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ELECTRON SPIN RESONANCE
OF PHOTOCHROMIC β-TETRACHLORO-α-KETONAPHTHALENE

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A triplet ESR spectrum has been observed in a powdered sample of β 2,3,4,4-tetra-chloro-α-keto-
aphtalene after UV irradiation. The spectrum could be reproduced by computer simulation using an
anisotropic g-tensor \( g_{xx} = 2.0095, \ g_{yy} = 2.0025, \ g_{zz} = 2.0023 \) and zero-field splitting parameters
\( D' \) and \( E' \) of 99 and 2.3 gauss respectively. The results are discussed in terms of the earlier proposed
photodissociation into a naphthoxyl radical and a chlorine atom.

In 1888 Zincke [1] observed that colourless
crystals of β-tetrachloro-α-ketonaphthalene
(βTKN) become amethyst coloured under the in-
this reaction is reversible and introduced the
term "phototropy". Nowadays the phenomenon is
generally called "photochromy". The first quan-
titative optical measurements were performed by
Weigert [3] who found that the electronic transition
moment of the absorption band that appeared
upon radiation lies in the plane of the naphthalene
ring.

Feichtmayr and Scheibe [4] have explained the
photochromic behaviour of βTKN as a reversible
photochemical dissociation reaction of the com-
ponent in the 2,3,4-trichloronaphthoxyl radical
and a chlorine atom as is depicted in fig. 1. On
the basis of Weigert's measurements they assign
the new absorption band to a \( ^\pi \rightarrow ^\pi^* \) transition of the
naphthoxyl radical.

Since the aromatic radical and the chlorine
atom each carry a free electron spin, the crys-
tal is expected to be paramagnetic in the "ex-
cited" state. An increase in the magnetic suscep-
tibility upon radiation has indeed been found by
Dörr and Engelman [5] but in spite of a number of
attempts [6] no ESR spectrum has been re-
ported. We have started to reinvestigate the
physics of the photochromic behaviour of βTKN
and we report here the first results of our ESR
measurements. After irradiating a powder of
βTKN at \( 180^\circ \)K for 20 minutes with a superhigh
pressure mercury arc type HP 125 W, an ESR
spectrum is obtained as shown in fig. 2. As is
immediately clear from the lineshape of this spec-
trum and from the fact that at 'half field' a weak
ESR signal can be detected \( (\Delta m = 2) \) tran-
sition) this spectrum arises from the magnetic coupling
between two unpaired electron spins. To make
this interpretation more reliable we have made a
computer simulation [7] of the spectrum based on
the spin Hamiltonian

\[
\mathcal{H} = \beta H g \cdot S + D S_2^2 + E(S_1^2 - S_2^2)
\]

(1)

where \( g \) is the anisotropic g-tensor, \( D \) and \( E \)
are the zero-field splitting (z.f.s.) parameters
and \( S = S_1 + S_2 \).

The result of such a simulation is also shown
in fig. 2, where a reasonable fit to the experimen-
tal spectrum could be obtained with the constants
inserted in the figure. The parameter \( E \) turned
out to be essential to reproduce the details of the
spectrum in spite of its smallness \( (E/D = 0.02) \).
As can be seen from fig. 2 the experimental ESR
spectrum shows a marked asymmetry. This can
be understood as follows: from a first order anal-
ysis based on the Hamiltonian (1) stationarity in
the resonance fields is obtained for the magnetic
field along the principal axes of the z.f.s. tensor
[6]. For a random orientation of the "triplet-mo-
lecules" some structure is thus produced in the
absorption at these magnetic field values. These fields are called the axial resonance fields and it can easily be shown that in a first order approximation these axial fields occur at

\[
\frac{g_e}{g_{xx}} [H_0 \pm \frac{1}{2}(D' + 3E')]
\]

and

\[
\frac{g_e}{g_{yy}} [H_0 \pm \frac{1}{2}(D' - 3E')]
\]

where \(D' = D/g_e \beta\), \(E' = E/g_e \beta\) and \(H_0 = h/\gamma g_e \beta\). Without \(g\)-anisotropy, the triplet ESR spectrum becomes symmetric (fig. 3a), but with \(g\)-anisotropy the spectrum becomes asymmetric (fig. 3b). In the case at hand a narrowing at low field and a broadening at high field of the spectrum occurs. Before discussing the z.f.s. constants we shall consider the central weak absorptions, which do not belong to the spectrum just discussed. These absorptions can be included in the simulation assuming a second two-electron spin system with very small z.f.s. parameters \((D' = 12\) gauss, \(E' = 0, g_{xx} = g_{yy} = 2.00400, g_{zz} = g_e = 2.00232\). We can interpret our observations in terms of the dissociation mechanism proposed by Feichtmayr and Scheibe [4] together with one consecutive reaction. We consider the triplet spectrum as aris-

![Fig. 2. Experimental and computer simulated ESR spectrum of UV irradiated βTKN powder.](image-url)

![Fig. 3. The position of the axial resonance fields for an isotropic and anisotropic g-tensor. At X, Y and Z the magnetic field lies along the x, y and z-axis of the z.f.s. tensor.](image-url)
ing from the magnetic coupling between a naphthoxyl radical and a chlorine atom while the central weak lines are probably due to the interaction between two naphthoxyl radicals.

In the latter case the chlorine atom initially formed abstracts a similar chlorine atom from a neighbouring ring. This reaction is similar to that observed by Kurita [9] after gamma-irradiation of oximes where initially formed hydrogen atoms react with hydrogen atoms from neighbouring oximes to form molecular hydrogen.

From the formula $D = \frac{3\mu_0 B^2 r^3}{2}$, one finds the value of 6.5 Å for the effective distance between the two unpaired spins. Let us assume in a first approximation that the triplet electrons are localized on the oxygen of the naphthoxyl radical and the free chlorine atom respectively. In this approximation the OCl-distance in the excited state is thus 6.5 Å. In fact delocalization of the electron on oxygen will occur so that the actual OCl-distance in the excited state can be somewhat smaller to yield the same $D$-value. A comparison with the OCl-distance of 5.4 Å [10] in the parent compound thus leads us to conclude that the chlorine atom moves only over a very small distance after leaving the ring, and it is therefore not surprising that a recombination reaction occurs. So far we have not discussed the fact that near the triplet state also a singlet state must be expected. The gap between these two states can be derived from temperature dependent measurements of the magnetic susceptibility assuming a temperature dependence

$$\chi = C\left(3 + e^{J/kT}\right)^{-1},$$

where $C$ is a constant and $J$ the magnitude of the gap. Tentative measurements yield for $J$ a value of $\approx 20$ cm$^{-1}$, with the singlet state as the ground state.

The lowering of the singlet state with respect to the triplet state may well be due to a mixing of the zero order singlet state $|\varphi_{s}(R_{Cl}^{*}, Cl^{*})\rangle$ with the charge transfer state $|\varphi_{CT}(R_{Cl}^{*}, Cl^{-})\rangle$. This charge transfer excitation incidentally offers an alternative explanation for the intense absorption in the visible by the newly formed radical system which has hitherto been assigned to a $\pi - \pi^*$ transition of the naphthoxyl radical. Optical and ESR measurements on single crystals are now in progress to clarify this and other questions pertaining to a better physical understanding of the photochromic behaviour of the compound at hand.

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