



CW-EPR study of 2,2,4,4-tetramethyl-3-pentanone oxime single crystals

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ABSTRACT

The electron paramagnetic resonance (EPR) spectra of gamma irradiated single crystals of 2,2,4,4-tetramethyl-3-pentanone oxime (TPO) have been examined between temperatures of 125 and 450 K. The spectra were found to be both dependent on temperature and orientation of single crystals with magnetic field. We attributed radiation damage centers to iminoxy radicals (RC=NO). There are two similar group of splitting in the spectra because of conformational isomers (R1, R2) of iminoxy radicals produced by gamma irradiation of TPO. Determined g-factor and hyperfine coupling constants for R1 and R2 conformers were found anisotropic with the average values $(g_{iso})_{R1}=2.01057$, $(g_{iso})_{R2}=2.009337$, $[(a_N)_{iso}]_{R1}=28.09$ G, $[(a_N)_{iso}]_{R2}=36.34$ G, $[(a_H)_{iso}]_{R2}=9.15$ G, respectively.

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1. Introduction

An oxime is one in a class of chemical compounds with the general formula $R'R''C=NOH$, where R' is an organic side chain and R'' is either hydrogen, forming an aldoxime, or another organic group, forming a ketoxime.

Oximes act as an antioxidant, radical scavenger, which find applications in textile, plastic, paint, detergent, and rubber industry. Oximes are used as a chemical building block for the synthesis of agrochemicals and pharmaceuticals. In medicine application, oxime structure is effective in cholinesterase reactivators to treat the poisoning by organophosphates. Generally, the oximes and their derivatives are used in photography, medical, agriculture field, textile industries, technological improvement, dye chemistry, and semi-conductor manufacture.

Because of these important usage of oximes, we identified the magnetic properties of a ketoxime: 2,2,4,4-tetramethyl-3-pentanone oxime (TPO) single crystals by using EPR.

Oximes exist as two geometric stereoisomers: a syn isomer and an anti isomer. Aldoximes, except for aromatic aldoximes, exist only as a syn isomer, while ketoximes can be separated almost completely and obtained as a syn isomer and an anti isomer. These stereoisomers are not there in TPO because of the same organic side chain ($R'=R''=C(CH_3)_3$), but there are conformational isomers because of the rotation of H atom given in Fig. 1. We can designate these conformers as R1 and R2. The $C\hat{N}O$ bond angle of R1 conformer is bigger than the angle of R2

conformer because of the repulsion effect between tertbutyl ($C(CH_3)_3$) group and H atom.

2. Experimental

The TPO ($C_9H_{19}NO$) powder was purchased from Merck. The samples were crystallized in the laboratory by slow evaporation from a concentrated solution in ethanol. The grown single crystals were irradiated with a ^{60}Co - γ -ray source at 0.99 kGy/h for about 96 h. After irradiation, the EPR spectra of the TPO crystals were recorded at 300 K at 10° intervals in the magnetic field, applied along each of the three crystallographic axes (x , y , and z) using a Bruker model EMX 081 X-band EPR spectrometer. Low- and high-temperature measurements were performed using a

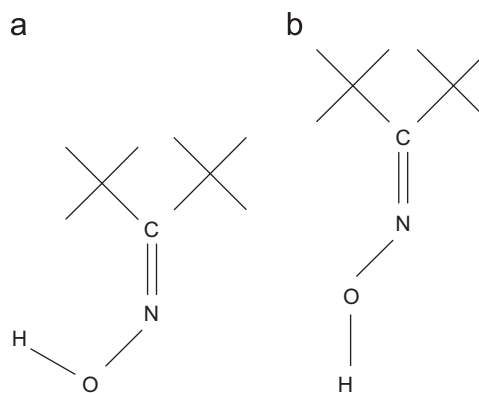


Fig. 1. Conformational isomers of TPO (a) R1 (b) R2.

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Bruker variable temperature-control unit. The magnetic field modulation frequency was 100 kHz. Bruker SimFonia software was used for spectral simulations. The g -factor of the conformers of the iminoxy radical were found by comparison with a DPPH sample ($g=2.0036$) (Weidner and Whitmer, 1953).

3. Results and discussion

We investigated magnetic properties of single crystals of TPO at 300 K using EPR. This temperature was used because of the higher resolution of the spectra than the other temperature measurements. The EPR spectrum of the paramagnetic species formed by gamma irradiation of TPO is anisotropic and has

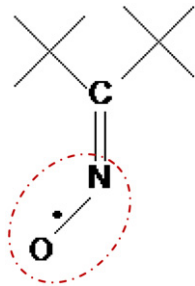


Fig. 2. Identified iminoxy σ -type neutral radical of TPO.

characteristic properties which belong to iminoxy σ -type neutral radical given in Fig. 2. Iminoxy radicals are characterized by relatively large isotropic hyperfine coupling

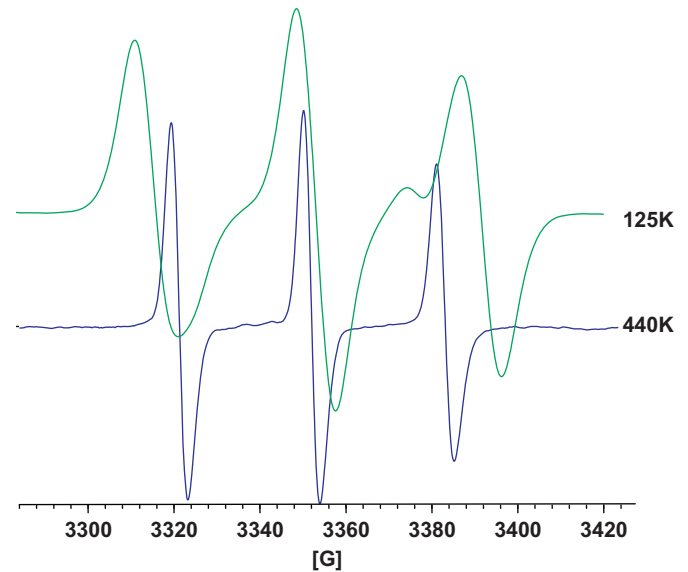


Fig. 3. EPR spectra of TPO at temperature of 125 and 440 K when the magnetic field oriented 0° to the z -axis.

Table 1

EPR parameters of the R1 conformational isomer of iminoxy radical.

(Conformer R1) $RC = \dot{N}O$		
$(A_N)_{R1}(G)$	$A_{xx} = 31.19$ $A_{yy} = 27.54$ $A_{zz} = 25.55$ $a_{iso} = 28.09$	$\begin{pmatrix} 0.006284488 & -0.235631238 & -0.971822219 \\ 0.953195577 & 0.295194430 & -0.065409785 \\ 0.302289094 & -0.925925574 & 0.226457800 \end{pmatrix}$
g_{R1}	$g_{xx} = 2.01186$ $g_{yy} = 2.01059$ $g_{zz} = 2.00925$ $g_{iso} = 2.01057$	$\phi_1 = 31^\circ \quad \phi_2 = 95^\circ \quad \phi_3 = 93^\circ$ $\begin{pmatrix} 0.309138587 & 0.938377511 & -0.154534724 \\ -0.622378577 & 0.322487070 & 0.713194922 \\ 0.719081526 & 0.124296968 & 0.683719257 \end{pmatrix}$
	$[(C_s^2)_N]_{R1} = 0.051$ $[(C_p^2)_N]_{R1} = 0.091$ $(\rho_N)_{R1} = 0.14$ $(\rho_O)_{R1} = 0.86$	$(C\dot{N}O)_{R1} = 118.14^\circ$

Table 2

EPR parameters of the R2 conformational isomer of iminoxy radical.

(Conformer R2) $RC = \dot{N}O$		
$(A_N)_{R2}(G)$	$A_{xx} = 39.92$ $A_{yy} = 35.64$ $A_{zz} = 33.45$ $a_{iso} = 36.34$	$\begin{pmatrix} 0.512829124 & -0.809636162 & 0.285474297 \\ 0.839096876 & 0.402437538 & -0.366006093 \\ 0.181446195 & 0.427239175 & 0.885744865 \end{pmatrix}$
$(A_H)_{R2}(G)$	$A_{xx} = 10.85$ $A_{yy} = 9.48$ $A_{zz} = 7.11$ $a_{iso} = 9.15$	$\begin{pmatrix} 0.956231210 & -0.239142073 & -0.168620703 \\ 0.25654462 & 0.406817321 & 0.876802177 \\ -0.141082468 & -0.881652276 & 0.450316556 \end{pmatrix}$
g_{R2}	$g_{xx} = 2.01033$ $g_{yy} = 2.00911$ $g_{zz} = 2.00857$ $g_{iso} = 2.00934$	$\begin{pmatrix} 0.239536109 & 0.936515793 & -0.256048085 \\ -0.850406490 & 0.329626132 & 0.410067573 \\ 0.468434898 & 0.119518963 & 0.875376470 \end{pmatrix}$
	$[(C_s^2)_N]_{R2} = 0.066$ $[(C_p^2)_N]_{R2} = 0.105$ $(\rho_N)_{R1} = 0.17$ $(\rho_O)_{R1} = 0.83$	$(C\dot{N}O)_{R2} = 116.35^\circ$

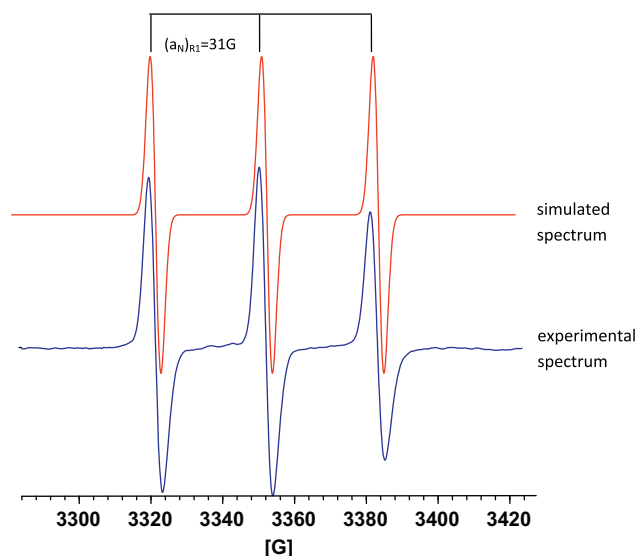


Fig. 4. Lower curve: EPR spectra of TPO at 440 K, when the magnetic field oriented 0° to the z-axis. Upper curve: simulation of the relevant spectra.

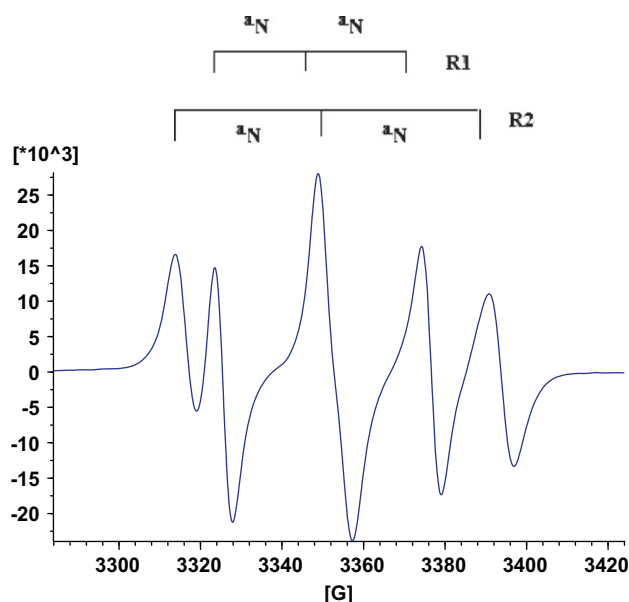


Fig. 5. EPR spectra of TPO at 300 K when the magnetic field oriented 80° to the z-axis.

constant due to the interaction with ^{14}N nucleus $(a_{\text{N}})_{\text{iso}} = 28 - 35$ G (Thomas, 1964; Symons, 1965; Gilbert and Norman, 1966; Fox and Symons, 1966). The unpaired electron is in an orbital derived from nitrogen sp^2 orbital and an oxygen p orbital, which lies in the nodal plane of the $\text{C}=\text{N}$ π -bond (Gilbert and Norman, 1966), hence the radicals are treated as σ -type.

Our results demonstrate that there are two conformational isomers (R1 and R2) of iminoxy radical. The spin density of the unpaired electron was determined for the R1 and R2 conformers and the results given in Table 1 and Table 2, were used for the calculation of the $\text{C}\dot{\text{N}}\text{O}$ bond angles in order with Coulson's formula (Atkins and Symons, 1967) given below

$$\theta = 2\text{Cos}^{-1}(\lambda^2 + 2)^{-1/2} \quad (1)$$

Here λ^2 is the hybridization ratio for the sp^n hybrid atomic orbital on the central atom and equal to C_p^2/C_s^2 ratio. Also, C_p^2 and

C_s^2 are the spin density distribution of the radical in the p and s orbital of the ^{14}N atom.

The angles of the $\text{C}\dot{\text{N}}\text{O}$ bond were found approximately 118.14° and 116.35° for R1 and R2 conformers, respectively. The bigger angle is because of the repulsion effect between tertbutyl group and the hydrogen atom.

We have calculated the relative orientations of the main directions the hyperfine tensors of the conformers R1 and R2. The values ϕ_1, ϕ_2, ϕ_3 given in Table 1 are the angles between the corresponding eigenvectors in experimental value of ^{14}N hyperfine coupling constant of R1 and R2 conformer.

The EPR parameters of the conformers were found temperature dependent. The EPR spectrum shown in Fig. 3 recorded at 440 K exhibits only a triplet ($(a_{\text{N}})_{\text{iso}} = 31$ G) with the g value $g_{\text{R1}} = 2.01098$ due to the ^{14}N nucleus of R1 conformational isomer of the iminoxy radical. It is clear that R2 conformer disappeared in high temperature measurements. The spectrum of R1 conformer

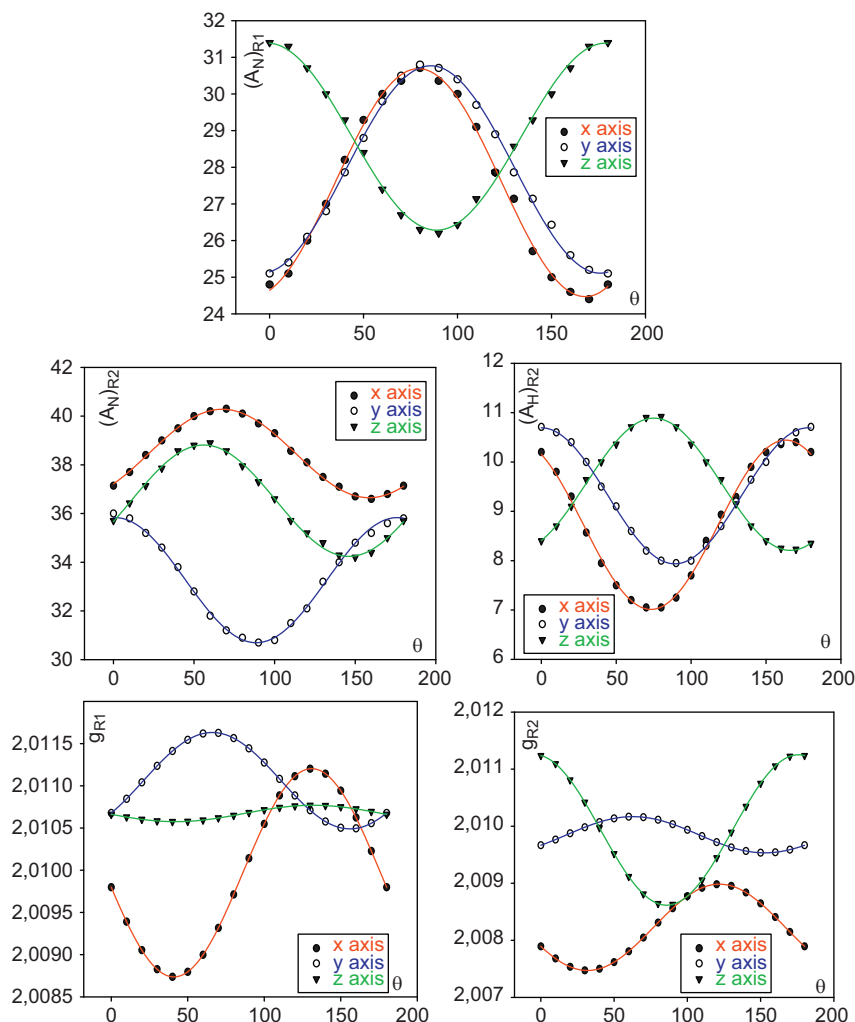


Fig. 6. Angular variations of the hyperfine interaction tensor, $A(\theta)$ and spectroscopic splitting tensor, $g(\theta)$, for the R1 and R2 conformers of the iminoxy radical produced in TPO at 300 K.

and simulation of relevant spectrum at 440 K are shown in Fig. 4. The EPR spectrum shown in Fig. 5 recorded at 300 K has 6 lines belong to the R1 and R2 conformers of the iminoxy radical. In addition to ^{14}N splitting, R2 conformer has also a small hydrogen splitting with the average value $(a_{\text{H}})_{\text{iso}}=9.15$ G, because the CNO bond angle of R2 smaller is than the angle of R1 and the unpaired electron is closer to hydrogens of tertbutyl group.

Since the amplitude of the peaks belonging to the each isomer radical are approximately of same magnitude for all directions, we have understood that the abundance ratio of the conformational isomers are nearly same.

Our values for R1 and R2 conformers given in Tables 1 and 2, respectively, are in agreement with the literature values of the several iminoxy radicals given in the references (Thomas, 1964; Symons, 1965; Gilbert and Norman, 1966; Fox and Symons, 1966; (Gilbert and Norman, 1968; Alberti et al., 1980; Kirste et al., 1988; Chmielewski et al., 1992; Jaszewski et al., 1999). The angular variations of the hyperfine interaction tensor, $A(\theta)$ and spectroscopic splitting factor tensor, $g(\theta)$, for the R1 and R2 conformers of the iminoxy radical produced in TPO are shown in Fig. 6.

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