

Direct analysis of hydrogen transfer reaction from *p*-benzosemiquinone radical to *p*-benzoquinone by time-resolved CIDNP method

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Abstract—The rate constant of the hydrogen transfer reaction from *p*-benzosemiquinone radical to *p*-benzoquinone was measured by the time-resolved CIDNP technique. The time dependence of the CIDNP intensity of the products, *p*-benzoquinone and *p*-hydrobenzoquinone, can be simulated by kinetic treatment. From the simulation, the rate constant of the hydrogen transfer is obtained.

INTRODUCTION

THE DEGENERATE hydrogen transfer reaction process of the intermediate radical, represented schematically as

$$\dot{\mathbf{R}}\mathbf{H} + \mathbf{R} \to \mathbf{R} + \dot{\mathbf{R}}\mathbf{H},\tag{1}$$

often plays an important role in the radical reactions. As the reactants and the products are identical, however, it is difficult to experimentally determine the rate constant of this reaction. For example, the reaction cannot be studied by optical spectroscopy such as transient absorption. One might perhaps examine the reaction by ESR spectroscopy [1-3]; the rate constant could be determined by the analysis of a modified Bloch equation [4, 5]. This method is, however, complicated and, moreover, the effect is very small in the case of hydrogen transfer from the paramagnetic species to the diamagnetic species. The time-resolved CIDNP method [6-8], on the other hand, is probably the most direct method to pursue the above reaction if the intermediate radical has nuclear spin polarization. In this case, reaction (1) can be represented as follows:

$$\dot{R}H^* + R \rightarrow R^* + \dot{R}H, \qquad (2)$$

where an asterisk denotes the nuclear spin polarized species. Since the CIDNP method can detect the nuclear spin polarized diamagnetic species, R^* , we can easily distinguish between the reactant and the product of the hydrogen transfer reaction. Further, with the time-resolved CIDNP method we can directly observe the dynamics of generation of the product that has nuclear spin polarization, and analyse the kinetics of this hydrogen transfer reaction [9].

In this paper, we try to measure the photo-induced hydrogen abstraction reaction of p-benzoquinone by the time-resolved CIDNP method and to estimate the rate constant of hydrogen transfer from the p-benzosemiquinone radical ($\dot{R}H$) to p-benzoquinone (R) with simulation by simple kinetics.

EXPERIMENTAL

The experimental set-up for the time-resolved CIDNP measurement is shown in Fig. 1. The light from a Lumonics EX-400 XeCl excimer laser ($\lambda = 308$ nm) excites a sample placed in a JEOL FX-100 NMR spectrometer, and CIDNP of the reaction product is measured. To remove the NMR signal of the reactants, the presaturation pulse sequence shown in Fig. 2 was applied [10]. Though the presaturation pulses should completely remove the signal of the reactants, a small amount of the NMR signal is observed owing to the nuclear spin relaxation during the delay time from the end of the presaturation pulse to the onset of the observation pulse (20 ms; see Fig. 2). The intensity of the signal thus produced by the relaxation is about one fiftieth of the normal NMR intensity at the Boltzmann equipment. The delay time from the laser pulse to the observation pulse was controlled



Fig. 1. Experimental set-up. The sample is excited by an XeCl excimer laser ($\lambda = 308$ nm) in an NMR magnet ($B_0 = 2.35$ T).

by a Stanford DG535 digital delay generator. The laser pulse length is 20 ns and the observation pulse length is $5 \mu s$ (= 30° tip angle).

We studied *p*-benzoquinone in chloroform- d_3 . *p*-Benzoquinone was recrystallized from ethanol. Commercial Aldrich 99.5% grade chloroform- d_3 was used without any further purification. The experiments were carried out for 0.01, 0.02 and 0.04 M solutions.

RESULTS AND DISCUSSION

The photo-induced hydrogen abstraction reaction of p-benzoquinone (BQ) has already been investigated [11] and the mechanism is shown in Fig. 3. The hydrogen donor RH is CHCl₃ included in a solvent.

In the high-field CIDNP experiment, the sign of the nuclear spin polarization is predicted by the KAPTEIN rule [12]. The KAPTEIN rule is expressed as $\Gamma = \mu \epsilon \Delta g A$. In our case, the precursor is the triplet ($\mu = +$), the g-factor difference ($\Delta g = g_{BQ} - g_{CHCl_3}$) is



Fig. 2. Pulse sequence. The first HS-90°-HS pulse sequence is the presaturation pulse sequence, which removes the contribution from the reactants. The delay time from the laser flash to the observation pulse, τ , is controlled by a digital delay generator.



Fig. 3. Reaction scheme of photo-induced hydrogen abstraction reaction of BQ. (a) Diffusion to free radical. (b) Geminate recombination. (c) Hydrogen transfer reaction. (d) Reaction from F-pair. An asterisk denotes the nuclear polarized species.

negative and the hyperfine coupling constant of BQ (A_{BQ}) is also negative [13]. Therefore, the sign of the geminate product $(\varepsilon = +)$ should be absorptive $(\Gamma = + + - - = +)$. On the other hand, the products from the free radical $(\varepsilon = -)$ should be emissive $(\Gamma = + - - - = -)$. Thus, the KAPTEIN rule predicts that the product generated in the process (b) in Fig. 3 has absorptive nuclear spin polarization and the products generated in the processes (c) and (d) have emissive polarization.

The NMR spectra observed during the photolysis of a 0.01 M BQ solution are shown in Fig. 4. The peak at 6.7 ppm is assigned to BQ, and the peak at 6.6 ppm is assigned to *p*-hydrobenzoquinone (BQH₂). Since the signal of BQ obtained before laser excitation is caused by the nuclear spin relaxation of BQ, the nuclear spin polarization can be obtained by subtracting this intensity from each CIDNP signal. The delay time dependence of the CIDNP intensity thus determined is shown in Fig. 5. The signal of BQ is absorptive at the early time and is converted to emission at the later time. The signal of BQH₂, on the other hand, is emissive at all times, and the intensity of the emissive peak increases with time.

The absorption in the earlier time region of BQ is observed as early as $2\mu s$. The sign of CIDNP indicates that the signal is caused by the nuclear spin polarization of the germinate product generated in the process (b) in Fig. 3. The emissive signal of BQ at the later time and the emissive signal of BQH₂ are both caused by the reactions from the free radical shown in the processes (c) and (d).

Under conditions of high magnetic field in our NMR magnet ($B_0 = 2.35$ T), we may consider only $S-T_0$ mixing. Since $S-T_0$ mixing does not bring out the nuclear spin flips, the total nuclear spin polarization of the products (BQ, BQH₂) must become zero at the end of the reactions. The experimental results, however, contradict this expectation. As the source of this residual polarization, we can conceive two mechanisms. One is the



Fig. 4. Observed NMR signals. (a) NMR. (b) CIDNP of delay time $\tau = 2 \mu s.$ (c) CIDNP of delay time $\tau = 10 \mu s.$ (d) CIDNP of delay time $\tau = 52 \mu s.$ The peak at 6.7 ppm is due to the proton of BQ, and the peak at 6.6 ppm is due to the proton of BQH₂.

existence of nuclear spin relaxation of the free radical, and the other is the existence of both electron spin polarization by the triplet mechanism (TM) and cross-relaxation.

If nuclear spin relaxation exists, the absorptive nuclear polarization of the geminate product (BQ) should be larger than those of the escaped products (BQ, BQH₂). We thus predict that the sum of the nuclear spin polarization of BQ and BQH₂ is absorptive after all the events of the chemical reactions, contrary to the experimental finding. Consequently, the mechanism due to the relaxation of the free radical can be ruled out.

Thus, the other mechanism, combination of TM and cross-relaxation, shown schematically in Fig. 6, is the most plausible. In this mechanism, the electron spin polarization created as a result of anisotropy in the intersystem crossing in the precursor molecule transfers to the nuclear spin polarization and thereby the anomalous nuclear spin polarization is created. This mechanism was first proposed by ADRIAN *et al.* [14]. Further, MENG *et al.* [15] in our laboratory have shown that the $\Delta m = 2$ dipole-dipole cross-relaxation process exists in BQ, in agreement with the emissive CIDNP.

The delay time dependence of the CIDNP intensity of BQ of different initial concentration is shown in Fig. 7. As is expected from Eqn (2), CIDNP intensity increases more rapidly as the concentration of BQ increases.



Fig. 5. Time dependence of CIDNP signals of proton of BQ (a) and proton of BQH_2 (b). CIDNP intensity is represented by the unit of the NMR signal of 1 M proton in the Boltzmann equilibrium.



Fig. 6. Mechanism creating the nuclear polarization of the reaction product by combination of triplet mechanism and cross-relaxation. For BQ, the intersystem crossing takes place preferentially to the top sublevel in the zero-field, and hence under the magnetic field the T_+ state is the most populated. The hyperfine coupling constant is negative. In this case the emissive nuclear spin polarization is created by the $\Delta m = 2$ cross-relaxation.



Fig. 7. Delay time dependence of CIDNP intensity of BQ for the concentrations of 0.01 (a), 0.02 (b) and 0.04 M (c). The CIDNP intensity increases more rapidly as the concentration of BQ increases.

We tried to simulate the time dependence of CIDNP intensity by kinetic analysis. In this paper we focus attention on the polarized product generated from the polarized free radical. We rewrite the reactions shown in (c) and (d) in Fig. 3 as follows:

$$BQH^* \bullet + BQ \xrightarrow{k_1} BQ^* + BQH \bullet$$
(3a)

$$BQH^* \bullet + BQH^* \bullet \xrightarrow{\kappa_2} BQ^* + BQH_2^*.$$
(3b)

The concentration of nuclear polarized BQ is so low compared with the initial concentration of BQ that the reverse process of (3a) can be ignored. Then we have the following kinetic equations:

$$\frac{\mathrm{d}[\mathrm{B}\mathrm{Q}\mathrm{H}^*\bullet]}{\mathrm{d}t} = -k_1[\mathrm{B}\mathrm{Q}][\mathrm{B}\mathrm{Q}\mathrm{H}^*\bullet] - 2k_2[\mathrm{B}\mathrm{Q}\mathrm{H}^*\bullet]^2 \tag{4a}$$

$$\frac{\mathrm{d}[\mathrm{BQ}^*\bullet]}{\mathrm{d}t} = k_1[\mathrm{BQ}][\mathrm{BQH}^*\bullet] + k_2[\mathrm{BQH}^*\bullet]^2 \tag{4b}$$

$$\frac{\mathrm{d}[\mathrm{BQH}_{2}^{*}]}{\mathrm{d}t} = k_{2}[\mathrm{BQH}^{*}\bullet]. \tag{4c}$$



Fig. 8. Results of the fitting. The left-side data are for BQ and the right-side data are for BQH₂. The concentrations are 0.01 (a, b), 0.02 (c, d) and 0.04 M (e, f). The best fit parameters are $k_1 = 2.8 \times 10^6 \, \text{s}^{-1} \, \text{M}^{-1}$, $k_2 = 2.7 \times 10^9 \, \text{s}^{-1} \, \text{M}^{-1}$, f = -200, $I_{\rm GP} = 8.6$ for (a), 17 for (c), 26 for (e). The initial radical concentration [BQH*•] was $1.84 \times 10^{-6} \, \text{M}$ for (a) and (b), $2.53 \times 10^{-6} \, \text{M}$ for (c) and (d), $4.56 \times 10^{-6} \, \text{M}$ for (e) and (f).

Since [BQ] is much larger than $[BQH\bullet]$, we can reasonably treat [BQ] as time independent. Under the initial conditions,

$$[BQ^*]_{t=0} = 0 \tag{5a}$$

$$[BQH_2^*]_{t=0} = 0, (5b)$$

the solutions of (4a)-(4c) are as follows:

$$[BQH^*\bullet] = \frac{k_1[BQ]_0[BQH^*\bullet]_0}{-2k_2[BQH^*\bullet]_0 + (2k_2[BQH^*\bullet]_0 + k_1[BQ]_0) e^{k_1[BQ]_0 t}}$$
(6a)

$$[BQ^*] = \frac{[BQH^* \bullet]_0}{2} \left(1 - \frac{k_1[BQ]_0}{-2k_2[BQH^* \bullet]_0 + (k_1[BQ]_0 + 2k_2[BQH^* \bullet]_0) e^{k_1(BQ)_0 t}} \right) + \frac{k_1[BQ]_0}{4k_2} \ln \left(1 + \frac{-2k_2[BQH^* \bullet]_0}{k_1[BQ]_0} (1 - e^{-k_1|BQ|_0 t}) \right)$$
(6b)

$$[BQH_{2}^{*}] = \frac{[BQH^{*}\bullet]}{2} \left(1 - \frac{k_{1}[BQ]_{0}}{-2k_{2}[BQH^{*}\bullet]_{0} + (k_{1}[BQ]_{0} + 2k_{2}[BQH^{*}\bullet]_{0}) e^{k_{1}[BQ]_{0}}}\right) - \frac{k_{1}[BQ]_{0}}{4k_{2}} \ln \left(1 + \frac{-2k_{2}[BQH^{*}\bullet]_{0}}{k_{1}[BQ]_{0}} (1 - e^{-k_{1}[BQ]_{0}'})\right).$$
(6c)

The CIDNP intensity is proportional to the concentration of the product and the enhancement factor, f, and is written as follows:

$$I_{\rm BQ} = f[\rm BQ^*] + I_{\rm GP} \tag{7a}$$

$$I_{BQH_2} = f[BQH_2^*], \tag{7b}$$

where I_{GP} is introduced to take into account the contribution from the geminate product. We estimate $[BQ^* \bullet]_0$ by dividing the loss of initial BQ by the number of the laser pulse. The values of $[BQ^* \bullet]_0$ thus determined are 1.838×10^{-6} , 2.530×10^{-6} and 4.559×10^{-6} M at, respectively, 0.01, 0.02 and 0.04 M of $[BQ]_0$. Thus, the unknown parameters are k_1 , k_2 , f and I_{GP} . We try to fit all the six sets of the data in Fig. 8 with the common k_1 , k_2 and f. I_{GP} need not be common. The results of the simulation are shown in Fig. 8 by solid curves. The parameters thus determined are:

$$f = -200 \pm 20 \tag{8}$$

$$k_1 = 2.8 \pm 0.5 \times 10^6 \,\mathrm{s}^{-1} \,\mathrm{M}^{-1}$$
 (9a)

$$k_2 = 2.7 \pm 0.5 \times 10^9 \,\mathrm{s}^{-1} \,\mathrm{M}^{-1}.$$
 (9b)

The value of k_1 is smaller than the diffusion-controlled rate constant by a factor of 10³. This is of the same order of magnitude as the rate constant of the hydrogen transfer from hydroxylbenzyl radical to benzaldehyde studied by TSENTALOVICH *et al.* [9]. The value of k_2 is nearly diffusion-controlled.

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