

## Electron Spin Resonance Spectra of Hydrogen-Bonded HO· Radicals

HIROSHI YOSHIDA\* and BENGT RANBY

Department of Polymer Technology,  
The Royal Institute of Technology,  
Stockholm 70, Sweden

Dixon and Norman observed the electron spin resonance (ESR) spectra of hydroxyl free radicals, HO·, generated in aqueous solution from the reduction of hydrogen peroxide with Ti(III) ions, using a flowing method where the free radicals were measured immediately after mixing the two reactants. They also studied the ESR spectra of many substances added to the reaction mixture.<sup>1,2</sup> Using their method, we obtained spectra which are thought to be due to HO· radicals, hydrogen-bonded to the oxygen atoms in trioxane molecules. The experimental arrangements used will be reported elsewhere.<sup>3</sup>

When 1,3,5-trioxane is added to the reactants, the spectra of the primary HO· radicals disappear and spectra related to trioxane appear as shown in Fig. 1. With a sufficient amount of trioxane added, the HO· spectra are completely converted to the trioxane spectra. The spectra related to trioxane are doublets with a very small splitting. Their  $g$ -value was  $2.003 \pm 0.002$ , while  $g = 2.013 \pm 0.002$  was recorded for the primary HO· radicals. The  $g$ -values were measured using a solution of diphenylpicrylhydrazyl ( $g = 2.0023$ ) in a mixture of acetone and water (1:3) as a standard.

Because of overlapping of the doublet components, it is difficult to measure absolute values for the doublet splitting. The temperature dependence of the relative  $\Delta H$  values (peak-to-peak distance of the derivative curves) was therefore examined (see Fig. 1), and the results are shown in Fig. 2. The doublet splitting is decreasing significantly with increasing temperature in the examined range.

ESR spectra from 1,4-dioxane obtained under similar conditions, were studied by

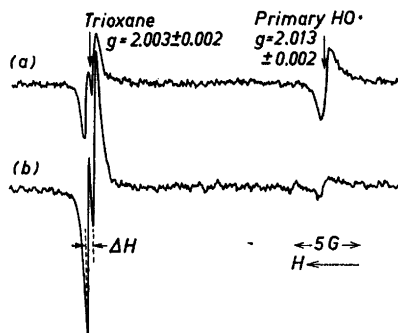


Fig. 1. ESR spectra from HO· radicals in a redox reaction system containing trioxane, measured at 23°C. Modulation width: 0.25 G. (a): trioxane concentration  $8.3 \times 10^{-3}$  mole/l. (b)  $16 \times 10^{-2}$  mole/l.

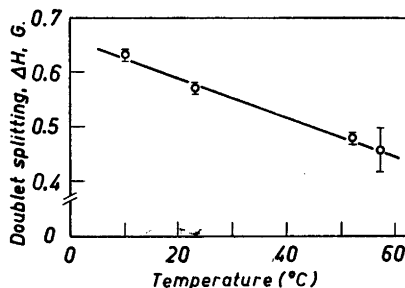
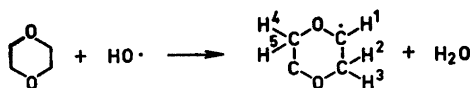


Fig. 2. Temperature dependence of the doublet splitting in the ESR spectra from the trioxane-HO· radical system.

Dixon and Norman.<sup>2</sup> The recorded spectra were completely different from those of trioxane. The dioxane spectra were attributed to the free radicals formed by hydrogen abstraction from the dioxane molecule by HO· radicals as follows:

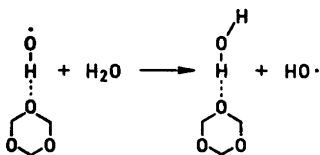


According to their interpretation the H<sup>1</sup> proton gives a hyperfine coupling constant of 17.2 G, and the H<sup>4</sup> and H<sup>5</sup> protons give 1.3 G. The sum of the hyperfine

\* Present address: Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka, Japan.

coupling constants due to  $H^2$  and  $H^3$  is 45.5 G. We also observed similar spectra for dioxane radicals.

Comparing the ESR spectra from trioxane and dioxane, the very small doublet splitting in the trioxane spectra cannot be attributed to any hydrogen atom in the trioxane molecule. Accordingly, it is reasonable that the doublet spectrum from trioxane is due to  $HO\cdot$  radicals hydrogen-bonded to oxygen in trioxane molecules. The unusually small doublet splitting and its temperature dependence may be interpreted in terms of a rapid exchange of hydrogen atoms with increasing rate at higher temperatures as follows:



Recently, Freed and Fraenkel reported a hyperfine splitting in ESR spectra thought to be due to protons involved in

intramolecular hydrogen bonds of anion radicals from naphthazarin.<sup>4</sup> Their discussion is based on similar arguments. The interpretation of hydrogen-bonded  $HO\cdot$  radicals in our case is supported by the observed shift in the  $g$ -values and the temperature dependence of the doublet splitting. These problems are being further studied. If the interpretation in our case is correct, the observed spectra indicate that  $HO\cdot$  radicals form hydrogen bonds with trioxane more readily than water molecules do.

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1. Dixon, W. T. and Norman, R. O. C. *J. Chem. Soc.* **1963** 97; Dixon, W. T., Norman, R. O. C. and Baley, A. L. *J. Chem. Soc.* **1964** 3625.
2. Dixon, W. T. and Norman, R. O. C. *Chem. Soc.* **1964** 4850.
3. Yoshida, H. and Rånby, B. *To be published.*
4. Freed, J. H. and Fraenkel, C. K. *J. Chem. Phys.* **38** (1963) 2040.

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