The Effect of Dissolved Paramagnetic Ion on the ESR Spectra of Diphenyl Nitric Oxide*

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In the preceding two papers[1,2], the author has reported on the study of the ESR spectra of diphenyl nitric oxide (DPNO) in crystalline states and in liquid solutions respectively.

During the course of the study, we noticed that dissolved oxygen[3] in solvents played a remarkable negative role in diminishing the proton hyperfine lines.

As will be shown in the succeeding section, the effect on the proton hyperfine lines of the presence of dissolved oxygen or other paramagnetic ions in solutions is to be explained not by chemical reaction but by magnetic dipole-dipole interaction.

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[1] Y. Deguchi, This Bulletin, 34, 910 (1961).

[2] Y. Deguchi, ibid., 35, 260 (1962).

[3] Y. Deguchi, *J. Chem. Phys.*, 32, 1584 (1960).

The same effect has already been recognized in the NMR experiments[4,5].

Experimental

All samples have been prepared by the same process as described in the preceding paper[3]. In order to investigate the dissolved oxygen effect, a valve with a tapered ground connector has been attached at one end of a sample tube connected to the vacuum line so that one can introduce air into the sample tube and remove air from it.

For the experiment of the foreign paramagnetic ion effect, a graduated cylinder containing a known volume of it with a certain concentration has been connected to the sample tube so that one can add each known amount of foreign paramagnetic ion to the sample successively. Here we used copper tetraphenyl porphyrin (CuTPP) as the foreign paramagnetic ion.

Results

With Dissolved Oxygen.—Figure 1 shows the effect of dissolved oxygen in solution on the ESR spectra of DPNO. Figure 1a is the spectrum of the degassed sample treated as in reference[3]. We can see the well-resolved proton hyperfine spectra in it. Figure 1b is the spectrum taken after opening the vacuum valve to introduce air into the sample tube. The proton hyperfine lines are all broadened, and only the nitrogen hyperfine lines remain. Again outgassing the sample, one can obtain the same well-resolved proton hyperfine lines in Fig. 1c as in Fig. 1a,

With Copper Tetraphenyl Porphyrin (CuTPP).—In the case of oxygen, it is difficult to control the concentration of oxygen in solution. Therefore, we here employed CuTPP as a foreign paramagnetic ion dissolved in solution.

Figure 2a is the spectrum of the degassed DPNO solution where no foreign paramagnetic ion coexists.

By the addition of 2/11 mg. of CuTPP to the solution, almost all the weak proton hyperfine lines disappear, as in Fig. 2b. Then by dissolving each known amount of CuTPP into the solution successively, as shown in Figs. 2c, 2d and 2e, the proton hyperfine lines become broader and broader until only the broad nitrogen splitting lines can be observed and all the proton hyperfine lines disappear.

Discussion

From the aforementioned experiments, we can conclude that this effect is caused by the magnetic dipole-dipole interaction of DPNO with dissolved oxygen or paramagnetic ions in the solutions.

By this interaction, the spin-lattice relaxation time (T_1) of DPNO will become shorter than when no dissolved paramagnetic ion is present in the solution. Thus, we can follow the theory of Bloembergen, Purcell and Pound[5] (BPP). In their case, the spin orientation of protons is relaxed by the dissolved paramagnetic ions, but in the present case the spin orientation of the unpaired electrons of the free radical will be relaxed by the dissolved paramagnetic ions.

Thus, instead of Eq. 54 in BPP's paper, we will obtain:

$$1/T_1 = 12\pi^2\gamma_e^2\eta N_{\text{ion}}\mu_{\text{eff}}^2/5\boldsymbol{k}T$$

where

γ_e: the gyromagnetic ratio of an electron,

η: the viscosity of the solvent at the temperature T°K,

N_{ion}: the number of dissolved paramagnetic ions per cm^3,

μ_{eff}: the magnetic moment of the dissolved paramagnetic ion in the Bohr magneton number,

$\boldsymbol{k}$: the Boltzmann constant,

T: the absolute temperature of the experiment.

In the case of dissolved oxygen, knowing that the solubility of oxygen, into ethyl alcohol is

$$143\times10^{-3}\ \text{cc. per 1 cc. of ethyl alcohol,}$$

we know that the N_{ion} for this case will be

$$3.844\times10^{18}\ \text{cm}^{-3}$$

Also the η for ethyl alcohol at 20°C is 1.20×10^{-2} poise, and the μ_{eff} for oxygen in the Bohr magneton number is 2.83.

Then we shall have

$$1/T_1 = 0.327\ \text{gauss}$$

Thus, it turns out that each proton hyperfine line of DPNO in degassed solutions will be broadened further by the amount of 0.327 gauss because of the presence of the dissolved oxygen. As stated, in the preceding papers[2,3], the separation between two successive proton hyperfine lines is about 0.98 gauss, and the half-widths of the sharpest lines in each group of the spectrum are of the order of 0.1 gauss. Thus, not every hyperfine lines will be reserved, and only the broad nitrogen hyperfine lines will be observed.

In the same way, foreign paramagnetic ion effect on the proton hyperfine lines can be explained. These results are tabulated in Table I.

There are other spin-lattice relaxation mechanisms such as the exchange interaction[6], the

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[4] F. Bloch, W. W. Hansen and M. Packard, *Phys. Rev.*, **70**, 474 (1946).

[5] N. Bloembergen, E. M. Purcell and R. V. Pound, ibid., **73**, 679 (1948).

[6] N. Bloembergen, *J. Chem. Phys.*, **72**, 572 (1957).

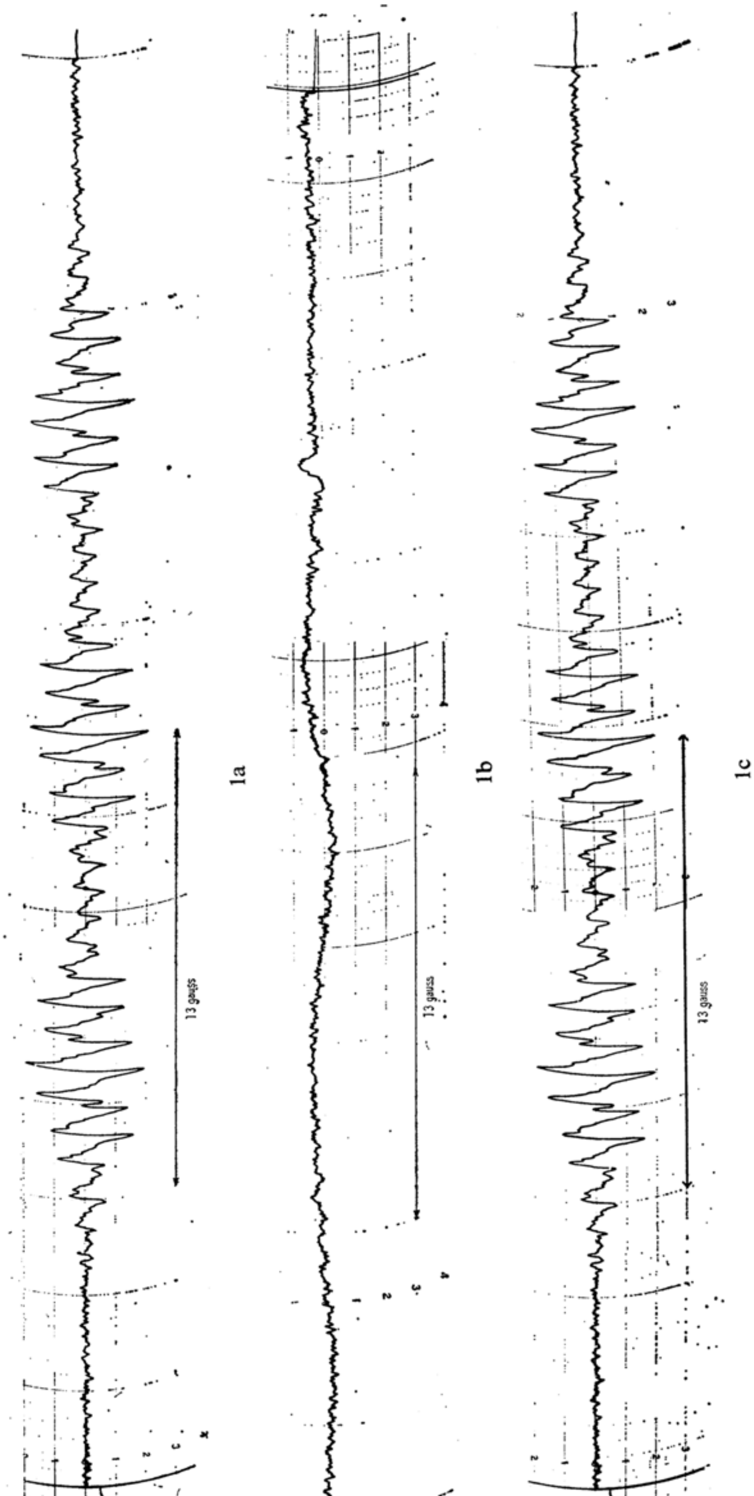
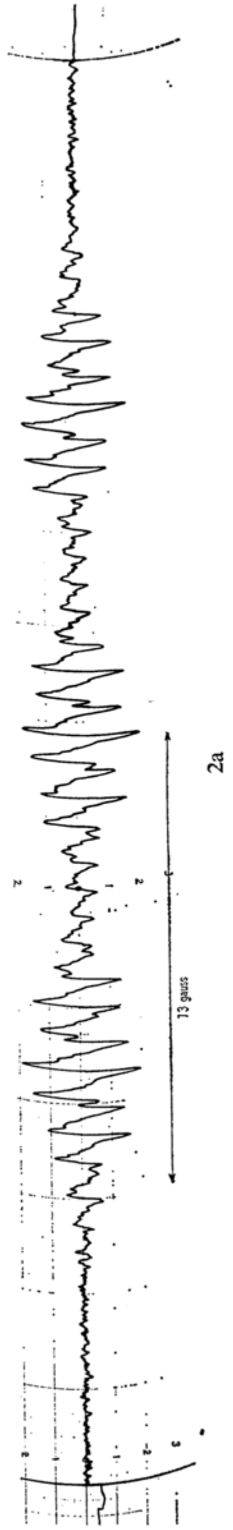
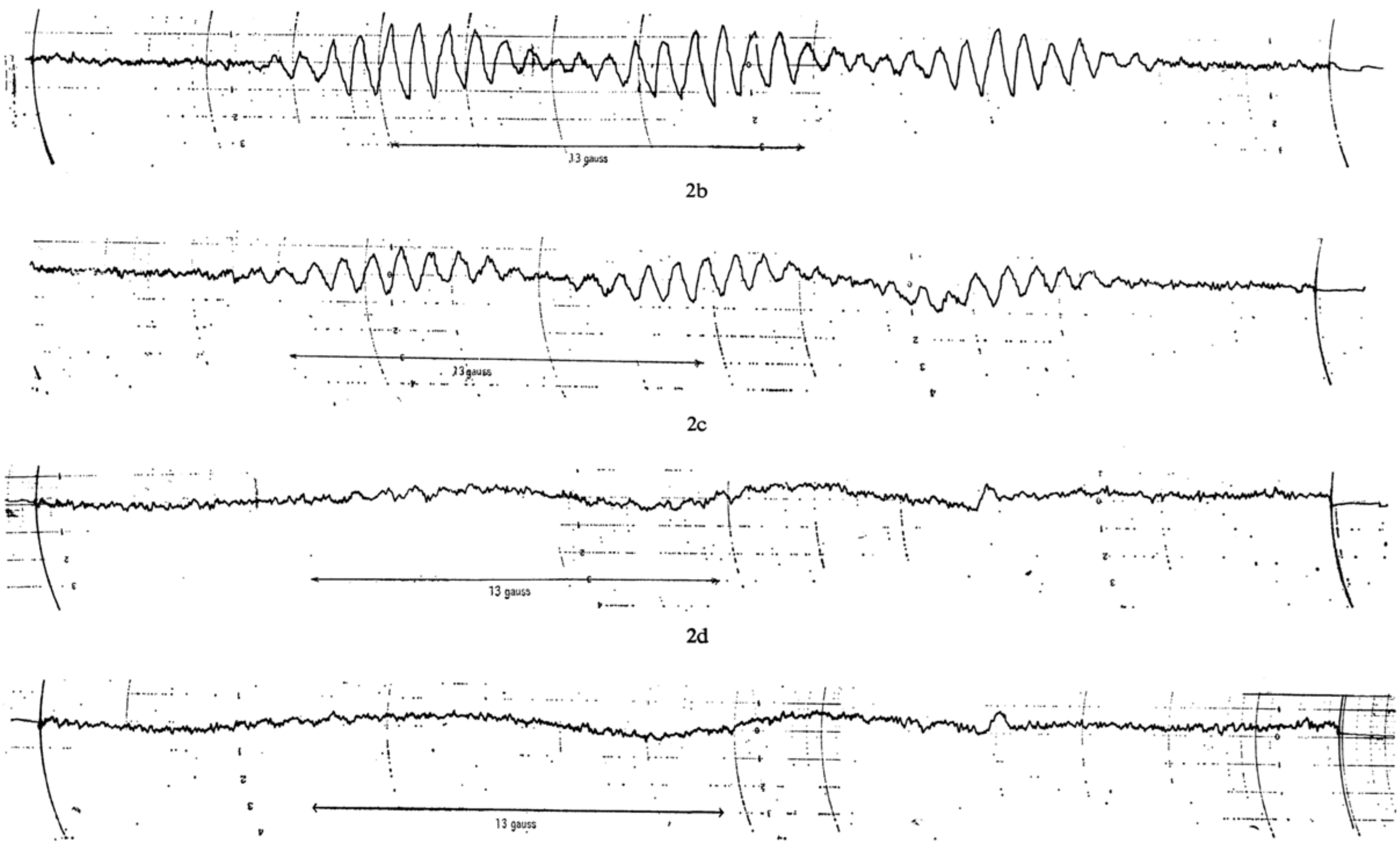


Fig. 1. Dissolved oxygen effect on the ESR spectra of DPNO. 1a: the spectrum of the degassed sample. 1b: the spectrum of the air introduced one. 1c: the spectrum of the again degassed one.



2a



2b

2c

2d

2e

Fig. 2. Dissolved paramagnetic ion effect on the ESR spectra of DPNO. 2a: no dissolved CuTPP presents. 2b, 2c, 2d and 2e: 2/11 mg., 6/11 mg., 10/11 mg. and 52/22 mg. of CuTTP are added into the DPNO sample successively.

TABLE I

Amounts of added CuTPP to the soln. of DPNO, mg.	No. of CuTPP molecules in the soln. per cc.	Increment of a half-width due to addition of CuTPP, gauss	Resulted half-width for the sharpest hf. line, gauss	Illustration of the spectra
0	0	0	0.1	Normal hf. lines appears.
2/11	0.211×10^{18}	0.055	0.1055	Almost all weak hf. lines disappear and the rest are broader.
6/11	0.632×10^{18}	0.165	0.265	Main hf. lines remain but are more broader.
10/11	1.054×10^{18}	0.274	0.374	Only 2 or 3 broad hf. lines remain but broad nitrogen hf. lines can be clearly observed.
52/22	1.097×10^{18}	0.286	0.386	All proton hf. lines disappear and only nitrogen hf. lines are left.

spin-orbit interaction⁽7⁾, etc. but in the case of organic free radicals one can neglect these interactions.

From the above discussion, then, one can conclude that dissolved oxygen or other paramagnetic ions in the solutions play an important role in the broadening of the proton hyperfine lines in the ESR spectra of organic free radicals through the spin-lattice relaxation.

Summary

The broadening effect of dissolved oxygen and foreign paramagnetic ions on the ESR spectra of the DPNO solution has been discussed. Using the BPP theory, it is explained that this effect is mainly caused by the magnetic dipole-dipole interaction of an electron with with a proton nuclear spin.

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(7) N. Bloembergen and L. O. Morgan, ibid., **34**, 842 (1961).