On the EPR Emission Spectrum of Transient Naphthosemiquinone Radical

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EPR spectrum in emission mode at the low-field hyperfine lines was observed for 1,4-naphthosemiquinone radical formed by the steady-state photolysis of solution of corresponding quinone in ethanol flowing through the cavity. Observed behavior of this spectrum was analyzed by a phenomenological way. The results support the view that the anomalous electron spin polarization is generated in the radical formation process. The conclusion was compared with the results of intermittent photolysis.

Since the first observation of EPR emission spectrum (more precisely emission-absorption combined spectrum) for H radical during the radiolysis of alkanes,1) chemically induced dynamic electron spin polarization (CIDEP) in short-lived free radicals has been reported2) and also generated theoretical interests.3) Among several theoretical attempts to interpret the anomalous spin polarization, the most promising mechanism at present seems to be a formation of radical pair, in which nonequilibrium populations of the spin levels arises from the combined effects of an exchange interaction between a radical pair and differences in the Larmor frequencies between the two radicals in the pair. This mechanism leads to the spin polarization which produces the EPR spectra composed of hyperfine lines both in emission and in enhanced absorption at such high field as 3000G. Fessenden applied this radical pair mechanism to interpret the anomalous spectra of H radical1c) and others4) and attained the conclusion that the nonequilibrium population was generated during the decay of the radicals by mutual recombination. This was the reason why the emission-absorption spectrum could be observed during the steady-state radiolysis, though the spin-lattice relaxation time should be much shorter than the chemical lifetime.

However, the radical pair mechanism does not seem to be a general and exclusive one for all CIDEP phenomena, because some photochemically generated transient free radicals were found to give EPR spectra entirely in emission. Among them, Wong and Wan studied the inversion from emission to absorption for 1,4-naphthosemiquinone radical formed in a solution of naphthoquinone in 2-propanol by intermittent photolysis, and found the time constant of about 300 μs for this inversion process.5) They mentioned also that all hyperfine lines of the radical exhibited the same behavior. They proposed, to interpret this observation, a mechanism where the spin polarization occurs in photoexcited naphthoquinone during the course of intersystem crossing from singlet to triplet state and it is retained when the triplet-excited naphthoquinone abstracts a hydrogen atom from solute.5e)

During the course of EPR study of short-lived free radicals under the steady-state photolysis of the solutions of quinones in ethanol, the present authors (H.Y. and T.W.) found an anomalous behavior of the spectrum due to 1,4-naphthosemiquinone radical which was recorded as a combination of emission and absorption.6) This appeared different from the results obtained by Wong and Wan under the intermittent photolysis. Therefore, the study is extended to elucidate the behavior of the spectrum under the steady-state photolysis and the difference between two different photolysis conditions and to understand fully the spin polarization mechanism in this particular free radical.

Experimental

The apparatus used has been described in detail elsewhere.7) EPR measurements were carried out with a conventional X-band spectrometer (Varian, E-3) during photolysis of flowing solution of 1,4-naphthoquinone (3.8 mM) in ethanol with unfiltered light from a super-high pressure mercury arc (Philips, SP 500). The effective volume of a quartz flat cell was 7×0.2×32 mm). Ethanol and naphthoquinone were of analytical grade and were used without further purification. The solution was purged with helium gas before use to remove dissolved oxygen.

Results

Typical examples of the observed spectra are shown in Fig. 1. Although the photochemical reactions involved and the observed hyperfine structures were reported previously,6) they are summarized here briefly. In a neutral solution, naphthosemiquinone anions and naphthosemiquinone radicals are formed simultaneously as shown in Fig. 1a. Their hyperfine structures are illustrated by the stick-spectra. The coupling constants for the anions are 3.25, 0.64 and 0.51 G (two equivalent protons for all three values), which agree with those reported by Wenkataraman *et al.*8) The radical spectrum is identified by referring to the spectrum observed

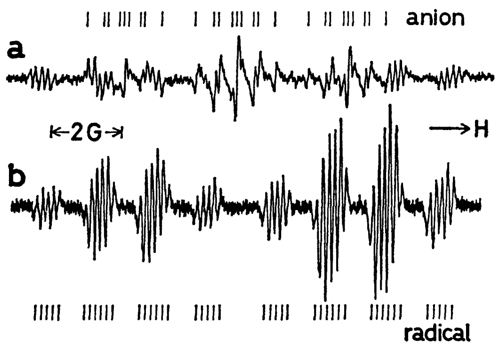

Fig. 1. EPR spectra observed during photolysis of 1,4-naphthoquinone (3.8 mM) (a) in ethanol at the residence time of the solution in the cell 0.07 s and (b) in ethanol with acetic acid (30 mM) at the residence time of 1.2 s.

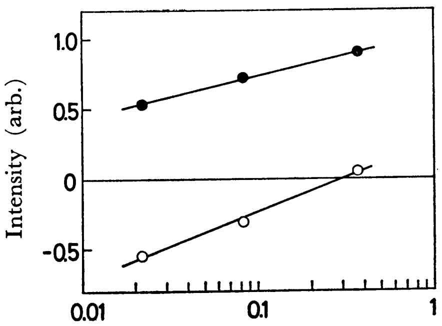

Fig. 2. Dependence of spectral line intensity of the naphthosemiquinone radical formed during the photolysis of naphthoquinone (3.8 mM) solution in ethanol on the residence time of the flowing solution in the cell at 20 °±3 °C, (○) average intensity of the second and fourth hyperfine lines from the low-field extreme and (●) that of the second and fourth lines from the high-field extreme.

when the solution is acidified with acetic acid (Fig. 1b). Its hyperfine coupling constants are temperature dependent and determined to be 6.80, 1.63 (2 protons), 1.50, 0.37 and 0.17 G (2 protons) at 34 °C.

The remarkable feature of the radical spectrum is that the intensity ratio of hyperfine lines depends very much on the flow rate of the solution. At the highest flow rate examined, a half of the spectrum at the low field is recorded as emission lines, whereas the high field half is in absorption (see Fig. 1a). The central part is too weak to be observed clearly. When the flow rate decreases, the emission lines gradually revert to normal absorption. The reversion of the spectrum is illustrated in Fig. 2 by the observed intensity of the second and fourth hyperfine lines from the low field end and those from the high field end as a function of the residence time of the solution in the cell (flow rate/cell volume) with other experimental conditions unchanged. It is surprising that the emission lines are observed not only under the intermittent photolysis condition⁵⁾ but also the steady-state photolysis condition. However, the spectrum is not entirely in emission in the latter case.

The chemical lifetime of the radical was estimated by means of a boxcar integrator and a rotating sector (11 cps) at the residence time of 1 s. The free radicals are thought to disappear by following a second-order kinetics, so that the lifetime may depend on the average concentration. However, the observed curve of radical formation and decay gives a rough estimate of the lifetime, 10 ms in the present photolysis condition.

Discussion

Normal steady-state photolysis is not a pertinent method to study the CIDEP phenomena in detail, because the observed spectra provide the information of spin populations in Zeeman sublevels averaged over the chemical lifetime of the free radical in question. However the steady-state photolysis method has some advantages, because the stability and sensitivity of the measurements are generally better than the time-resolved EPR measurement with flash (or intermittent) photolysis. Therefore, the anomalous behavior of the EPR spectra observed by this method indicates unequivocally, though qualitatively, something about CIDEP. In this discussion, we shall not go into the mechanism of spin polarization in detail but try to interpret phenomenologically the present observations.

Emission-absorption spectra are observed by the steady-state photolysis at high flow rates, but the chemical lifetime of free radicals as well as the residence time of the solution is very much longer than the spin-lattice relaxation time of the free radicals. This seems to indicate that the anomalous spin population is not generated in the radical formation process but by a continuous "pumping" during the decay of the radicals. For simplicity, let us consider a model radical with single proton. According to Fessenden's treatment based on the radical pair theory,⁴⁾ the spin populations are well approximated by the following differential equations:

$$\mathrm{d}(n_2-n_1)/\mathrm{d}t = -\{[(n_2-n_1)-\beta(n/4)]/T_1\} - f_\mathrm{R}k''(n/4)^2 \tag{1}$$

$$\mathrm{d}(n_4-n_3)/\mathrm{d}t = -\{[(n_4-n_3)-\beta(n/4)]/T_1\} + f_\mathrm{R}k''(n/4)^2 \tag{2}$$

where the subscripts 1,2,3 and 4 indicate the Zeeman sublevels $(\alpha_\mathrm{e}, \alpha_\mathrm{N})$, $(\beta_\mathrm{e}, \alpha_\mathrm{N})$, $(\alpha_\mathrm{e}, \beta_\mathrm{N})$ and $(\beta_\mathrm{e}, \beta_\mathrm{N})$, β the Boltzmann factor given by $h\nu/kT$, f_R the fractional degree of polarization induced by the recombination reaction, and k'' the second-order decay constant. For the steady-state photolysis of flowing solution, the number of total spin n changes as the following function of photolysis time, t,

$$n = (c/2k'')^{1/2}\tanh\{(2k''c)^{1/2}t\} \tag{3}$$

when the free radicals in question disappear by a second-order reaction, which should be additionally taken into account. c is the rate of radical formation. The observed intensity of the low-field hyperfine line is proportional to $\tau^{-1}\int_0^\tau (n_2-n_1)\mathrm{d}t$, where τ represents the residence time of solution in the cell.⁹⁾ Although the integration cannot be given analytically, Eqs. (1) and (2) indicate the qualitative nature of the low-field emission line. For the emission line to be observed, (n_2-n_1) should be negative, which turns out that $\mathrm{d}(n_2-n_1)/\mathrm{d}t$ should be negative in an appropriate range of time. Under proper conditions (strictly speaking, when $\beta<k''f_\mathrm{R}T_1(n''_\mathrm{s}/4)$), the emission line develops in $\tau\approx1/k''n''_\mathrm{s}$ and its intensity reaches $\beta(n''_\mathrm{s}/4)\{1-f_\mathrm{R}k''T_1(n''_\mathrm{s}/4)/\beta\}$ at $\tau=\infty$ where n''_s is the steady-state value of $n(=\sqrt{c/2k''})$. The observation that the emission lines are recorded only for big flow rate, or short residence time τ (see Fig. 2) is just contrary to what is theoretically expected on the basis of the phenomenological analysis and excludes the possibility of generation of the anomalous spin population during the decay of radicals.

An alternative approach is that the CIDEP phenomena observed in steady-state photolysis and intermittent photolysis experiments are from the same origin, that is, the anomalous spin polarization generated at the moment of radical formation when, no matter what the operative mechanism is, both (α_e, α_N) and (α_e, β_N) sublevels are overpopulated. Then Eqs. (1) and (2) are modified as follows,

$$\mathrm{d}(n_2-n_1)/\mathrm{d}t = -\{[(n_2-n_1)-\beta(n/4)]/T_1\} - f_\mathrm{F}(c/2) \tag{4}$$

$$\mathrm{d}(n_4-n_3)/\mathrm{d}t = -\{[(n_3-n_4)-\beta(n/4)]/T_1\} - f_\mathrm{F}(c/2) \tag{5}$$

under the assumption that the radical lifetime is much longer than T_1, where f_F represents the fractional degree of polarization induced in the radical formation process. The steady-state treatment can be applied to Eq. (4) except for the small time interval $t \lesssim T_1$, and the approximate relation

$$n_2 - n_1 = \beta(n/4) - f_\mathrm{F}(c/2)T_1 \tag{6}$$

is obtained.

For simplicity, let us assume at first that the radical disappears in the following first-order decay:

$$n = (c/k')\{1-\exp(-k't)\}, \tag{7}$$

where k' represents the first-order decay rate constant. From (6) and (7), the line intensity is derived as

$$\frac{1}{\tau}\int_0^\tau (n_2-n_1)\mathrm{d}t = \beta(\mathrm{n}'_\mathrm{s}/4)\{[1-(2f_\mathrm{F}k'T_1/\beta)] - (1/k'\tau)[1-\exp(-k'\tau)]\}, \tag{8}$$

where n'_s represents the steady-state value of n, c/k'. If $2f_\mathrm{F}k'T_1>\beta$, the emission line is observed regardless of the residence time τ. Even if $2f_\mathrm{F}k'T_1$ is smaller than β but not very much, the line can be in emission at such a low flow rate as $\tau \sim 1/k'$, as shown in Fig. 3. In this case, the line reverts from emission to absorption with increasing τ. If one takes values 1.48×10^{-3} for Boltzmann factor β for 9300 MHz at room temperature, $10^2\,\mathrm{s}^{-1}$ for k' and, arbitrarily 10^{-5} s for T_1, $f_\mathrm{F}=0.7$ well develops the emission line. This f_F value turns out that the enhancement factor $f_\mathrm{F}/2\beta$ of 250, which is compared with the value of 313 estimated by Wong *et al.* for naphthosemiquinone radical based on the intersystem crossing mechanism.[3e)]

For the second-order decay, the line intensity is derived from equations (3) and (6) and expressed by a somewhat complex form as

$$\frac{1}{\tau}\int_0^\tau (n_2-n_1)\mathrm{d}t = \beta(n_\mathrm{s}''/4)\{(\sqrt{2k''c}\cdot\tau)^{-1} \times \ln[\cosh(\sqrt{2k''c}\cdot\tau)] - 2f_\mathrm{F}\sqrt{2k''c}\cdot T_1/\beta\} \tag{9}$$

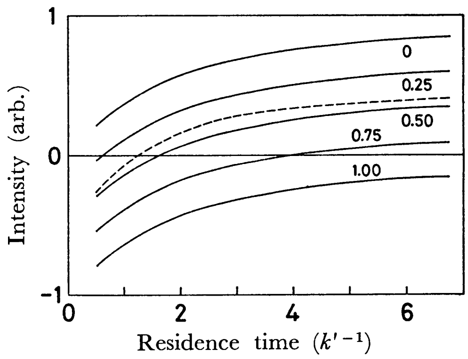

Fig. 3. Dependence of line intensity on the residence time of flowing solution expected from Eq. (8) for the first-order decay of radical. The value of parameter $2f_\mathrm{F}k'T_1/\beta$ for each curve is shown in the figure. The dependence for the second-order decay based on Eq. (9) is shown only for $2f_\mathrm{F}\sqrt{2k''c}\cdot T_1=$ $=0.5$ by a dashed line. The intensity 1.0 corresponds to the Boltzmann distribution and negative intensities represent spectral lines in emission.

The intensity increases from negative to positive value and approaches to the limiting value of $\beta(n''\mathrm{s}/4)\{1-2f_\mathrm{F}\cdot\sqrt{2k''c}\cdot T_1/\beta\}$ in similar manner as that for the first-order decay. The difference in the dependence of the intensity upon τ is not significant between the second-order decay and the first-order one, as shown in Fig. 3 representatively for $2f_\mathrm{F}\sqrt{2k''c}\cdot T_1/\beta=0.5$. Therefore, behavior of the spectrum is not seriously affected by the mode of radical decay except for unrealistically small values of τ.

It is most crucial to test whether the totally emissive spectrum immediately after the photolysis with pulsed light can be recorded as the emission-absorption spectrum under the steady-state photolysis. Really it can if f_F and/or T_1 are dependent on the nuclear spin state (in the simplified single proton model radical, dependent on the state α_N or β_N) as shown in Fig. 3. Assuming that the value of $2f_\mathrm{F}\sqrt{2k''c}\cdot T_1$ is slightly smaller for the high field lines in naphthosemiquinone radical spectrum, they revert to absorption, as a function of τ, much quicker than the low field lines do.

Paramagnetic relaxation times were tried to be measured from the cw saturation and the line width. They were estimated as $T_1 \sim T_2 \sim 10^{-6}$ s and their dependence on hyperfine lines could not be observed. However, the relaxation times based on the cw saturation may not be reliable enough to be involved in the present discussion of CIDEP. In addition, it was claimed by Atkins *et al.*[10)] that a simple T_1 determination using the saturation properties of an emission is invalid.

In conclusion, the latter approach is reasonable to interpret the emission-absorption spectrum of naphthosemiquinone radical observed during steady-state photolysis of the flowing solution of naphthoquinone in ethanol. Although the flow rate is very slow compared with T_1, the anomalous spin polarization observed is generated at the radical formation rather than at the radical recombination. It was shown that the emission-absorption spectrum in the present study can be consistent, by choosing proper parameters, with the totally emissive spectrum previously observed by the intermittent photolysis. However, to attain the rigid conclusion, it is essentially desirable to examine the behavior of the emission lines of this particular radical by a time-resolved EPR measurements for a long time duration after a photolysis pulse, even though it may be difficult experimentally because of weak signal intensities.

Finally, it should be noted that the hyperfine lines at the high field of the naphthosemiquinone radical spectrum are in reduced absorption, as the population difference between electronic Zeeman sublevels is smaller than that in Boltzmann distribution as illustrated in Fig. 3. This feature is in contrast to the enhanced absorption observed for the high-field line of the H radical spectrum in which the radical pair mechanism is operative at the radical disappearance. The present investigation suggests that the reduced absorption may sometimes occur for the electron paramagnetic resonance of short-lived free radicals which are known to give asymmetric EPR spectra very often.

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