Electron Spin Resonance of Radical Pairs in X-Irradiated Single Crystals of Clathrate Complex of Hydroquinone with Acetonitrile

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In the previous papers,[1-3] radical pairs trapped in X-irradiated crystals of oxime compounds have been studied by ESR. This paper will report the first observation of pairwise trapping of phenoxy radicals in X-irradiated crystals of clathrate complex of hydroquinone with acetonitrile.

Figure 1 shows a typical X-band ESR spectrum observed at 77°K for the single crystal irradiated at 77°K. The spectrum consists of three sets of doublets with unidentified lines at the center.

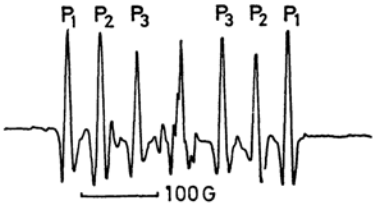


Fig. 1. Second derivative ESR spectrum at 77°K of a single crystal of clathrate complex of hydroquinone with acetonitrile irradiated at 77°K. The doublets P_1, P_2 and P_3 are ascribed to the same radical pairs with different orientation. The direction cosines of the external magnetic field with respect to the crystal axes [1$\bar{1}$0], [110] and [001] are (0.766, 0.643, 0.000).

The angular dependence of the doublet has the feature characteristic of the transition $\Delta M=\pm1$ of a triplet state and can be fitted to a spin Hamiltonian for a triplet state ($S=1$, $\Delta M=\pm1$),

$$\mathscr{H} = \beta \boldsymbol{HgS} + \boldsymbol{SDS}$$
$$= \beta \boldsymbol{HgS} + D\left(S_z^2 - \frac{1}{3}S^2\right) + E(S_x^2 - S_y^2). \quad (1)$$

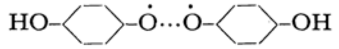
The principal elements of the fine structure tensor **D** for one of the doublets are given in Table 1. The vector $\boldsymbol{R}$ between two unpaired electrons is parallel to the direction for D_{zz} and R is found to be 5.1 Å from the relation, $R=30.6\ D^{-1/3}$, where D and R are expressed in Gauss and in Å, respectively. Comparison of $\boldsymbol{R}$ with the interatomic distances determined by X-ray analysis[4] indicates that the triplet state arises from a radical pair  which is derived from two hydroquinone molecules with the shortest intermolecular distance among six hydroquinone molecules surrounding the acetonitrile molecule (Fig. 2). Non-vanishing value of E shows that the unpaired electron is delocalized over the whole phenoxy radical. Radical pairs responsible for other two sets of the doublets are related to the pair given in Table 1 by rotation $\pm 2\pi/3$ about the c axis of the crystal. This fact is compatible with the hexagonal symmetry of the crystal. The spectrum of the powdered sample has absorption peaks corresponding to the transitions of $\Delta M=\pm1$ as well as of $\Delta M=\pm2$.

TABLE 1. PRINCIPAL VALUES AND PRINCIPAL DIRECTIONS OF FINE STRUCTURE TENSOR

The directions are expressed in direction cosines with respect to the crystal axes [1$\bar{1}$0], [110] and [001].

$D_{xx}=-62.8$ G	(0.234,	−0.461,	0.856)
$D_{yy}=-74.0$ G	(−0.846,	0.338,	0.413)
$D_{zz}=137.2$ G	(0.479,	0.821,	0.310)
$D=205.6$ G, $E=5.6$ G, $g=2.004-2.008$			

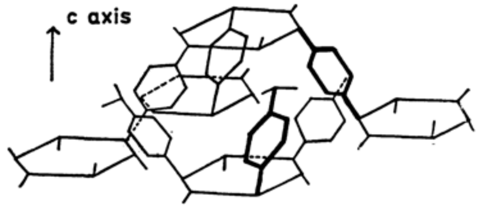


Fig. 2. Stereoscopic representation of the clathrate complex of hydroquinone. The two hydroxy radicals are drawn with heavy lines. Larger hexagons represent the hydrogen bonds and smaller hexagons represent benzene rings (after Palin and Powell[4]).

The absorptions of the radical pairs disappeared in half an hour 190°K, and the unidentified absorptions give rise to new absorption spectra which can be attributed to a radical CH_2CN. Irradiated clathrate complexes of hydroquinone with SO_2, CO_2, HCl and CH_3OH showed ESR spectra due to radical pairs.

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