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CIDEP Study of Photooxidation Reaction of Carbazole by Maleic Anhydride

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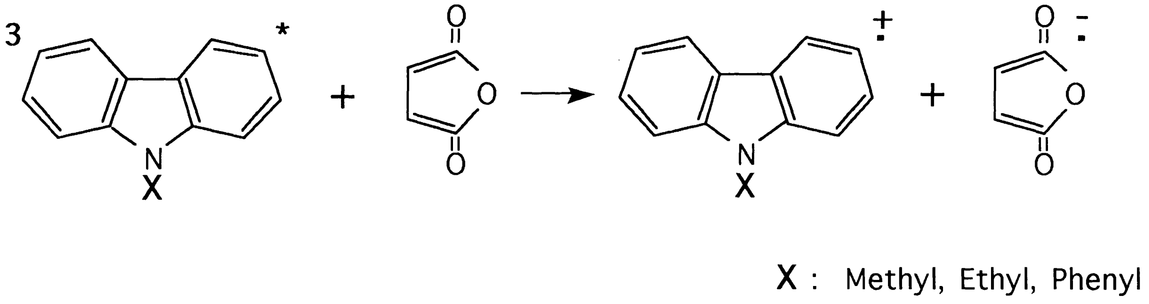
Photooxidation reaction of carbazole by maleic anhydride was studied by a time-resolved ESR method. Emissively spin polarized maleic anhydride anion radical and neutral carbazole N-center radical were detected. According to the CIDEP data, it is concluded that the reaction takes place through the excited triplet state of carbazole and fast deprotonation takes place from carbazole cation. This reaction is different from those of the other N-substituted carbazoles.

Some aromatic amines such as *N,N,N',N'*-tetramethyl-1,4-phenylenediamine (TMPD) and carbazoles (Czs) are known to be easily photoionized or photooxidized in polar media.[1, 2] According to our previous works of TMPD,[3)] maleic anhydride (MA) worked as a good oxidant and the anion radical of MA was identified as the CIDEP (chemically induced dynamic electron polarization)[4)] spectrum of the triplet precursor. This data provided important information of anomalous interaction of a radical-ion pair (RIP) such as level-crossing. Photoexcited triplet states of N-substituted Czs such as *N*-methyl-, *N*-ethyl- and *N*-phenylcarbazoles were also oxidized by MA. These reactions showed peculiar phenomena of CIDEP, which were tentatively explained by the sign inversion of the exchange interaction of RIP and level-crossing.[5)]



(1)

Here the asterisk and the superscript number denote the excited state and the spin multiplicity, respectively. These CIDEP data of TMPD and N-substituted Czs were mainly explained by the Coulomb interaction of the transiently formed RIP, namely, the confinement of the RIP in a solvent cage. The behavior of a transient RIP is of great interest, because it is thought to be one of ideal systems to be investigated as the spin-chemistry aim, namely, CIDEP, CIDNP (chemically induced dynamic nuclear polarization), external and internal magnetic field effect on chemical reaction, and so on.

In the present report, the CIDEP study of the photooxidation reaction of carbazole (Cz) with MA is presented. This system was proved to be photooxidized through the excited triplet state of Cz and fast deprotonation from the carbazole cation took place immediately after the charge transfer reaction in contrast to the other Czs cases.

The CIDEP spectra were measured by an X-band time-resolved ESR spectrometer without field modulation. The excitation pulsed light source was an excimer laser (Lambda Physik LPX-100, XeCl) with a wavelength of 308 nm. G.R. grade Cz, MA and 2-propanol provided by Wako Pure Chemicals were used as received. Deuterated MA (MA-d_2, 98% D) was supplied by Cambridge Isotope Laboratories. The concentration of Cz was about 2 x 10^{-2} M (mol dm^{-3}) and that of MA was changed between 10^{-4} and 10^{-2} M to control the reaction rate. Under the present conditions, the laser light was exclusively absorbed by Cz. The solution was deoxygenated by bubbling with pure nitrogen gas prior to the flowing through a flat quartz cell installed in an ESR cavity.[6)]

Figure 1a shows the typical CIDEP spectrum observed immediately after the laser excitation. The triplet spectrum appeared near the center with emissive pattern was assigned to the anion radical of MA, and a weak and widely spread spectrum having emissive pattern especially at the lower resonant field portion was assigned to the neutral N-center Cz radical (carbazyl radical). The simulated spectra of the anion and N-center radicals are shown in Fig. 1b. The hyperfine coupling constants (hfc) of 0.615 mT was used as two equivalent protons of the MA anion radical, and the values of 0.71, 0.43 and 0.11 mT were employed for a nitrogen, 1.3.6.8 position protons and 2.7 position protons of the Cz radical, respectively. The hfc values of the N-center radical were in good agreement with the reported ones in solid conditions.[7)] The hfc of the anion radical was a bit smaller than those observed in previous

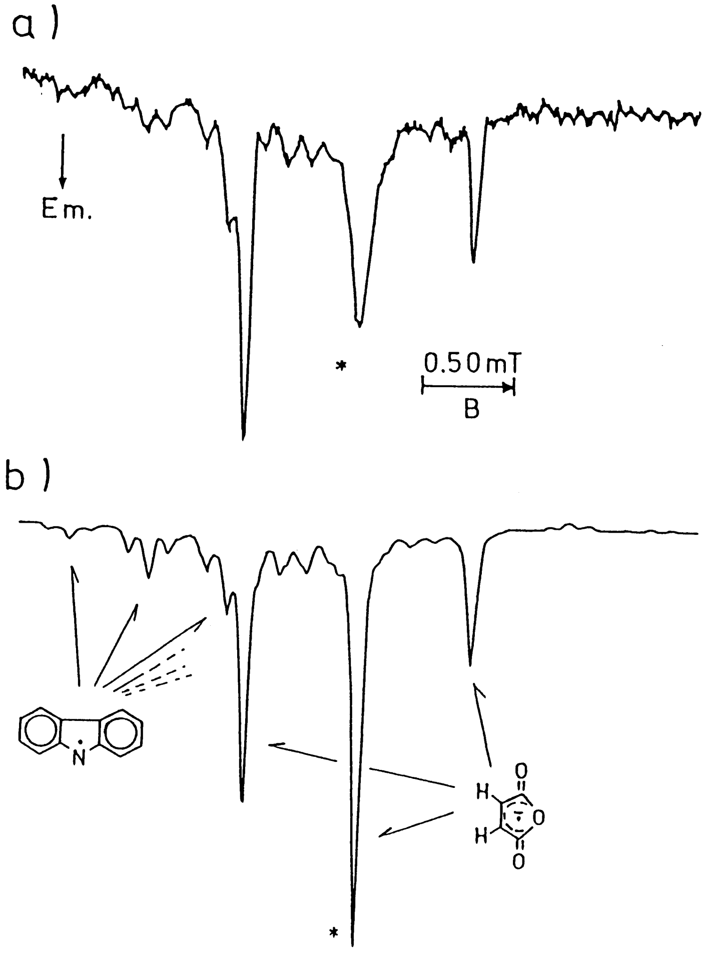


Fig. 1. a) CIDEP spectrum (0.5 - 0.7 μs) observed in the laser photolysis of Cz/MA system in 2-propanol at room temperature. [MA] = 2 x 10^{-2} M. b) Computer simulated CIDEP spectrum of $^{\cdot}$Cz and $MA^{\cdot -}$ with emissive TM polarization and E/A of RPM.

systems[3, 5] and the center line (as shown by an asterisk) was seriously broadened compared to the simulated one. This difference from the ordinary CIDEP spectrum of the MA anion radical was explained by the line-width alternation due to the chemical exchange phenomenon.[8, 9] In the present system, a protonated solvent alcohol molecule may exist near the carbonyl portion of MA anion radical and the position of the protonated alcohol molecule switches between two carbonyl groups of MA. The small hfc of the protons of this anion radical may also be rationalized by the slight penetration of the unpaired electron to the protonated alcohol.

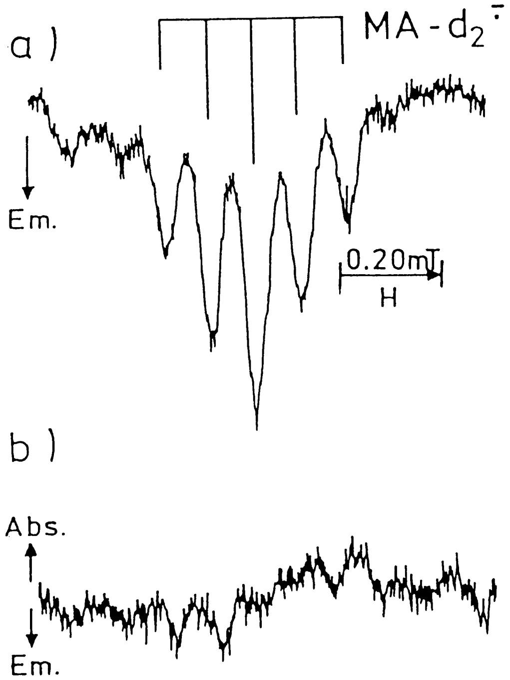
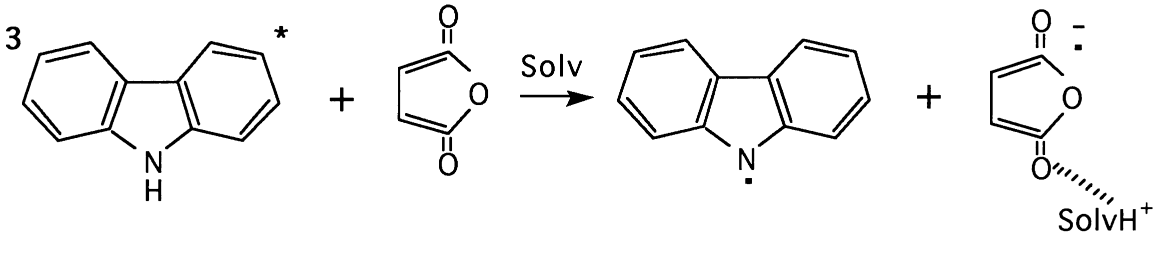


Fig. 2. CIDEP spectra of the anion radical of $MA\text{-}d_2$ observed in the system of $Cz/MA\text{-}d_2$ in 2-propanol at room temperature. a) $[MA\text{-}d_2]$ = 2 x 10^{-2} M (0.5 - 0.7 μs) and b) $[MA\text{-}d_2]$ = 2 x 10^{-3} M (0.8 - 1.0 μs).

Figure 2a and b show the CIDEP spectra observed in the photolysis of the system of Cz and $MA\text{-}d_2$ in 2-propanol. As shown in this figure, a quintet spectrum of the anion radical of MA whose hfc of the deuterons is 1/6.5 of that of protons appears. Under the high concentration condition of $MA\text{-}d_2$ (Fig. 2a), the spectrum shows slightly distorted emission which is due to the TM and slight contribution of the RPM. Under the low concentration of $MA\text{-}d_2$ (Fig. 2b), the spectrum shows very weak but apparent E/A pattern due to the RPM. This weak RPM signal intensity is explained by the small hfc of deuterons. The quintet spectrum does not show apparent line broadening phenomenon of the chemical exchange, but it is also explained by the small hfc value of deuteron because the chemical exchange frequency which modifies the hf line of the proton of $MA^{\bullet -}$ must be too high to modify that of the deuteron. The other weak peaks superimposed on those of the anion radical were assigned to the N-center radical from Cz. This experiment of the isotope effect gave sure confirmation of the assignment of each species moreover provided the information of the spin-polarization. The main part of this reaction is expressed as follows:



(2)

where Solv and $SolvH^+$ mean solvent molecule and its protonated one, respectively.

The distortion from the simple symmetric pattern of the present CIDEP spectra was explained by the combination of the emissive triplet mechanism (TM) and the radical pair mechanism (RPM). In fact, by diluting the concentration of MA the emissive spectral pattern changed to the low field emissive and high field absorptive (E/A) pattern due to the triplet precursor RPM because of the slow reaction rate of eq. 2 which makes the appearance of TM polarization difficult. In the cases of TMPD and N-substituted Czs, additional total emissive (absorptive in case of N-substituted Czs) spectral patterns which were tentatively explained by level crossing phenomenon appeared probably due to the strong confinement of RIP by Coulombic force in 2-propanol. Therefore, the interaction of RIP in the present case is very weak or does not exist because of the short duration of RIP interaction or no existence of RIP. The charge transfer reaction followed by the deprotonation from the Cz cation radical may occur in this system according to the similarity to the cases of the other Czs. The whole reaction scheme including the spin interaction as the radical pair may be expressed as follows:

$$^{3}\mathrm{Cz}^{*} + \mathrm{MA} \longrightarrow {}^{3}[\mathrm{Cz}^{\cdot+} + \mathrm{MA}^{\cdot-}] \qquad \text{(Charge transfer)} \qquad (3)$$

$$^{3}[\mathrm{Cz}^{\cdot+} + \mathrm{MA}^{\cdot-}] + \mathrm{Solv} \longrightarrow {}^{3}[{}^{\cdot}\mathrm{Cz} + \mathrm{MA}^{\cdot-}\cdots\mathrm{SolvH}^{+}] \qquad \text{(Deprotonation)} \qquad (4)$$

$$^{3}[{}^{\cdot}\mathrm{Cz} + \mathrm{MA}^{\cdot-}\cdots\mathrm{SolvH}^{+}] \longleftrightarrow {}^{1}[{}^{\cdot}\mathrm{Cz} + \mathrm{MA}^{\cdot-}\cdots\mathrm{SolvH}^{+}] \qquad \text{(S-T}_0\text{ mixing)} \qquad (5)$$

$$^{1}[{}^{\cdot}\mathrm{Cz} + \mathrm{MA}^{\cdot-}\cdots\mathrm{SolvH}^{+}] \longrightarrow \text{Products} \qquad \text{(Recombination)} \qquad (6)$$

$$^{1,3}[{}^{\cdot}\mathrm{Cz} + \mathrm{MA}^{\cdot-}\cdots\mathrm{SolvH}^{+}] \longrightarrow {}^{\cdot}\mathrm{Cz} + \mathrm{MA}^{\cdot-}\cdots\mathrm{SolvH}^{+} \qquad \text{(Escaping)} \qquad (7)$$

here, the bracket indicates the radical pair in a solvent cage. However, we cannot exclude the hydrogen transfer reaction to MA followed by the deprotonation from the ketyl-type radical at this stage.

In conclusion, the photoexcited Cz reacts with MA in 2-propanol through the triplet state and the anion radical of MA which shows the chemical exchange phenomenon appears. The counter radical is the neutral N-center radical which may be formed by the deprotonation of the transient cation radical. In this system the interaction of RIP is not thought to be important and a separated proton exists near the MA anion radical as an adduct to a solvent molecule.

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