Chemically Induced Dynamic Electron and Nuclear Polarization in the Photolysis of 1,4-Benzoquinone in 2-Propanol. The Radical-Pair Theory or the Photochemical Model?

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Abstract: In the photolysis of 1,4-benzoquinone in 2-propanol, *both* CIDEP of the intermediate semiquinone radicals and CIDNP of the reaction products at high and low fields have been observed and correlated. The results indicate that while the CIDNP observation can be satisfactorily explained by the radical-pair theory, the CIDEP observation is more consistent with the photochemical triplet model. It was disappointing, however, that CIDNP was not observable in the photoreduction of benzoquinone by 2,6-di-*tert*-butylphenol.

Our recent studies in CIDEP in quinone photochemical systems[1] have led us to propose a photochemical triplet model based on the optically spin polarized triplets of the parent quinone and their subsequent hydrogen abstraction with retention of polarization in the resultant radicals. The model was first formulated by a static, random distribution of triplets[2,3] and a recent treatment by Atkins and Evan[4] modified the static system to recognize the rotating triplet as a dynamical problem. While a possible connection between CIDEP and CIDNP has been generally recognized,[5-9] few studies heretofore have been directed toward a correlated experimental investigation of both CIDEP and CIDNP of the same chemical system. We wish to report here such a study on the photolysis of 1,4-benzoquinone (Q) in 2-propanol.

The photochemistry of 1,4-benzoquinone in 2-propanol has been well established and the mechanism can be represented by the following reactions.

$$\mathrm{Q} + h\nu \longrightarrow {}^1\mathrm{Q}^* \rightsquigarrow {}^3\mathrm{Q} \qquad (1)$$

$${}^3\mathrm{Q} + (\mathrm{CH_3})_2\mathrm{CHOH} \longrightarrow \dot{\mathrm{Q}}\mathrm{H} + (\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} \qquad (2)$$

$$(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} + \mathrm{Q} \longrightarrow (\mathrm{CH_3})_2\mathrm{CO} + \dot{\mathrm{Q}}\mathrm{H} \qquad (3)$$

$$2\dot{\mathrm{Q}}\mathrm{H} \longrightarrow \mathrm{QH_2} + \mathrm{Q} \qquad (4)$$

While the intermediate semiquinone radical $\dot{\mathrm{Q}}\mathrm{H}$ has been observed by ESR,[10,11] CIDEP of this 1,4-benzosemiquinone radical has eluded[12] previous detection using only a rotating sector and 100-kHz modulation. Our new detection system now employs a 5-nsec nitrogen pulse laser and a 2-MHz modulation unit and this has enabled us to observe the CIDEP of the semiquinone radical in 2-propanol. It is therefore possible to compare directly the experimental CIDEP and CIDNP results of this chemical system.

Experimental Section

1,4-Benzoquinone (Aldrich) was purified by vacuum sublimation. 2,4-Di-*tert*-butylphenol was recrystallized from benzene. In all experiments, the sample solutions contained in 4-mm o.d. Pyrex tubings were degassed and sealed off under 10^{-5} Torr vacuum. All runs were at room temperature unless otherwise specified.

In CIDEP study, a Varian 4502 X-band spectrometer using 2-MHz modulation was employed. The basic Micronow 2-MHz modulation unit was modified for our system and a home-made modulation coil was fitted onto the wall of the V4534 optical cavity. The light source is an Avco 20 kW nitrogen pulse laser with a tunable dye laser accessory. Only the nitrogen laser output was used in these experiments. The light pulse has a width of 3-5 nsec and was triggered by the Nicolet 1074-instrument computer. A Biomation 610B transient recorder with 100-nsec resolution was used to measure the changes in ESR signal amplitude at some predetermined constant magnetic field and the information was fed into the Nicolet 1074 for time averaging. Details of the electronics of the system will be described elsewhere.

In CIDNP study, a Bruker HX60 spectrometer and an auxiliary magnet system with a variable field between 5 to 8000 Gauss were used. The spectrometer probe was modified to allow irradiation by light from a 200 W Hg high-pressure lamp, equipped with Pyrex lens. For the low-field experiments, the sample was irradiated for 10 sec while in a 4 in. electromagnet (Walker 4HF) with a preset constant magnetic field. The field was measured by a gaussmeter (RFL Industries Model 505). The irradiated sample was then transferred to the spectrometer for CIDNP observation. The spectrometer was prelocked on the hydroxylic proton of 2-propanol and preset at the appropriate frequency of observation. It was found that under the experimental conditions, the time between irradiation at low field and observation in the spectrometer could be kept at 8 sec. The CIDNP spectra were recorded with repeated scans until the signals have relaxed to the thermal value. The spectrometer sensitivities settings were kept constant throughout a series of CIDNP experiments.

Results and Discussion

CIDEP Study. In the CIDEP study of the photoreduction of 1,4-benzoquinone in 2-propanol, the semiquinone radical was readily observed but the counter 2-propanol radical escaped experimental observation for similar reasons involved in other substituted quinone studies.[13] It was, however, established that the semiquinone radical polarization is in the totally emissive mode. Figure 1 represents a typical transient polarized ESR signal at a constant field showing the initially emissive signal relaxing to the thermal equilibrated absorptive mode. Further study using a benzene solution of benzoquinone and 2,6-di-*tert*-butyl-4-methylphenol as the hydrogen donor[14] established that both the semiquinone radical and the corresponding phenoxy radical exhibit total emission. The emission relative amplitude of the radicals was found to increase with the increasing phenol concentration. These experimental observations are consistent with the photochemical triplet theory[2,3] but cannot be satisfactorily accounted for by the simple radical-pair theory. For example, the S-$\mathrm{T_0}$ mixing would predict opposite polarization for the semiquinone radical and the phenoxy radical; the S-$\mathrm{T_{-1}}$ mixing, which is expected at low field, can explain the signs of the polarization but fails to account for the concentration dependence of the phenol.

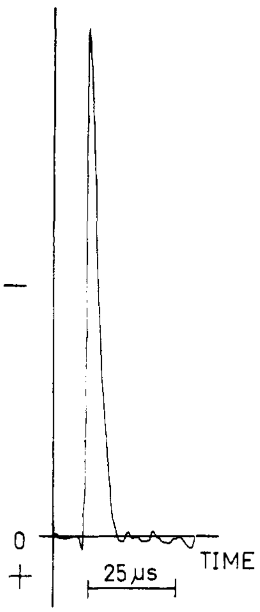
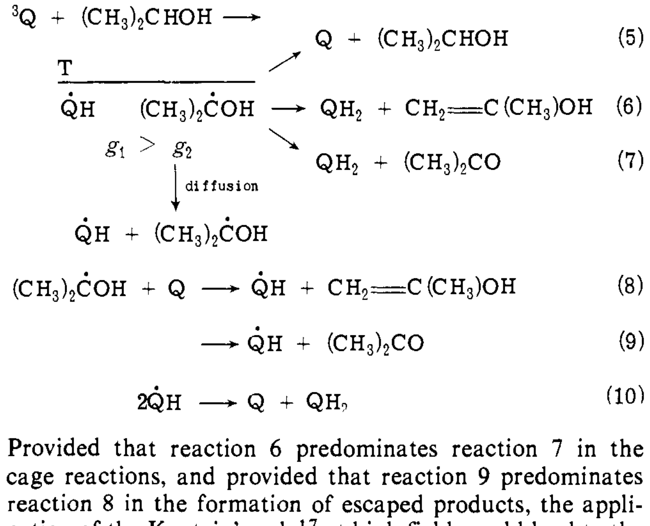


Figure 1. The time dependence of electron polarization of 1,4-benzosemiquinone radicals after the pulse-laser photolysis of benzoquinone in 2-propanol. The + sign indicates absorption and the − sign emission.

High-Field CIDNP Study. In the photolysis of benzoquinone in 2-propanol at high field, the product acetone showed CIDNP in the enhanced absorption mode and the product QH_2 was emissive. The interpretation of these observations was aided by studying the photochemical reaction in CD_3CN solvent.[15] Here the product enol $CH_2{=}C(CH_3)OH$ was identified[16] and the CIDNP of this enol is in the net emissive mode (Figure 2) along with the other product acetone being in the enhanced absorption mode. These CIDNP observations can be readily explained in terms of the S-T_0 mixing and the following reaction scheme.



$$^{3}Q + (CH_3)_2CHOH \longrightarrow \overline{\dot{Q}H \quad (CH_3)_2\dot{C}OH}^{\,T}$$

$$\longrightarrow Q + (CH_3)_2CHOH \qquad (5)$$

$$\longrightarrow QH_2 + CH_2{=}C(CH_3)OH \qquad (6)$$

$$\longrightarrow QH_2 + (CH_3)_2CO \qquad (7)$$

$$g_1 > g_2 \quad \Big\downarrow \text{diffusion}$$

$$\dot{Q}H + (CH_3)_2\dot{C}OH$$

$$(CH_3)_2\dot{C}OH + Q \longrightarrow \dot{Q}H + CH_2{=}C(CH_3)OH \qquad (8)$$

$$\longrightarrow \dot{Q}H + (CH_3)_2CO \qquad (9)$$

$$2\dot{Q}H \longrightarrow Q + QH_2 \qquad (10)$$

Provided that reaction 6 predominates reaction 7 in the cage reactions, and provided that reaction 9 predominates reaction 8 in the formation of escaped products, the application of the Kaptein's rule[17] at high field would lead to the CIDNP of the enol and QH_2 in the emissive mode and the acetone in the enhanced absorption mode.

In order to gain some insight on the above reaction scheme, the CIDNP intensity of the product acetone was studied as a function of the concentrations of the reactant benzoquinone. Concentrations ranging from 0.00063 to 0.3 *M* of benzoquinone in 2-propanol were first investigated. It was found that for concentration range between 0.025 and 0.2 *M*, the CIDNP intensity of acetone initially increased with irradiation time and then reached a steady-state value. After the interruption of irradiation, the acetone signal was allowed to relax to its thermal intensity and the difference between these two intensities was taken as the polarization intensity of the acetone. For concentration at 0.00063 *M*, the CIDNP intensity first passed through a maximum and then decreased. The polarization factor was taken as the difference between the maximum intensity and the thermal value. The variation of the polarization intensity of acetone with benzoquinone concentrations is shown in Figure 3.

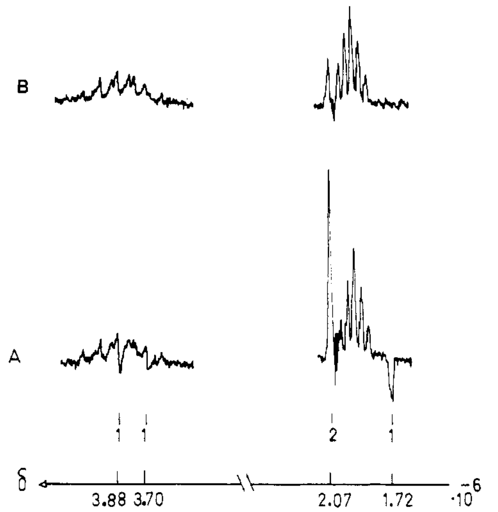


Figure 2. CIDNP spectra (a) during and (b) after the photolysis of 1,4-benzoquinone and 2-propanol in CD_3CN. The enol is labeled **1** and acetone as **2**.

In photochemical reactions, the rate of radical-pair formation is usually independent of the precursor concentration[18] under constant light absorbed intensity and the CIDNP intensity during photolysis will build up to a steady-state value.[17] This explains the results for the benzoquinone concentrations between 0.025 and 0.2 *M* in which light was totally absorbed by benzoquinone and the abstraction reaction 2 was rate determining. On the other hand, complete light absorption was not achieved at low benzoquinone concentration, 0.00063 *M*, and the radical-pair formation rate is therefore dependent upon the quinone concentration, or the amount of light absorbed.

According to the above reaction scheme, the polarization of acetone in reaction 9 should be dependent upon the benzoquinone concentration, as observed in the concentration range between 0.025 and 0.2 *M* in Figure 3. However, in the diffusion model of the CIDNP theory,[17] a second encounter of the geminate pair is necessary for the observation of the polarization. Here an increase in quinone concentration increases the efficiency of the scavenging process 9 and thus reduces the possiblility of a second encounter for the geminate pair and the observable CIDNP intensity. Therefore, the experimental results indicated that when this effect is dominant the observed CIDNP intensity will fall with increasing quinone concentration.

Another important consideration also presents itself at low quinone concentrations. At a concentration below 0.025 *M* for benzoquinone, the rate constant for reaction 9 can be estimated at about 8×10^5 l. mol^{-1} sec^{-1}.[19] Thus τ_s for the 2-propanol radical is of the order of 10^{-4} sec. This is comparable to the nuclear relaxation time of 10^{-4} to 10^{-5} sec of the radical.

Low-Field CIDNP Study. The dominance is supported by a field dependence study of the CIDNP in the product acetone. When the photolysis was carried out at fields below about 1600 G, the observed CIDNP (at 14,000 G) of the product acetone changed from enhanced absorption to an

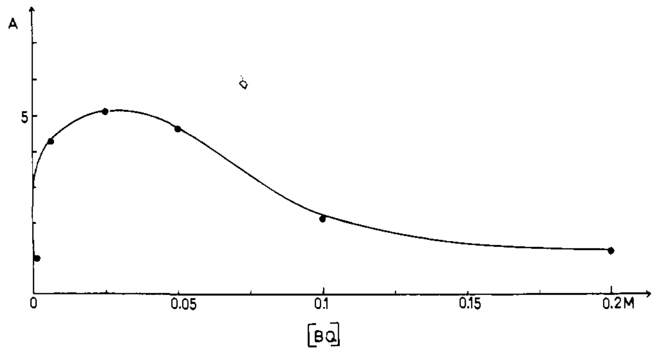


Figure 3. Variation of acetone high-field CIDNP intensity with 1,4-benzoquinone concentrations in 2-propanol during photolysis.

emission mode. Such a cross-over is consistent with the radical-pair theory that the S-T_{-1} mixing becomes dominant at low fields. A detailed theoretical and experimental low field study of benzoquinone and substituted benzoquinones will be published elsewhere. It is of interest to note here that in the present photochemical system, the crossover occurs at a relatively high field as compared to the known systems in literature. Still, the field of 1600 gauss is considerably lower than the 3300 gauss field used in the CIDEP experiments. It appears from the CIDNP experiments that S-T_0 mixing is dominating at such a 3300-G field. It must be noted that the S-T_0 mixing, however, cannot explain the CIDEP results of the present system.

A more critical CIDNP experiment on the photoreduction of benzoquinone with phenol in deuterated benzene could have provided further information on the polarization mechanism, since the radical pair here would have negligible difference in g values and the net effect cannot appear at high field with S-T_0 mixing dominating. The experiment indeed showed that no CIDNP was observed from the quinone, QH_2, or the phenol at high field. Unfortunately, no CIDNP could be observed even at low fields when the polarization should mainly result from S-$T_{\pm1}$ mixing. There are a number of kinetic arguments which could lead to such observation of no CIDNP at low fields. We prefer not to speculate on these reasons until further low-field studies are completed.

Thus, we now face the dilemma: radical-pair theory or the photochemical triplet theory? We believe that there may be some chemical systems where the radical-pair theory can correlate both CIDNP and CIDEP results. The photolysis of acetone in 2-propanol may just be such a case[15,20-22]. In the present photochemical system with benzoquinone and 2-propanol, we are inclined to believe that the photochemical triplet theory is consistent with the CIDEP results. Since the main concern of the photochemical mechanism is the relative populations of the triplet sublevels, the S-T_0 mixing might slightly disturb the electron polarization. At fields when S-T_{-1} becomes important, treatment of the radical pair should take into account that unequal populations of the triplet sublevels might result initially from a polarized triplet precursor.

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