Tetrahedron Letters No.39, pp. 4203-4206, 1968. Pergamon Press. Printed in Great Britain.

EPR CONTRIBUTION TO INVESTIGATIONS OF THE AUTOOXIDATION MECHANISM OF 2-TERT.ALKYLHYDROQUINONES

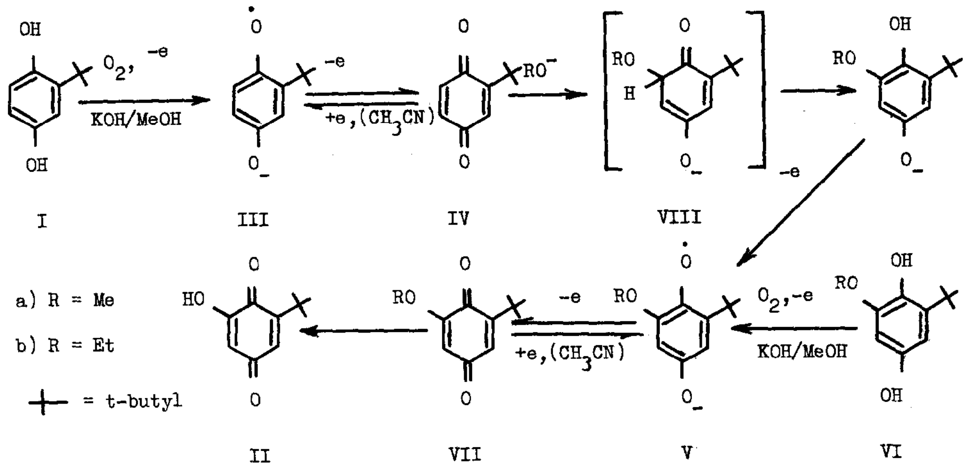
J. Pilař, I. Buben, and J. Pospíšil

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

(Received in UK 4 June 1968; accepted for publication 2 July 1968)

For a detailed elucidation of the mechanism of aerial oxidation of 2-tert.alkylhydroquinones (I) by oxygen in a medium of methanolic KOH solution we have tried to identify by the EPR method the radical intermediates of this reaction, the final products of which are 2-tert.alkyl-6-hydroxy-1,4-benzoquinones (II) (1). In the first step aerial oxidation of hydroquinones in alkaline medium causes the formation of p-semiquinone radicals which are unstable when exposed to the air (2,3). With regard to the influence of the composition of the oxidising medium (content of alcohol and alkaline hydroxides) on the yield of hydroxyquinones (II) (1), the chemical participation of the medium in certain oxidation stages must also be taken into account. Observations of Reitz et al. (4) support this statement. They find that during oxidization of hydroquinone by air in methanolic sodium methoxide a secondary radical appeared after the primary p-benzosemiquinone radical had disappeared. The EPR spectrum of this secondary radical was identical with that of 2,5-dimethoxy (or ethoxy)-p-semiquinone if the oxidation was made in methanol (or in ethanol). On this basis the authors believe that alkoxyl groups are added to the aromatic ring in the course of oxidation.

For our study we selected 2-tert.butylhydroquinone. The radicals formed by aerial oxidation of this compound were studied by the EPR method using a continuous flow method. Close to the resonator cavity, two solutions were mixed, one of them was a 10^{-3}M solution of the hydroquinone derivative under study in a 75% aqueous methanol and the second one was a 20 % KOH solution in the same solvent. Differing from oxidation done in a preparative manner (1), the solutions contained only dissolved atmospheric oxygen. On passage through the resonator cavity we observed the EPR spectrum of the primary radical which was the eight-line spectrum of 2-tert.butyl-p-semiquinone (III). A spectrum of the same type was obtained by Stock and Suzuki (5) by aerial oxidation of 2-tert.butylhydroquinone in acetonitrile in the presence of different bases, and by Ryba et al. (6) in the one-electron reduction of 2-tert.butyl-1,4-benzoquinone (IV) in acetonitrile. When the flow was stopped the spectrum of the primary radical disappeared slowly, being overlapped



by the spectrum of the secondary radical (Fig. 1 a). Interpretation of this spectrum showed that in the secondary radical interaction of the unpaired electron takes place with three equivalent and two non-equivalent protons. With regard to the final oxidation product and the facts observed by Reitz et al. (4) this conclusion led us to assume that the secondary radical formed in the reaction is 2-tert.butyl-6-methoxy-p-semiquinone (V a). This assumption was confirmed by the spectrum of 2-tert.butyl-6-methoxy-p-semiquinone (Fig. 1b). This radical was prepared by means of aerial oxidation of 2-tert.butyl-6-methoxyhydroquinone (VI a) under the same conditions as used to oxidise 2-tert.butylhydroquinone in aqueous methanol and also in water without alcohol. A comparison of the spectra in Figs. 1a and 1b shows clearly that in Fig. 1a the spectrum of 2-tert.butyl-6-methoxy-p-semiquinone is confused by the spectrum of the primary radical, of which only the two side and centre lines are visible due to the low intensity of this spectrum. The correctness of the interpretation of the spectrum of 2-tert.butyl-6-methoxy-p-semiquinone is confirmed by the simulated spectrum (Fig. 1c) which was calculated from the splitting constants given in Table 1 with the assumption that the shape of the spectral line is Lorentzian and its width is $\Delta H_{1/2}$ = 400 mG. We have obtained a spectrum of the same type by means of electrolytic reduction of 2-tert.butyl-6-methoxy-1,4-benzoquinone (VII a) in acetonitrile. There was only a small difference in the splitting constants (see Table 1), due to the solvent effect.

Under the same conditions we have furthermore studied the course of aerial oxidation of 2-tert.butylhydroquinone in 75 % aqueous ethanol. The result of this experiment was the same as in the aqueous methanol; only the spectrum of the secondary radical was of a different type. Its

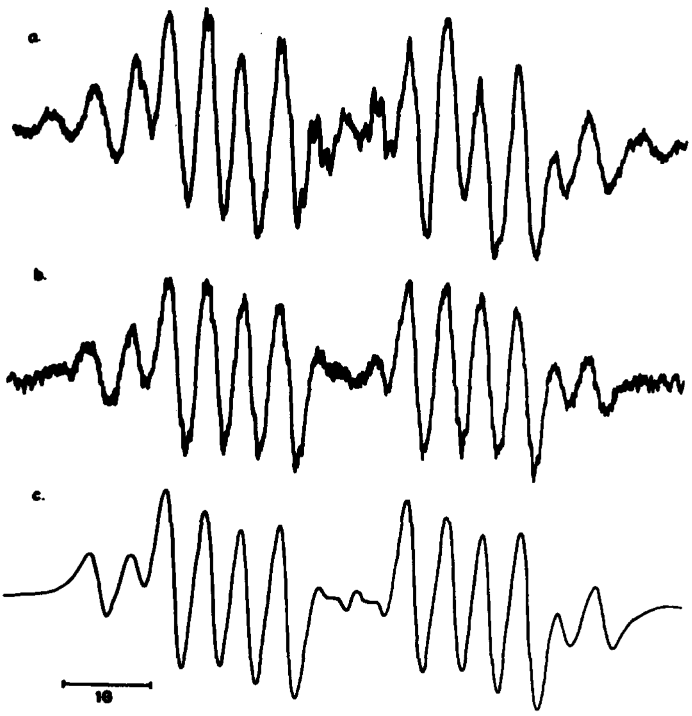


Fig. 1

a. EPR spectrum of the secondary radical occuring in aerial oxidation of 2-tert.butylhydroquinone in 75 % MeOH + 25 % H_2O; b. EPR spectrum of 2-tert.butyl-6-methoxy-p-semiquinone in 75 % MeOH + + 25 % H_2O; c. Simulated spectrum of 2-tert.butyl-6-methoxy-p-semiquinone calculated from splitting constants given in Table 1.

TABLE 1

Splitting Constants (in gauss)

		a^H_{ring}(d)		a^H_{alkoxy}
2-tert.butyl-6-methoxy-p-semiquinone	(a)	2,72 ± 0,05	0,44 ± 0,02	0,84 ± 0,02
	(b)	3,12 ± 0,05	1,00 ± 0,02	0,64 ± 0,02
2-tert.butyl-6-ethoxy-p-semiquinone	(c)	2,72 ± 0,05	0,44 ± 0,02	1,00 ± 0,02

(a) measured in 75 % MeOH + 25 % H_2O; (b) measured in CH_3CN; (c) measured in 75 % EtOH + 25 % H_2O; (d) it is impossible to decide from the EPR data which splitting corresponds to a proton in position 3 and which to a proton in position 5 of the aromatic ring interpretation showed that it corresponds to a radical in which a unpaired electron interacts with two equivalent and two non-equivalent protons. In agreement with the preceding case we ascribed it to 2-tert.butyl-6-ethoxy-p-semiquinone (V b).

The interpretation of model results obtained with the use of 2-tert.butylhydroquinone and substances derived from it shows that under the oxidation conditions described, the alcohol used as reaction medium participates temporarily in the reaction mechanism. Since hydroxyquinones (II) are also formed in the oxidation of 2-tert.alkyl-1,4-benzoquinones (IV) (1), it may be assumed that the anion RO^- is temporarily bound in position 6 of this quinone which is formed in the course of the oxidation process; furthermore that a hypothetical anion (VIII) is created and that the anion-radical (V) is gradually formed. Stone and Waters (7) tried to explain our earlier results obtained in the oxidation of 4-methyl and 4-tert.octylpyrocatechol by the introduction of the HO^- anion into the alkyl-1,2-benzoquinone molecule, similarly. The formation of the anion-radical (V) agrees with the result of oxidation done by preparative means (1), in which the final product, the hydroxyquinone (II), is formed immediately on acidification of a solution of 2-tert. butyl-6-methoxy-1,4-benzoquinone (VII a); the latter substance is, moreover, subject to more changes in a strongly alkaline oxidising medium.

REFERENCES

1. I. Buben and J. Pospíšil, Tetrahedron Letters, **1967**, 2123; Collection Czech.Chem.Commun., in press.
2. B. Venkataraman, B. G. Segal, and G. K. Fraenkel, J.Chem.Phys., **30**, 1006 (1959).
3. M. Adams, M. S. Blois, Jr., and R. H. Sands, J.Chem.Phys., **28**, 774 (1958).
4. D. C. Reitz, J. R. Hollahan, F. Dravnieks, and J. E. Wertz, J.Chem.Phys., **34**, 1457 (1961).
5. L. M. Stock and J. Suzuki, J.Am.Chem.Soc., **87**, 3909 (1965).
6. O. Ryba, J. Pilař, and J. Petránek, Collection Czech.Chem.Commun., **33**, 26 (1968).
7. T. J. Stone and W. A. Waters, J.Chem.Soc., **1965**, 1488.
8. J. Pospíšil and V. Ettel, Collection Czech.Chem.Commun., **24**, 729 (1959).