SEPARATION OF FREE RADICALS BY PAPER CHROMATOGRAPHY

![Fig. 1. E.p.r. spectrum of the primary Ionol radical](image)

1961

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Abstract

Full Text

PHYSICAL CHEMISTRY

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SEPARATION OF FREE RADICALS BY PAPER CHROMATOGRAPHY

(Presented by Academician V. N. Kondrat' ev, April 7, 1961)

It is known ([1,2]) that many alkyl-substituted phenols, upon oxidation, are capable of forming kinetically stable radicals. The formation of radicals occurs by abstraction of the hydroxyl hydrogen. Such primary phenoxy radicals, as a result of subsequent reactions, give products which, in turn, can also form secondary stable radicals. Since the formation of primary and secondary radicals proceeds simultaneously and in parallel, radicals of both, and sometimes of several, types are usually present in the reaction mixture. Investigation of these processes by the method of electron paramagnetic resonance under ordinary conditions is hindered by the superposition of the spectra of the radicals and by the difficulty of interpreting them. To ensure reliable spectral analysis, preliminary separation of the radicals and investigation of their e.p.r. spectra separately are necessary. We carried out the separation in the case of the radicals of 2,6-di-tert-butyl-4-methylphenol (Ionol).

Fig. 1. E.p.r. spectrum of the primary Ionol radical

The e.p.r. spectrum of the primary Ionol radical is shown in Fig. 1. A quadruplet with a splitting between components of 11.4 oersted and an intensity ratio of 1 : 3 : 3 : 1 arises from interaction of the unpaired electron with the protons of the methyl group in the para position to the oxygen atom. Each component of the quadruplet is split into three lines with an intensity ratio of 1 : 2 : 1 and a spacing between them of 1.7 oersted. This splitting occurs on two equivalent protons in the meta position of the benzene ring. Splitting on the meta protons, as well as the small magnitude of the splitting on the protons of the methyl group in comparison with the CH_3 radical (26 oersted) ([3]), testifies to delocalization of the unpaired electron over the ring, which is one of the reasons for the stability of this radical. The primary radical is formed when Ionol is oxidized by lead dioxide, when it reacts with benzoyl peroxide and cyclohexyl percarbonate, and also during photolysis and radiolysis of Ionol ([4]). When Ionol is oxidized by lead dioxide, secondary radicals appear simultaneously with the

Fig. 3. EPR spectrum of the secondary ionol radical in the solid phase

Figure 2: Fig. 3. EPR spectrum of the secondary ionol radical in the solid phase

primary radical, considerably complicating the pattern of the e.p.r. spectrum.

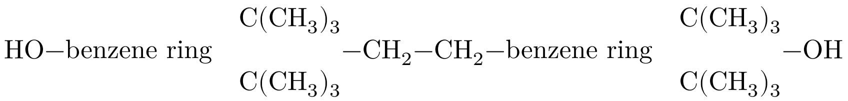
For separation of the radicals, paper chromatography was used (^{5}). Toluene, ethyl alcohol, and carbon tetrachloride were used as the mobile phase. Samples were taken from the oxidizing hydrocarbon solution of Ionol and applied as a strip near the lower edge of the filter-paper tape. After drying, the tape was lowered by its lower edge into the solvent serving as the mobile phase. The best separa-

separation occurred upon elution with 96% ethyl alcohol. In this case the applied strip of the oxidized ionol solution was clearly separated into two fronts: the lower—orange, with $Rf = 0$, and the upper—yellow, with $Rf = 1$. A typical chromatogram is shown in Fig. 2 (see inset to p. 1023). After drying, the chromatogram on the paper was cut into sections, each of which was placed in the resonator of an EPR-2 spectrometer (^{6}), and the EPR spectra were then recorded. It was shown that the first yellow section of the chromatogram gives an EPR spectrum exactly coinciding with the spectrum shown in Fig. 1.

The second orange section gives a spectrum representing a doublet with a component intensity ratio of $1:1$ and a splitting of 14.5 oersted (Fig. 3). After wetting this section of paper with a solvent (benzene, toluene, CCl_4), this spectrum changed into another—a triplet with a component intensity ratio of $1:2:1$ and a splitting between them of 8.2 oersted (Fig. 4). Each component of the triplet is split into 3 lines with an intensity ratio of $1:2:1$ and a distance between them of 1.8 oersted. After evacuation of the solvent, and also upon freezing the solution with liquid nitrogen, the triplet again changes into a doublet. Such triplet-doublet transitions are reversible. In the solid phase (crystal or frozen solution) a doublet is always observed; in solution, a triplet. The observed transitions do not depend on the presence of paper in the solution or on the presence of atmospheric oxygen. The latter causes only a blurring of the hyperfine structure of the triplet components.

Fig. 3. EPR spectrum of the secondary ionol radical in the solid phase

Analysis of the EPR spectrum shown in Fig. 4 indicates that it should be assigned to the secondary radical obtained from the phenol



$$\text{HO—benzene ring}\ \begin{matrix}C(CH_3)_3\\ \\ C(CH_3)_3\end{matrix}\text{—}CH_2\text{—}CH_2\text{—benzene ring}\ \begin{matrix}C(CH_3)_3\\ \\ C(CH_3)_3\end{matrix}\text{—OH}$$

by abstraction of one of the hydroxyl hydrogens. Indeed, such a phenol is one

Fig. 4. EPR spectrum of the secondary ionol radical in solution

Figure 3: Fig. 4. EPR spectrum of the secondary ionol radical in solution

of the main products of ionol oxidation (^{7}).

Fig. 4. EPR spectrum of the secondary ionol radical in solution

The triplet-doublet transformations are explained as follows. In solution, free rotation takes place around the aralkyl C—C bond, and the unpaired electron interacts with each of the two equivalent protons of the CH_2 group. In the solid phase, owing to the rigidity of the structure of the surrounding lattice, the tetrahedral angles at the carbon atom in the CH_2 group are arranged so that interaction of the unpaired electron occurs only with one proton of the CH_2 group, lying in the plane perpendicular to the plane of the π-orbital of the unpaired electron. At room temperature in the crystal, torsional vibrations around the

this C–C bond. The splitting between the components of the doublet in this case is 14.5 oersteds. The presence of a more rigid lattice (at liquid-nitrogen temperatures) restricts the possibility of such motions still further, and, correspondingly, the splitting between the components of the doublet increases to 18.5 oersteds, while each of the components broadens.

Thus, analysis of EPR spectra makes it possible to judge the behavior of radicals in solution and in a rigid lattice.

In addition to separating radicals of different types, it is possible to separate radicals from the molecules corresponding to them. Such a separation was carried out by us for the system diphenylpicrylhydrazyl–diphenylpicrylhydrazine. By the chromatographic method, using aqueous-alcoholic mixtures of definite composition as the mobile phase, it proved possible to separate molecules and radicals that had first been applied, in the form of a mixture, to the lower edge of a strip of filter paper. In this case the leading front of the chromatogram, moving together with the solvent, contained radicals, while the second, immobile front contained molecules firmly adsorbed on the paper.

We believe that the application of chromatography opens up the possibility of separating and isolating stable radicals, which will help to investigate more deeply the structure and behavior of such radicals.

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Received
3 IV 1961

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