaired electron with two nitrogen atoms.

For the purpose of isolating and analyzing the stable product III, oxidation with a MEABP-to-PB ratio of 1:1 was carried out in air. The product was then isolated by chromatography on alumina; its benzene solution gave an h.f.s. spectrum (Fig. 1d). The molecular weight of this product, determined by the ebullioscopic method [6], as well as analysis for nitrogen, confirm the supposition that oxidized molecules of the original MEABP undergo pairing, with addition of peroxide residues as well.

For III mol. wt. calculated 595.7, found 582.9

Found, %: N 4.69; 4.73
Calculated, %: N 4.70

The spectrum obtained from the oxidation product in vacuum differs somewhat from the spectrum obtained upon oxidation in air (Fig. 1a and d). Analysis of the experimental spectrum d showed that the h.f.s. is also due to interaction of the unpaired electron with two nitrogen atoms. In the present case, however, the interaction with one nitrogen is somewhat greater. This is evident from the changed ratio of the hyperfine-coupling constants, which is now ~ 0.78. Such a change probably arises from the influence of atmospheric oxygen on the oxidation products. This supposition is also confirmed by the fact that spectrum e, after the ampoule is opened, is transformed after several hours into spectrum d.

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