ENDOR-study of radical pairs in single crystals of potassium hydrogen malonate

R. Knopp und A. Müller

Institut für Biophysik und Physikalische Biochemie,
Universität Regensburg, Postfach 397, D-8400 Regensburg

Recently it has been shown that irradiation of single crystals of potassium hydrogen malonate ($KOOC \cdot CH_2 \cdot COOH$) with X-rays at 77 K yields two types of radical pairs (1). These are composed of the same monoradicals but are different in the orientation of the vector $\vec{r}$ linking the radicals of a pair. Each type of pairs exists in three modifications, which are related by small irreversible changes of their fine structure with rising temperature.

ENDOR results obtained from one type of pairs and from the corresponding monoradical confirm the conjecture that changes of the electron-electron dipole splittings at about 160 K are related to a structural relaxation of the stressed molecule after abstraction of one hydrogen from the methylene carbon changing its hybridization from sp^3 to sp^2. In the ENDOR spectra this manifests itself by a disappearing site splitting of the α-proton resonances of both the monoradical and the pair. The change of the fine structure at about 240 K is accompanied by a renewed splitting of the ENDOR line of the pair only.

Another interesting result obtained by the ENDOR measurements is a difference between the hyperfine splitting of the α-protons of the pair and the corresponding monoradical. This difference is attributed to a *transferred hyperfine interaction* and can be a measure of the direct overlap of the coupled unpaired electrons (2). It is the first time that this effect has been observed in noncovalently bonded pair systems.

1) Knopp, R. and Müller, A., (1981), Molec. Phys., 42, 1245.
2) Owen, J. and Harris, E.A., (1972), *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum Press), p. 427.