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PHOTOCHEMICAL REDUCTION OF p-BENZOQUINONES STUDIED BY CIDNP TECHNIQUE

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Photo-reduction of p-benzoquinone and its methyl- or chloro-derivatives has been investigated using the CIDNP technique. Strongly polarized PMR signals due to p-benzoquinones themselves, active reaction intermediates and hydroquinones were observed during the course of the reactions. From these results, the reaction scheme of these photo-reductions was proposed.

Photo-reduction of p-benzoquinone or chloranil in the presence of hydrogen donors has been well known.[1-3] However, systematic studies or details of the reaction mechanism have not yet been published. In this research photo-reduction of p-benzoquinone and its methyl- or chloro-derivatives has been investigated using the CIDNP technique.

p-Benzoquinone and its methyl- or chloro-derivatives dissolved in a suitable solvent are photochemically reduced in the presence of hydrogen donors, i.e., xanthene, 9,10-dihydroanthracene, fluorene or diphenylmethane, to give hydroquinone, quinhydrone and/or their methyl- and chloro-derivatives. During the course of the photo-reductions, strongly polarized PMR signals (enhanced absorption or enhanced emission signals) due to the benzene ring protons and/or the methyl protons of the hydroquinones produced can be observed. Unexpectedly, at the same time the benzene ring protons and/or the methyl protons of p-benzoquinones themselves show strongly polarized PMR signals during the course of the reactions, as shown in Fig. 1. On the other hand, in the absence of the hydrogen donors p-benzoquinones show no such polarized PMR signals when they were irradiated in an inert solvent. Further the strongly polarized signals due to active reaction intermediates, i.e., exciplexes which are not accumulated in the reaction system as the reaction products after prolonged irradiation, could be observed during the course of the photochemical reactions. The assignment of the polarized signals to the active reaction intermediates may be rationalized with the following facts; i) stable compounds which show the same signals are not accumulated in the reaction system after prolonged irradiation, ii) the signals 4 and 6 in Fig. 1-A, or the signals 5, 6, 7, and 8 in Fig. 1-B could not be observed during the course of the photochemical reaction when xanthene-9-d_2 was used as a hydrogen donor (see Fig. 1-A-c and Fig. 1-B-c).

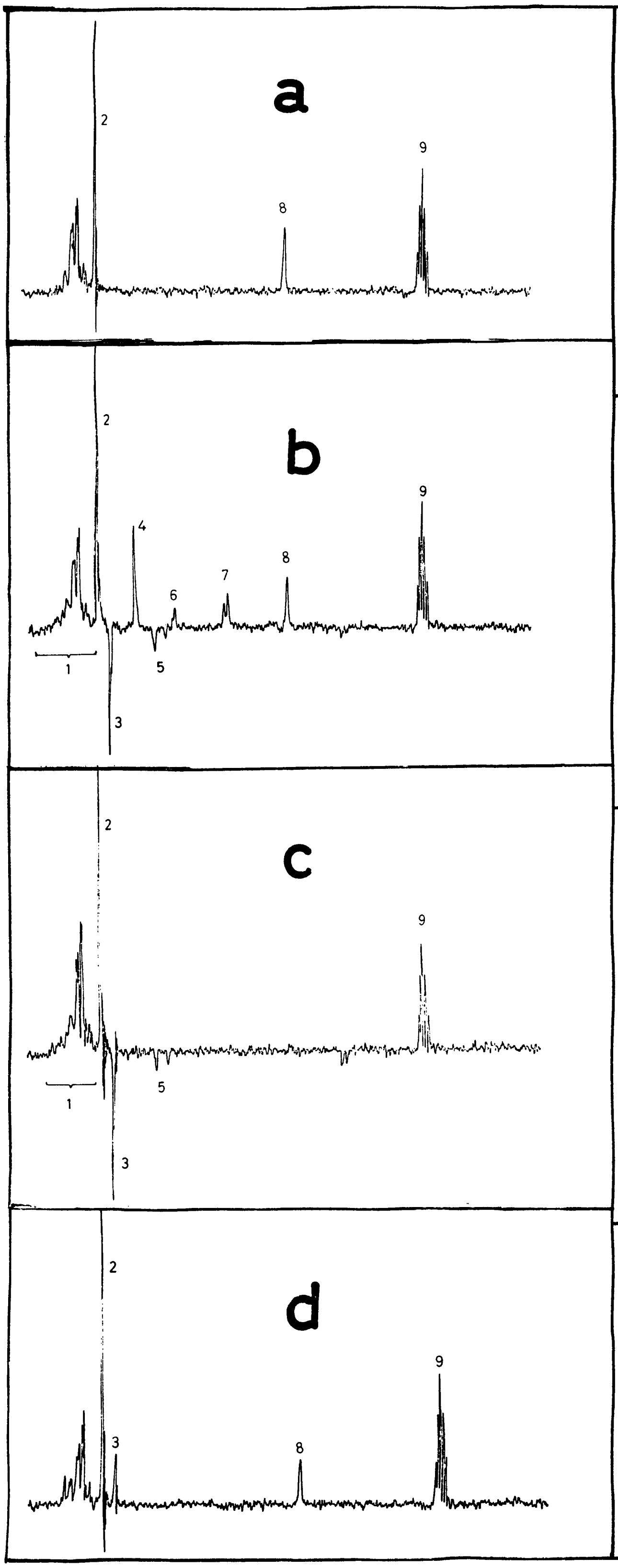
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Fig.1 - A

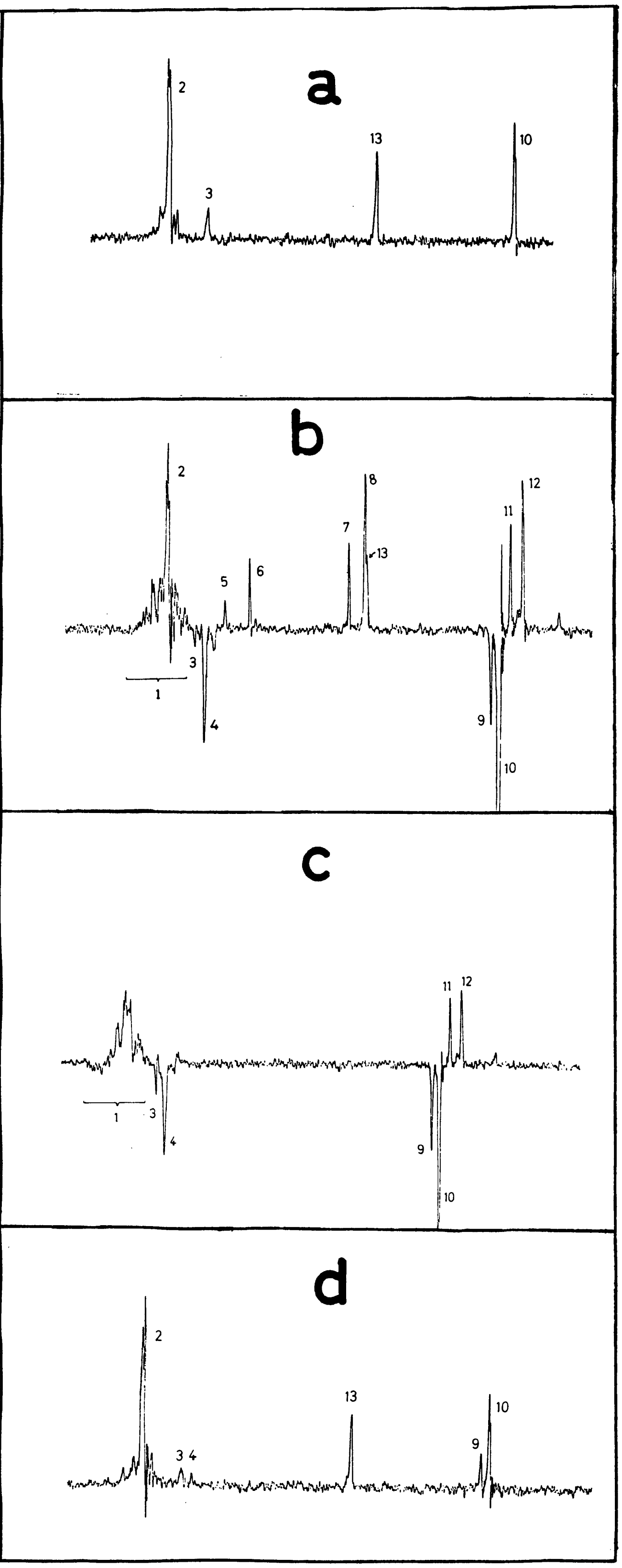
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Fig.1 - B

Fig. 1-A Photochemical Reaction of p-Benzoquinone with Xanthene in Acetone-d_6.

(a) Before irradiation. Signal 2: the benzene ring protons of p-benzoquinone; signal 8: the 9-methylene protons of xanthene; signal 9: the methyl protons of acetone mixed in acetone-d_6.

(b) During irradiation. Signals 1, 2, 3, 4, 5, and 7: the polarized signal.

(c) During irradiation. Instead of xanthene, xanthene-9-d_2 was used. Signals 4, 6, and 7 disappeared (compare this spectrum with Fig. 1-A-b).

(d) After prolonged irradiation. Signal 3: the benzene ring protons of hydroquinone accumulated.

Fig. 1-B Photochemical Reaction of 2,6-Dimethyl-p-benzoquinone with Xanthene in Carbon Tetrachloride.

(a) Before irradiation. Signal 2: the aromatic ring protons of xanthene; signal 3: the benzene ring protons of 2,6-dimethyl-p-benzoquinone; signal 10: the α-methyl protons of 2,6-dimethyl-p-benzoquinone; signal 13: the 9-methylene protons of xanthene.

(b) During irradiation. Signals 1, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12: the polarized signal.

(c) During irradiation. Instead of xanthene, xanthene-9-d_2 was used. Signals 5, 6, 7, and 8 disappeared (compare this spectrum with Fig. 1-B-b).

(d) After prolonged irradiation. Signals 4 and 9: the benzene ring protons and the α-methyl protons of 2,6-dimethyl-p-benzoquinone accumulated.

Therefore, the signals were based on the methylene protons of xanthene rest in exciplexes. The signals appear in one pair (signals 4 and 6 in Fig. 1-A), if quinone has the C_{2v} symmetry axis perpendicular to the benzene ring; but the signals appear in two pairs (signals 5 and 6, and 7 and 8 in Fig. 1-B), if quinone has no such a symmetry axis. p-Benzoquinone, 2,5-dimethyl-p-benzoquinone, 2,5-dichloro-p-benzoquinone or duroquinone belong to the former and 2-methyl-p-benzoquinone, 2,6-dimethyl-p-benzoquinone or 2,6-dichloro-p-benzoquinone belong to the latter. This may be reflection of the arrangement of quinone and xanthene rest in the exciplex., and iii) considerably complexed signals (signal 1 in Fig. 1-A or in Fig. 1-B) appear in the aromatic ring proton region, and the signals can not be assigned to those of reactants or reaction products.

p-Benzoquinones examined are the followings; p-benzoquinone, 2-methyl-p-benzoquinone, 2,5-dimethyl-p-benzoquinone, 2,6-dimethyl-p-benzoquinone, 2,3,5-trimethyl-p-benzoquinone, duroquinone, 2-chloro-p-benzoquinone, 2,5-dichloro-p-benzoquinone, 2,6-dichloro-p-benzoquinone, 2-ethyl-p-benzoquinone, and 2-isopropyl-p-benzoquinone. All of these p-benzoquinone behave quite analogously to p-benzoquinone itself during the course of the photochemical reduction in the CIDNP examinations without any exceptions. The typicals are shown in Fig. 1. Features of the polarized PMR signals observed are summarized in Table 1. However, some features of the polarized PMR signals are solvent-dependent.

Table 1 Features of The Polarized PMR Signals at 60 MHz.

Hydrogen Donor: Xanthene; Solvent: CCl_4; Room Temperature

	Polarized PMR Signals						
Quinones	Hydroquinones		p-Benzoquinones		Exciplexes		
	ring-H,	α-H	ring-H,	α-H	quinone-rest		xanthene-rest
					ring-H[a]	α-H[b]	$9\text{-}CH_2$[c]
p-Benzoquinone	E	-	A	-	E	-	A
2-Methyl-p-benzoquinone	(E)	E	A	E	(E)	A	A
2,5-Dimethyl-p-benzoquinone	(E)	E	A-E	E	(E)	A	A
2,6-Dimethyl-p-benzoquinone	E	E	E	E	(E)	A	A
2,3,5-Trimethyl-p-benzoquinone	E	E	E	E	( )	A	A
Duroquinone	-	E	-	E	-	A	A
2-Chloro-p-benzoquinone	E	-	A-A	-	( )	-	A
2,5-Dichloro-p-benzoquinone	E	-	E	-	(E)	-	A
2,6-Dichloro-p-benzoquinone	E	-	(E)	-	( )	-	A
2-Ethyl-p-benzoquinone	( )	E	A	E	E	A	A
2-Isopropyl-p-benzoquinone	( )	E	A	E	E	A	A

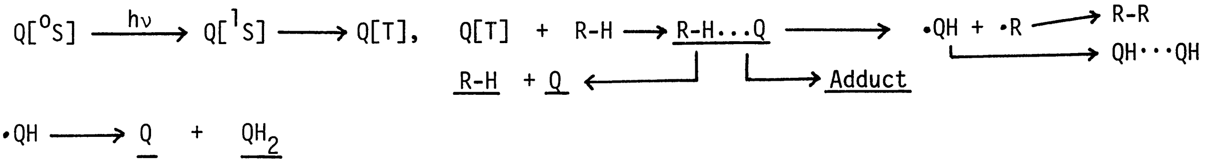
A: enhanced absorption signal; E: enhanced emission signal; ( ): means somewhat ambiguous.

[a] Signals due to the benzene ring protons of p-benzoquinone rest in the exciplex.

[b] Signals due to the α-methyl protons of methyl substituted p-benzoquinone rest in the exciplex.

[c] Signals due to the 9-methylene protons of xanthene rest in the exciplex. These signals disappear when xanthene-9-d_2 was used as a hydrogen donor.

From the experimental results explained above, the following reaction scheme is presented tentatively.



Q: p-benzoquinones; R-H···Q: exciplexes; QH: semiquinone radicals; QH····QH: quinhydrone; Adduct: 1,2- or 1,4-adducts. The compounds underlined show the polarized signal.

A C-60 HL-type NMR spectrometer(JEOL) and a 500 W high-pressure mercury-arc lamp were used in this experiment. Method of CIDNP examinations used was described in elsewhere.[4)]

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2) A. Schönberg and A. Mustafa, ibid., 1944, 67.

3) R. F. Moore and W. A. Waters, ibid., 1953, 3405.

4) K. Maruyama, H. Shindo, T. Otsuki, and T. Maruyama, Bull. Chem. Soc. Japan, 44, 2756 (1971).

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