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# EPR STUDY ON THE RECRYSTALLIZED SAMPLES OF PIPERDINYLOXY 2,2,6,6 TETRAMETHYL RADICAL

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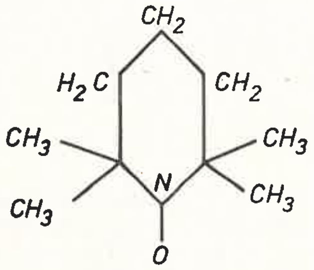
Electron spin resonance (ESR) studies in recrystallized samples of piperdinyloxy 2, 2, 6, 6 tetramethyl (TEMPO) were made. The samples were prepared by recrystallizing them from a number of organic solvents, and the values of linewidths and *g*-factor were determined experimentally. The shape of the ESR lines was also determined. The shape of the ESR lines remains unchanged, but the linewidth and *g*-values are found to be different from that of the parent free radical. The changes thus produced in the linewidth and *g*-values have been explained on the basis of a complex formation.

## 1. *Introduction*

It was found from earlier studies [1–6] that electron spin resonance (ESR) spectra of free radicals, after their recrystallization from different solvents, show notable changes in the lineshapes, linewidths, and *g*-values from those of their parent free radical.

In view of this interesting fact a detailed ESR study was carried out on a free radical piperdinyloxy 2, 2, 6, 6 tetramethyl also known as TEMPO which is a stable nitroxide radical and is widely used as a spin labelling agent, i.e. in the study of liposomes [7] and fragmented sarcoplasmic reticulum [8]. It has a structural formula as given below.



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For preparing recrystallized samples of this radical, equal amounts of it were dissolved in trichloroethylene, acetone, ethyl alcohol, carbon tetrachloride, methyl alcohol, toluene, and tetrahydrofuran (THF). The solution of TEMPO thus prepared was concentrated using a water bath and then was kept at the room temperature for slow evaporation of the organic solvent. After two to three days when the solvent was completely evaporated, the sample, which was left behind was kept in a vacuum dessicator to remove the loosely bound solvent molecules, if any.

The ESR spectra of samples of TEMPO recrystallized from different organic solvents were recorded at room temperature (ESR spectra of recrystallized samples from toluene and THF were recorded at 0°C as their melting point was around the room temperature).

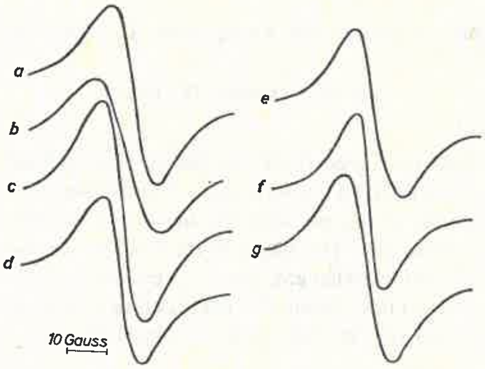

Fig. 1. ESR spectra of recrystallized polycrystalline samples of TEMPO. Spectra (a-g) are respectively for the samples of TEMPO recrystallized from trichloroethylene, acetone, ethyl alcohol, carbon tetrachloride, methyl alcohol, toluene and tetrahydrofuran

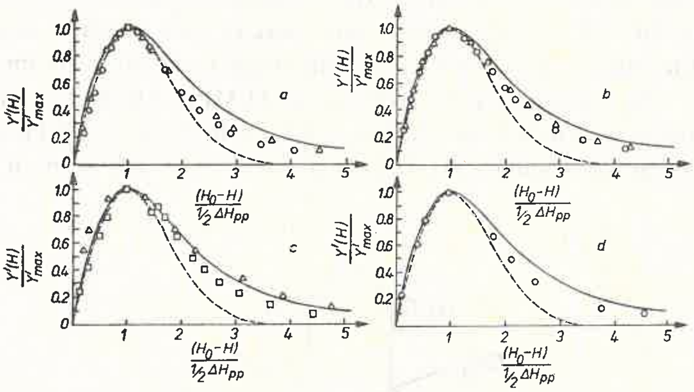

Fig. 2. Plots of calculated values of $Y'(H)/Y'_{\max}$ versus $(H_0-H)/\frac{1}{2}\Delta H_{pp}$ along with the observed values ta ke from the observed ESR spectra of samples of TEMPO recrystallized from different solvents: a) ——— — theoretical Lorentzian line shape, – – – — theoretical Gaussian line shape, ○ — observed points for TEMPO/acetone, Δ — observed points for TEMPO/trichloroethylene; b) ○ — observed points for TEMPO/ethyl alcohol, Δ — observed points for TEMPO/carbon tetrachloride; c) □ — observed points for TEMPO/$CH_3OH$, Δ — observed points for TEMPO/toluene; d) ○ — observed points for TEMPO/TH

A varian E-12 ESR spectrometer was used for recording the ESR spectra. Fig. 1 a-g show the ESR spectra of the recrystallized TEMPO samples.

The lineshape of all the records was tested using the following relations [9]

$$\frac{Y'(H)}{Y'_{\max}} = \frac{32}{9}\left(\frac{H-H_0}{\Delta H_{\mathrm{pp}}}\right)\left[1+\frac{1}{3}\left(\frac{H_0-H}{\frac{1}{2}\,\Delta H_{\mathrm{pp}}}\right)^2\right]^{-2} \quad \text{for Lorentzian lineshape,}$$

and

$$\frac{Y'(H)}{Y'_{\max}} = e^{1/2}\left(\frac{H_0-H}{\frac{1}{2}\,\Delta H_{\mathrm{pp}}}\right)\exp\left[-\frac{1}{2}\left(\frac{H_0-H}{\frac{1}{2}\,\Delta H_{\mathrm{pp}}}\right)^2\right] \quad \text{for Gaussian lineshape,}$$

where $\Delta H_{\mathrm{pp}}$ is the full width between maximum slope points. The normalized theoretical Lorentzian and Gaussian line shape graphs for arbitrary values of $Y'(H)/Y'_{\max}$ and $(H_0-H)/\frac{1}{2}\Delta H_{\mathrm{pp}}$ along with the values of $Y'(H)/Y'_{\max}$ for different values of $(H_0-H)/\frac{1}{2}\Delta H_{\mathrm{pp}}$ were taken from the spectra of recrystallized samples (see Fig. 2).

## 2. *Results and discussion*

From Fig. 2, it is seen that the lineshape remains Lorentzian in all recrystallized samples since most of the experimental points are close to the theoretically drawn Lorentzian curve. It is well known [10] that during the process of recrystallization, either some molecular addition complexes are formed, or the solvent molecules enter into the free radical crystal lattice and thus modify the crystal structure of the free radical and influence the spacing between them. But the Lorentzian nature of the ESR lines for all recrystallized samples given here simply suggests that exchange interaction which is very much dependent on the distance between free radical molecules and changes very much with a slight change of the spacing, has not been modified to the extent of affecting the lineshape. It also suggests that the dipolar broadening which is also dependent on the distance between the paramagnetic centres has not been modified to such an extent that it may change the shape of the ESR lines.

The values of the peak to peak linewidth, *g*-value, and lineshape of the TEMPO and recrystallized samples in different solvents are given in Table I.

From Table I it is clear that ESR lines are broader than the line due to parent radical for recrystallized samples from trichloroethylene, acetone, ethyl alcohol, carbon tetrachloride, methyl alcohol, and THF, where the line due to recrystallized sample from toluene is narrower than the line due to parent radical. On the basis of the results given in Table I, it can be said qualitatively that the factors which affect the linewidth viz. dipole-dipole interaction and exchange interaction for a free radical have been modified sufficiently after recrystallization from different solvents. A decrease in the linewidth after recrystallization from toluene may be explained as follows: Parent radical (which was supplied by Dr. M. Borghini of CERN, Geneva) is a recrystallized sample of TEMPO from diethyl ether. It is possible that after recrystallization of this sample from toluene the distance between the TEMPO molecules reduces and thus increases the exchange interaction

TABLE I

Data of linewidth, *g*-value and lineshape of TEMPO and recrystallized samples of TEMPO

| Sample | Temperature (in °C) | Linewidth $\Delta H_{pp}$ (in Gauss) | *g*-value | Lineshape |
|---|---|---|---|---|
| TEMPO (Polycrystalline) | 20 | 9.7 | 2.0066 | Lorentzian |
| TEMPO recrystallized from | | | | |
| Trichloethylene | 20 | 13.25 | 2.0065 | Lorentzian |
| Acetone | 20 | 18.00 | 2.0065 | Lorentzian |
| Ethyl alcohol | 20 | 13.00 | 2.00654 | Lorentzian |
| Carbon tetrachloride | 20 | 11.60 | 2.00636 | Lorentzian |
| Methyl alcohol | 20 | 14.00 | 2.00654 | Lorentzian |
| Toluene | 0 | 9.12 | 2.0066 | Lorentzian |
| THF | 0 | 14.25 | 2.0061 | Lorentzian |

which in turn decreases the linewidth of ESR signal. A definite and quantitative interpretation of the change in linewidth in terms of various interactions can only be presented on the basis of various linewidth theories viz. those due to Van Vleck [11], Anderson and Weiss [12] and Kubo and Tomita [13]. Out of these theories Kubo and Tomita's theory is most exhaustive and explains the results in most of the cases. For carrying the calculations on the basis of Kubo and Tomita's theory, one requires the value of mean spin distance, and the exact value of mean spin distance can only be obtained if one knows the micro-chemical analysis of the recrystallized samples. This could not be done in the present case since the indicators required for this purpose are not known to the best of our knowledge.

The *g*-values of all recrystallized samples of TEMPO are shown in Table I. From Table I it is apparent that the *g*-values of all recrystallized samples are different. However, they are not much different from that of the parent free radical. The *g*-values of the samples of TEMPO, recrystallized from different organic solvents, are not equal to 2.0023 which is the value of *g* for a free radical having an unpaired electron which is completely free from the orbital effect, indicating that in these samples the electron magnetic moment is not free from orbital effects. This can be studied in terms of $\delta g$, which is the deviation in the *g*-value of the substance and is a measure of a change in the contribution of a spin--orbit interaction in the magnetic moment of the electron giving out ESR spectrum, due to formation of molecular addition complexes of the free radical with the solvent molecules. $\delta g$ is equal to $2\lambda/\Delta$ [14–16], where $\lambda$ is a spin orbit coupling constant and $\Delta$ is the separation of energy between the ground orbital state and the next higher state. A change in deviation $\delta g$ in recrystallized polycrystalline samples suggests simply that the modifications in the values of $\lambda$ and $\Delta$ of the free radical after its recrystallization from various solvents are different. The nature of the modification and its magnitude depends on the type of the solvent used for recrystallization. In the free radicals, the spin orbit coupling coefficient is small. The value of $\Delta$ for free radicals is very large and change in its value after recrystallization is not sufficient to produce an accountable change in the $g$-value of the recrystallized samples [5]. The change in $\lambda$ may occur as it depends upon the nature of the lattice, which is sufficiently modified after recrystallization. The change in $\lambda$ may be sufficient to produce a measurable change in the $g$-value of the recrystallized sample. But since the nature of the sample is polycrystalline, one can only get an averaged value of $g$-factor for all possible orientations of the crystallites present in the polycrystalline recrystallized samples. Therefore, no definite conclusion can be drawn from the change in the $g$-value of these samples. Some definite conclusion can only be drawn if a single crystal study is carried out for these complexes. No attempt for growing single crystals of recrystallized samples was made due to prohibitive cost of the free radical TEMPO. The sample which has been used in the present investigations was provided by Dr. M. Borghini of CERN (Geneva). Larger amount of the sample could not be obtained. Since the single crystal study of recrystallized samples could not be done due to its non-availability, no quantitative conclusion could be made here from the $g$-factor measurements about the changes in $\lambda$ and $\Delta$ after recrystallization.

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