Chemically Induced Dynamic Nuclear Polarization in the Photochemical Reaction of Phenanthraquinone with Hydrogen Donors. I. Kinetics of Nuclear Spin Polarization[1]

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(Received February 23, 1971)

Strongly-enhanced NMR signals were observed in the photo-induced hydrogen abstraction reaction of phenanthraquinone with several hydrogen donors in benzene. Chemically-induced dynamic nuclear polarization was kinetically treated in the photochemical reaction during the course of irradiation by visible light and shut-off. It was found that the relaxation time of the nuclear-spin system under the irradiation is shorter by a factor of 2 to 4 than that in the black-out stage and that the enhancement factor for the methine proton of the 1,2-adduct of phenanthraquinone was evaluated as 1000—2000.

Of the products of the rapid radical reaction, their proton NMR spectra are often observed as an enhanced absorption and/or emission line during the course of the reaction.[2–11] This phenomenon is called "chemically-induced dynamic nuclear polarization (CIDNP)"[3]

Since the discovery of this phenomenon by Fischer and Bargon,[2,3] many kinds of radical reactions have been investigated by several workers from the standpoint of CIDNP.[4–9] Thus, Closs and his co-workers[10] and Kaptein and Oosterhoff[11] recently proposed a model of a radical pair as an intermediate of the reaction, and showed that the CIDNP phenomenon originates from the mixing between the electronic singlet and triplet states of the radical pair. Their theory (CKO theory)[10,11] seems to have been accepted as the explanation of CIDNP phenomenon.

CIDNP is dynamic in its nature; nevertheless, no phenomenological treatments have been made from the point of view of kinetics. For simplicity, we preferred the photo-induced chemical reaction to any other type of radical reaction, that is, the hydrogen abstraction reactions of phenanthraquinone with fluorene, xanthene, diphenylmethane, and 9,10-dihydroanthracene in benzene. In these reactions, the 1,2-type adduct[12] of phenanthraquinone with hydrogen donors mentioned above is known to be mainly produced.[13]

The NMR singlet spectrum of the methine proton of the adduct of each of hydrogen donors revealed a strongly-enhanced absorption; the nuclear-spin polarization of this methine proton will be kinetically discussed.

Experimental

Materials. Phenanthraquinone was prepared by oxidation of phenanthrene with pottassium dichromate and was repeatedly purified by the recrystallization method from its acetic acid solution. It has a mp of 202—206°C and $\lambda_{\max}=410$—$420\ \mathrm{m}\mu$ in the UV spectrum. Commercially-available guaranteed-grade reagents, used as hydrogen donors to phenanthraquinone, were used without further purification. A benzene solution of 2.3×10^{-2} M of phenanthraquinone and 1.0M of the hydrogen donor was sufficiently degassed in vacuum and submitted to NMR measurements.

Apparatus. The NMR spectra were observed at 60 MHz by the use of a spectrometer of the C-60HL type (JEOL· Co. Ltd.). A saw-tooth wave generator (JEOL. Co. Ltd.) was used to measure the variation in the spectrum intensity with the time.

In order to induce a photochemical reaction within the NMR probe, we modified the probe for introducing UV or visible light as follows. The light source (Ushio high-pressure Hg lamp, 500W) is placed above the magnet. The focused light from the source is guided into the probe through a hole, reflects once on the aluminum mirror attached within the probe, and then arrives at the sample. In order to be used effectively, the light is forced to pass to the sample again by means of a concave aluminum mirror.

Theory

Phenanthraquinone (PQ) I in benzene is photochemically excited to a triplet state, II, with a fairly long lifetime, τ; II returns to a singlet ground state with the emission of fluorescence.[14]

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[1] This work has been done at the Department of Chemistry, College of Liberal Arts and Science, Kyoto University.

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[10] G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2183 (1970); G. L. Closs, C. E. Doubleday, and D. R. Paulson, *ibid.*, **92**, 2185 (1970); G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2186 (1970).

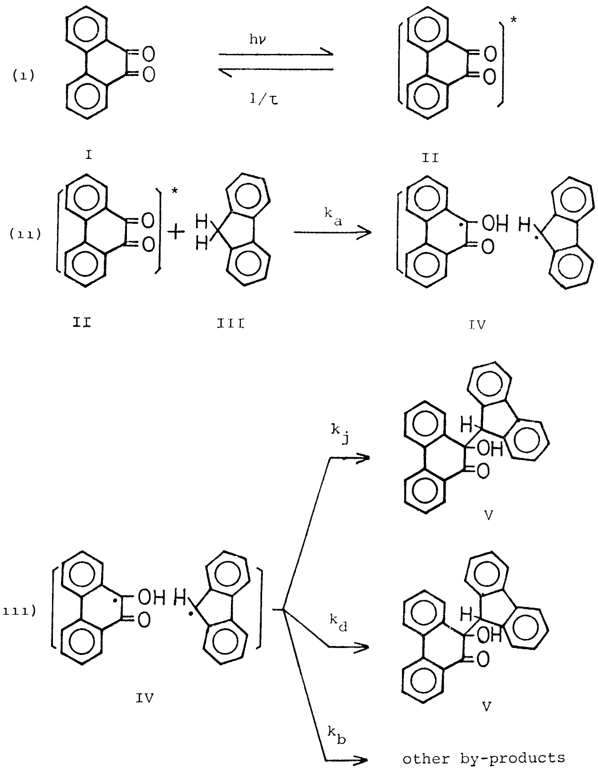
[11] R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969).

[12] See structure V.

[13] These reactions are, in general, very clean, and almost all of the products are 1,2-type adducts. The details of the structure of the photo-adduct will be reported in the near future.

[14] Although PQ is activated to an excited singlet state at first through $n\rightarrow\pi^*$ excitation, the molecule is transformed to a triplet state by inter-system crossing.

When a hydrogen donor (III), for instance, fluorene, is present, hydrogen abstraction reaction easily proceeds with a specific rate constant of k_a, simultaneously, a radical pair, IV, may be formed, as was assumed in CKO theory.[10,11]



The radical pair, IV, was assumed to yield the products through three processes. One is the process producing the 1,2-adduct V directly from the radical pair. The specific rate constant of this process, k_j, is assumed to depend on the nuclear spin state of the 1,2-adduct, in accordance with the CKO theory. Thus, the nuclear-spin polarization occurring in the adduct is produced only through this process. The second process, occurring with a rate constant of k_d is related to the separation and recombination of the radical pair to give the 1,2-adduct. However, the nuclear-spin polarization of the adduct generated through this process is considered to be less important in our system.[15]

The last process of the three is assumed to be associated with the process giving other by-products.

For convenience, we may rewrite the reaction processes, (i), (ii), and (iii), as follows:

$$\begin{tikzcd}
 & & & Z_j^* \\
X \arrow[r, shift left, "k_0"] & X^* \arrow[l, shift left, "1/\tau"] \arrow[r, "k_a"] & Y \arrow[ur, "k_j"] \arrow[r, "k_d"] \arrow[dr, "k_b"'] & Z_j' \\
 & & & \text{by-products}
\end{tikzcd}$$

Also, the nuclear-spin system polarized through the reaction process mentioned above will, with the relaxation time, T_1, approach the thermal equilibrium;

$$Z_j \underset{1/2T_1(k,\,j)}{\overset{1/2T_1(j,\,k)}{\rightleftarrows}} Z_k$$

where the two suffixes, j and k, represent, respectively, jth and kth nuclear spin state of the 1,2-adduct, and where $T_1(j,k)$ is the relaxation time between jth and kth nuclear-spin states. The population of the jth nuclear spin state of the 1,2-adduct, $[Z_j^*]+[Z'_j]$, is denoted by $[Z_j]$.

In the case of a sufficiently concentrated solution of PQ, the increase in the rate of X*, k_o, may be considered to be independent of the concentration of PQ, [X]. It depends only on the intensity of the light used; that is, this reaction process is of the zeroth order. The reaction process from X* to Y may be regarded as quasi-first order because of the large excess of the hydrogen donor compared with that of PQ. The other processes are first order in their natures. Thus, we may write the rate of chemical change during the course of the light irradiation as follows;

$$\frac{d[X^*]}{dt} = k_0 - (1/\tau + k_a)[X^*] \tag{1}$$

$$\frac{d[Y]}{dt} = k_a[X^*] - \sum_j (k_j + k_d + k_b)[Y] \tag{2}$$

$$\frac{d[Z_j]}{dt} = (k_d + k_j)[Y] - \sum_k 1/2T_1^*(j,\,k) \times (\langle[Z_j]-[Z_k]\rangle - \langle[Z_j]-[Z_k]\rangle_0) \tag{3}$$

where $\langle[Z_j]-[Z_k]\rangle_o$ is the difference in populations between the jth and kth energy levels in the thermal euilibrium; the use of T_1^* in place of T_1 indicates the relaxation time during irradiation.

As the signal of photo-adduct in the thermal equilibrium can not be observed even after the chemical change proceeded, the term $\langle[Z_j]-[Z_k]\rangle_o$ may be ignored in Eq. (3). In general, a solution of Eq. (3) can not be analytically obtained, so we will deal with the case of the single spin system alone. In such a case, we can replace Eq. (3) by;

$$\frac{d[Z_1]}{dt} = (k_d + k_1)[Y] - 1/2T_1^*\langle[Z_1]-[Z_2]\rangle \tag{4}$$

$$\frac{d[Z_2]}{dt} = (k_d + k_2)[Y] - 1/2T_1^*\langle[Z_1]-[Z_2]\rangle \tag{5}$$

From Eqs. (4) and (5), we obtain;

$$\frac{d\langle[Z_1]+[Z_2]\rangle}{dt} = \sum_{j=1}^{2}(k_j + k_d)[Y] \tag{6}$$

$$\frac{d\langle[Z_1]-[Z_2]\rangle}{dt} = (k_1 - k_2)[Y] - 1/T_1^*\langle[Z_1]-[Z_2]\rangle \tag{7}$$

On integrating Eqs. (1) and (2), and considering that X* and Y are zero when t is zero, the concentrations of PQ* and the radical pair are given by;

$$[X^*] = \frac{k_0}{1/\tau + k_a}(1 - e^{-t/\tau - k_a t}) \tag{8}$$

$$[Y] = \frac{k_0 k_a}{1/\tau + k_a}\left\{\frac{1}{\sum(k_j + k_d + k_b)}(1 - e^{-\Sigma(k_j + k_d + k_b)t}) - \frac{1}{\sum(k_j + k_d + k_b) - 1/\tau - k_a}(e^{-t/\tau - k_a t} - e^{-\Sigma(k_j + k_d + k_b)t})\right\} \tag{9}$$

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[15] This can be concluded from the following two experimental observations: i) the rate of hydrogen abstraction by phenanthraquinone and the successive recombination of radicals formed are usually too fast for intermediate radicals to be observed by the ESR technique, and ii) the fact described in footnote 13).

Since it is reasonable that $\sum(k_j+k_d+k_b) \gg 1/\tau+k_a$ and $1/T_1{}^*$, the solutions of Eqs. (6) and (7) can be approximated by;

$$\langle[\mathrm{Z}_1] + [\mathrm{Z}_2]\rangle = \frac{k_0 k_d(k_j+k_d)}{(1/\tau+k_a)\sum(k_j+k_d+k_b)} \times \left(t + \frac{1}{1/\tau+k_a}\mathrm{e}^{-t/\tau-k_a t}\right) \tag{10}$$

$$\langle[\mathrm{Z}_1] - [\mathrm{Z}_2]\rangle = \frac{k_0 k_a(k_1-k_2)T_1{}^*}{(1/\tau+k_a)\sum(k_j+k_d+k_b)}\left\{(1-\mathrm{e}^{-t/T_1{}^*}) - \frac{1/T_1{}^*}{1/T_1{}^*-1/\tau-k_a}(\mathrm{e}^{-t/\tau-k_a t}-\mathrm{e}^{-t/T_1{}^*})\right\} \tag{11}$$

by using Eq. (9).

Next, let us consider the case when the irradiation is shut off at a certain time, $t=t_o$, after the establishment of a steady-state nuclear polarization. The rate of the chemical reaction (1) is replaced by;

$$\frac{\mathrm{d}[\mathrm{X}^*]}{\mathrm{d}t} = -(1/\tau+k_a)[\mathrm{X}^*] \tag{12}$$

On integrating Eqs. (2), (9), and (12) under appropriate initial conditions,[16] the expression of $\langle[\mathrm{Z}_1]-[\mathrm{Z}_2]\rangle$ is given by Eq. (13);

$$\langle[\mathrm{Z}_1] - [\mathrm{Z}_2]\rangle = \frac{k_0 k_a(k_1-k_2)T_1}{(1/\tau+k_a)\sum(k_j+k_d+k_b)} \times \left\{\frac{1/T_1}{1/T_1-1/\tau-k_a}\mathrm{e}^{-(1/\tau+k_a)(t-t_0)} - \frac{1/\tau+k_a}{1/T_1-1/\tau-k_a}\mathrm{e}^{-(t-t_0)/T_1}\right\} \tag{13}$$

after being approximated in the same manner as was done in Eqs. (10) and (11). The relaxation time under the off-irradiation is denoted by T_1 in order to distinguish it from the relaxation time under the irradiation, $T_1{}^*$.

If $1/T_1{}^*$ and $1/T_1 \ll 1/\tau+k_a$, the signal intensity in the irradiating stage increases in accordance with the following expression;

$$\langle[\mathrm{Z}_1] - [\mathrm{Z}_2]\rangle = \frac{k_0 k_a(k_1-k_2)T_1{}^*}{(1/\tau+k_a)(k_1+k_2+2k_d+2k_b)}(1-\mathrm{e}^{-t/T_1{}^*}) \tag{14}$$

as may be found from Eq. (11). On the other hand, the signal after blacking-out is diminished exponentially as follows;

$$\langle[\mathrm{Z}_1] - [\mathrm{Z}_2]\rangle = \frac{k_0 k_a(k_1-k_2)T_1}{(1/\tau+k_a)(k_1+k_2+2k_d+2k_b)}\mathrm{e}^{-(t-t_0)/T_1} \tag{15}$$

as may be seen from Eq. (13). We obtain the envelope curve depicted by signal peaks during the irradiation and black-out.

The enhancement factor is defined by;

$$P = \frac{\langle \mathrm{I}\rangle - \langle \mathrm{I}\rangle_0}{\langle \mathrm{I}\rangle_0} \simeq \frac{\langle \mathrm{I}\rangle}{\langle \mathrm{I}\rangle_0} = \frac{\langle[\mathrm{Z}_1]-[\mathrm{Z}_2]\rangle}{\langle[\mathrm{Z}_1]-[\mathrm{Z}_2]\rangle_0} \tag{16}$$

where $\langle \mathrm{I}\rangle_o$ is the expectation value of the spin-angular momentum in the thermal equilibrium. The value of $\langle[\mathrm{Z}_1]-[\mathrm{Z}_2]\rangle_o$ can be obtained from the value of $\langle[\mathrm{Z}_1]+[\mathrm{Z}_2]\rangle$ on the basis of Boltzmann's law. Thus, the enhancement factor at a certain time in a steady-state can easily be found from Eqs. (10) and (11);

$$P = \frac{(k_1-k_2)T_1{}^*}{(k_1+k_2+2k_d+2k_b)t} \cdot \frac{2kT}{\Delta E} \tag{17}$$

where ΔE is the energy difference between the two energy levels of the spin system; k, Boltzmann constant, and T, the absolute temperature.

Results

Phenanthraquinone (PQ) is photochemically induced to yield its 1,2-adducts in the presence of hydrogen donors. For example, when a solution of 2.3×10^{-2}M of PQ and 1.0M of fluorene in benzene was irradiated inside the probe, an enhanced singlet line of the methine proton of the 1,2-adduct was observed at a field lower by about 45 Hz from the chemical shift of the methylene protons of fluorene. This is shown for fluorene and xanthene in Fig. 1. That such an absorption line is strongly enhanced is shown by its collapse after the irradiation was shut off.

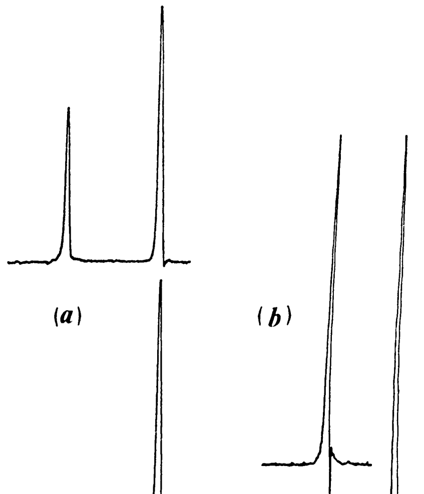

Fig. 1. Enhanced and normal NMR spectra in the photochemical reaction of phenanthraquinone (2.3×10^{-2}M) with hydrogen donor (1.0M) in benzene.

The envelope curves of the singlet lines in Figs. 2 and 3 were obtained at 70°C by field scanning repeated with a saw-tooth wave of 1 Hz for both fluorene and xanthene. Figures 4—6 show the envelope curves for the adducts of fluorene, xanthene, diphenylmethane, and 9,10-dihydroanthracene at 30° and 50°C. As can be seen from these figures, the signal intensity increases exponentially just after the application of light and then establishes its steady-state. When the irradiation is shut off at a certain time, $t=t_o$, signal is diminished exponentially. The values of the loga-

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[16] The initial conditions, that is, the concentrations of X,* Y, and $<[\mathrm{Z}_1]-[\mathrm{Z}_2]>$ at $t=t_0$ may be given by the respective values at $t=\infty$ in Eqs. (8), (9), and (11); $[\mathrm{X}^*]=k_0/(1/\tau+k_a)$, $[\mathrm{Y}]=k_0k_a/(1/\tau+k_a)\times\sum(k_j+k_d+k_b)$ and $<[\mathrm{Z}_1]-[\mathrm{Z}_2]>=k_0k_a \times T_1{}^*/(1/\tau+k_a)\sum(k_j+k_d+k_b)$ were used.

rithms of the signal intensities, $I_\infty - I_t$ and I_{t-t_0}, are plotted against the time (see Fig. 7). Here, I_∞ and I_t represent the signal intensities at the steady-state and at a certain time, t. As may be seen in Fig. 7, the fact that these plots fall on a straight line indicates an exponentially time-dependent nature of the signal intensity. Thus, it may be found that the relaxation times, T_1^* and T_1, in Eqs. (14) and (15) can be determined from the slopes of straight lines in Fig. 7. The values of T_1^* and T_1 are given in Table 1.

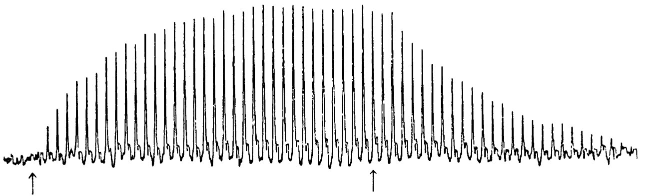

Fig. 2. Envelope curve of enhanced signals due to the methine proton of the adduct of fluorene (field-scanning with saw-tooth wave of 1 Hz, 70°C). Arrows in figure indicate a starting point of the irradiation, $t=0$ and a point of the black-out $t=t_0$.

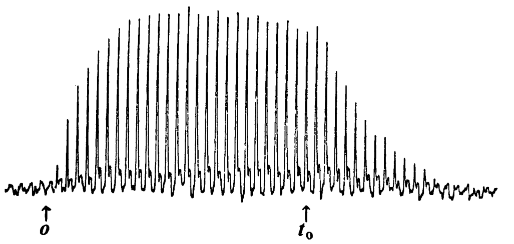

Fig. 3. Envelope curve of enhanced signals due to the methine proton of the adduct of xanthene at 70°C.

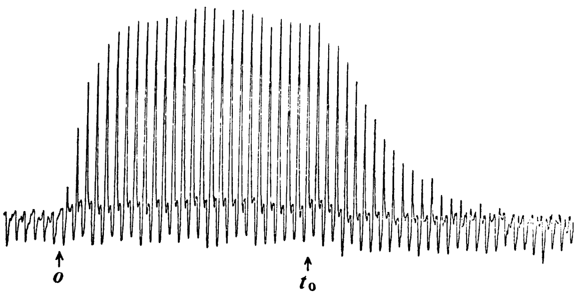

Fig. 4. Envelope curve of enhanced signals due to the methine proton of the adduct of fluorene at 50°C.

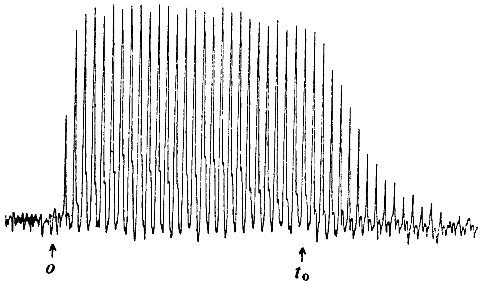

Fig. 5. Envelope curve of enhanced signals due to the methine proton of the adduct of xanthene at 50°C.

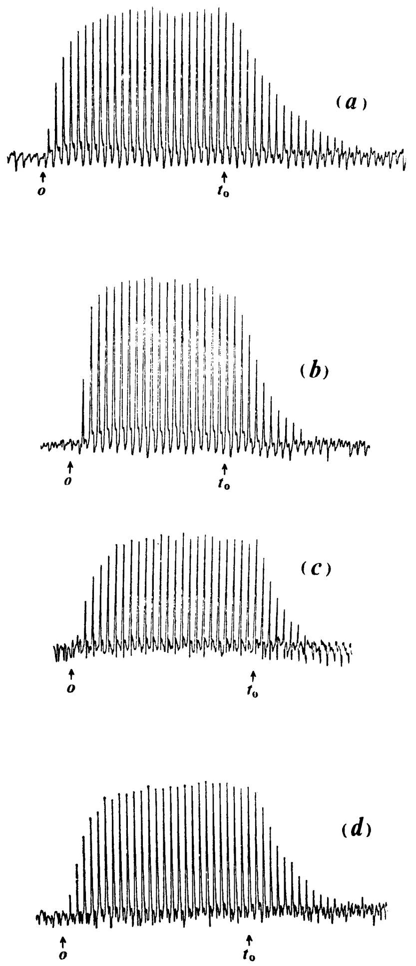

Fig. 6. Envelope curves of enhanced signals due to the methine proton of the adducts of fluorene (a) and xanthene (b) at 30°C, and those of diphenylmethane (c) and 9,10-dihydro-anthracene (d) at 50°C.

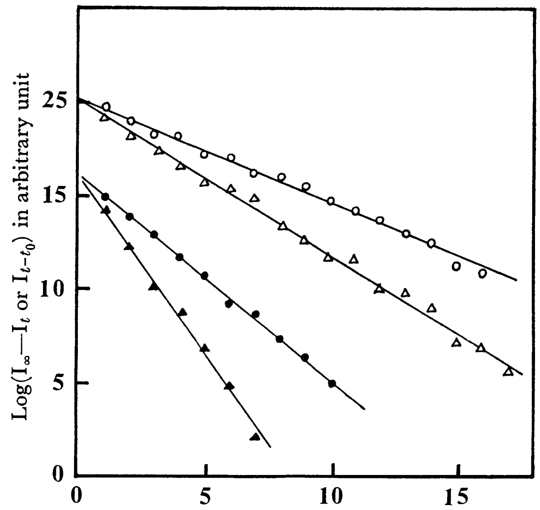

Fig. 7. The time-dependent intensity change of enhanced signals for the adducts of fluorene and xanthene.

△: $\log(I_\infty - I_t)$ for fluorene after the irradiation
○: $\log I_{t-t_0}$ for fluorene after the black-out
▲: $\log(I_\infty - I_t)$ for xanthene after the irradiation
●: $\log I_{t-t_0}$ for xanthene after black-out

TABLE 1. RELAXATION TIMES T_1* AND T_1 EVALUATED FROM THE ENVELOPE CURVES OF THE ENHANCED SIGNALS

Hydrogen donors	Temperature(°C)	T^*_1 (sec)	T_1 (sec)	Signal intensity[a)]
Fluorene	30	2.1	6.8	
	50	2.6	7.0	2.0
	70	6.6	9.4	
Xanthene	30	1.0	3.6	
	50	0.9	4.3	2.3
	70	3.0	4.6	
Diphenylmethane	50	2.3	3.2	1.8
9,10-Dihydroanthracene	50	2.6	4.4	3.9

a) See the text.

Now, we are interested in the relative values of $\langle[Z_1]-[Z_2]\rangle$, which are proportional to the signal intensity. The intensity ratios of the enhanced signal to the intensity per proton of a methylene group of a given hydrogen donor (concentration; 1.0M) in a benzene solution were evaluated as shown in the last column in Table 1.

Discussion

The envelope curves of enhanced signals are shown in Figs. 2 to 6; the figures represent the typical nature of these photochemical reactions. Contrary to the usual conception of photochemical reactions, in the photo-induced CIDNP examined here the rate constants of nuclear polarization after the irradiation and black-out differed by a factor of about 2 to 4 (see Table 1). It was mentioned in the previous section that the rate constants for nuclear-spin polarization are controlled by the relaxation times of the nuclear-spin system.

For fluorene at 50°C, the relaxation time during the irradiation is 2.6 sec and that under the black-out is 7.0 sec. It is found that the value of T_1* is generally smaller than that of T_1 and that the ratio of T_1^*/T_1 approaches a unit value with an increase in the temperature. These facts may be responsible for the presence of paramagnetic species during the irradiation, whose concentration must decrease with an increase in the temperature. This is because the relaxation time is inversely proportional to the concentration of paramagnetic species.[17)] The steady-state concentration of PQ* is given by (see Eq. (4));

$$[X^*] = \frac{k_0}{1/\tau+k_a}$$

Since the specific rate, k_a, can be considered to increase with an increase in the temperature in the temperature range of 30° to 70°C, the steady-state concentration of PQ* decreases with an increase in the temperature, as may be seen from the last equation. On the other hand, the value of T_1 may well give the usual relaxation time because of the rapid collapse of PQ* just after blacking-out. The facts that the T_1^*/T_1 ratio is smaller than the unit value and that it increases with an increase in the temperature can reasonably be explained in terms of the presence of activated phenanthraquinone PQ* during the irradiation of light.

The enhancement factor, P, is defined as the expression (16); hence, it is experimentally determined from the ratio of the intensity of the enhanced signal to that of the standard solution as follows;

$$P = \frac{[Z]_s}{[Z]_p} \times \frac{I_p}{I_s} \tag{18}$$

where $[Z]_p$ and $[Z]_s$ are the concentration of the proton associated with the enhanced signal and that of the standard methylene protons of hydrogen donors respectively. I_p and I_s represent the signal intensity of the enhanced and that of the standard protons.

In our case, the increase in the rate of the adduct, $[Z]_p=[Z_1]+[Z_2]$, is given by Eq. (10). Since phenanthraquinone exclusively yields 1,2-adducts, $2k_b$ can be neglected compared with $(k_1+k_2+2k_d)$. Thus, one obtains the following expression for the increase in the rate of the 1,2-adduct in the steady-state polarization;

$$[Z]_p = k_0t$$

The light was very difficult to apply uniformly over the whole of the sample; hence, the exact value of k_0 could not be determined. However, it may be roughly evaluated as below. When the irradiation was kept on continuously, the steady-state polarization was found to be suddenly broken at a certain time, t_b, which was about 100 sec or more at 50°C in all of our experiments. This is the time where the zeroth-order approximation can not hold any longer for the reaction process from X to X*; thus, the concentration of phenanthraquinone at t_b is found to be rather small. Thus, the ratio of the initial concentration of phenanthraquinone to the time, $[X]_0/t_b$, may be taken as the value of k_0. Remembering that $[X]_0=2.3\times 10^{-2}$M, we find that $k_0 \gtrsim 2\times10^{-4}$ mol/l/sec.

The value of I_p/I_s is in the range of 2 to 4 (see Table 1). Since $[Z]_s$ is 1.0M, we find that the enhancement factor, P, should amount to the value of 1000—2000 at $t=10$ sec just after the irradiation.

The authors wish to thank Mr. Shozo Shimizu (JEOL (USA), Inc.) for his helpful suggestions for modifying the NMR probe for photochemical reactions.

[17)] I. Solomon, *Phys. Rev.*, **99**, 559 (1955).