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Photo-induced Condensation Reaction of *p*-Quinones with Aldehydes

Kazuhiro MARUYAMA and Yo MIYAGI

Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606

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Synopsis. The quantum yield of a photo-induced condensation product between a *p*-quinone and an aldehyde was determined, the reaction course being investigated by CIDNP technique.

Quantum Yield of the Reaction. Qualitative inspection on photo-induced reaction of *p*-quinones with aldehydes has been reported by Bruce and Cutts.[1] Their conditions for the reaction were unusual; a quinone dissolved in an aldehyde was subjected to irradiation to yield acylated hydroquinone derivatives. In the present investigation a more dilute mixture of *p*-quinone and aldehyde in a suitable solvent was irradiated by Xenon arc lamp. The quantum yields of major products, 2-acylated hydroquinones, are given in Tables 1—3 for several combinations of *p*-quinones and aldehydes.

Monochromatic light of 445 nm was used in the reaction of *p*-benzoquinone, and that of 425 nm in the reaction of 1,4-naphthoquinone. Each absorption band corresponds to the n→π^* excitation band of the respective carbonyl groups.

TABLE 1. YIELDS OF 2-ACETYLHYDROQUINONE(**7**) IN THE PHOTOCHEMICAL REACTION OF *p*-BENZOQUINONE AND ACETALDEHYDE[a]
(monochromatic light: 445 nm, solvent: acetonitrile)

Time (min)	Yield of **7** (%)[b]	Yield of **7** per hour (%/hr)	Quantum yield
0	—	—	
30	1.44	2.8_5	
65	3.09	2.8_9	
95	4.60	2.9_0	0.55_9
125	5.82	2.7_9	
155	7.12	2.7_6	
185	8.32	2.7_6	

a) Initial concentrations of *p*-benzoquinone and acetaldehyde were 0.01 and 0.1 mol/l. b) Determined by absorption at 360 nm.

TABLE 2. YIELDS OF 2-PROPIONYL-1,4-NAPHTHOHYDROQUINONE(**8**) IN THE PHOTOCHEMICAL REACTION OF 1,4-NAPHTHOQUINONE AND PROPANAL[a]
(monochromatic light: 425 nm, solvent: acetonitrile)

Time (min)	Yield of **8** (%)[b]	Yield of **8** per hour (%/hr)	Quantum yield
30	2.7_2	5.4_3	0.51_8
60	4.9_0	4.9_0	0.47_8
90	6.6_7	4.4_4	0.42_4
120	8.4_0	4.2_0	0.40_1
150	9.8_3	3.9_3	0.37_6

a) Initial concentrations of 1,4-naphthoquinone and propanal were 0.005 and 0.05 mol/l. b) Determined by absorption at 390 nm.

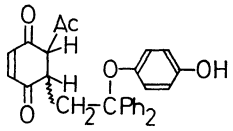
TABLE 3. QUANTUM YIELDS OF 2-ACYL- OR 2-AROYLHYDROQUINONES IN THE PHOTOCHEMICAL REACTION OF *p*-BENZOQUINONE AND ALDEHYDES
(monochromatic light: 445 nm, solvent: acetonitrile)

Aldehyde	$[BQ]_0$[a]: [RCHO]	Quantum yield[b]
CH_3CHO	1 : 100	0.78_5
CH_3CHO	1 : 50	0.69_9
CH_3CHO	1 : 10	0.55_9[c]
CH_3CHO	1 : 4	0.56_7
C_2H_5CHO	1 : 5	0.55_4
C_3H_7CHO	1 : 10	0.57_4
C_6H_5CHO	1 : 10	0.54_7

a) Initial concentration of *p*-benzoquinone, $[BQ]_0$, was 0.01 mol/l. b) Mean quantum yield during 90 min reaction. The yields were determined by absorption at 360 nm. c) Mean quantum yield during 95 min reaction.

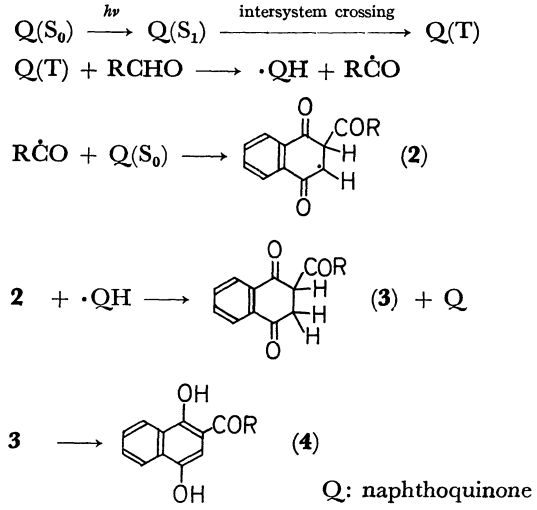
The mean quantum yields estimated in the duration of every 30 min remain constant in the reaction of *p*-benzoquinone with aldehydes, but they change with time in the reaction of 1,4-naphthoquinone with propanal. This can be ascribed to the quenching effect by the major product, 2-acyl-1,4-naphthohydroquinone, accumulated in the reacting solution. The following indirect evidence deduced from the investigation of the reaction by means of CIDNP would support the view. The fresh solution of 1,4-naphthoquinone and an aldehyde dissolved in carbon tetrachloride showed fairly strong polarized PMR signals during the course of irradiation, but the intensity is strongly depressed without exception when the corresponding 2-acyl-1,4-naphthohydroquinones were added to the solutions.

Reaction Mechanism. Thus, 2-acylated hydroquinone was obtained from *p*-quinone and aldehyde in a free form or in the form of quinhydrone addition compound.[2] On the mechanism of these condensation reactions, Bruce and Cutts included the addition of acyl radical to the quinone followed by subsequent enolization of the primary adduct.[1] In the reaction of *p*-benzoquinone with acetaldehyde they obtained the scavenged product (**1**) of the reactive intermediate radical by 1,1-diphenylethylene added in the reaction system.



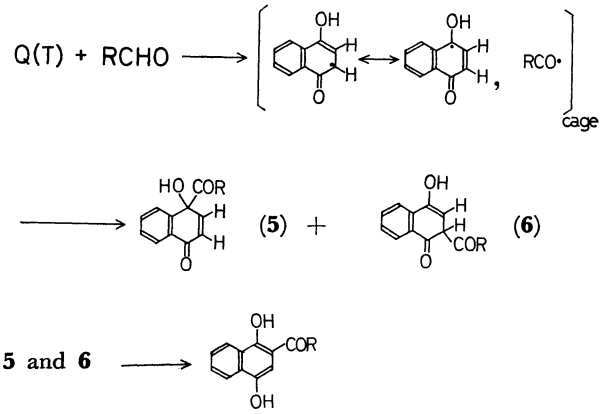
(**1**)

According to this mechanism the reaction should proceed as follows.



Scheme 1.

The reaction could proceed in part through the above reaction scheme, but our investigation by CIDNP technique revealed a modified aspect. The polarized PMR signal (multiplet, emission and absorption) observed in the region δ=3.70—4.30 and the polarized signal (emission) due to 2,3-protons of naphthoquinone can be interpreted by this mechanism. However, both the strongly polarized signals (emission) in the region δ=6.25—6.45 and the strongest polarized alkyl proton signal or signals (absorption) of acyl group suggest the concomitant generation of **5** or **6** through direct recombination of the radical pair in an original solvent cage[3] (Fig. 1), (Scheme 2). The polarized emission signals observed in the region δ=6.25—6.45 can be reasonably interpreted by taking account of the olefinic protons of **5** and **6**. No evolution of carbon monoxide during the course of irradiation supports our scheme.



Scheme 2.

Experimental

Quantum yields were determined by the use of ferrous succinate as an actinometer. Monochromatic light was attained with a Shimadzu RF-501 spectrophotometer. CIDNP examinations were carried out with a JEOL 60 MHz NMR spectrometer (solvent; CCl_4). Details are described elsewhere.[4]

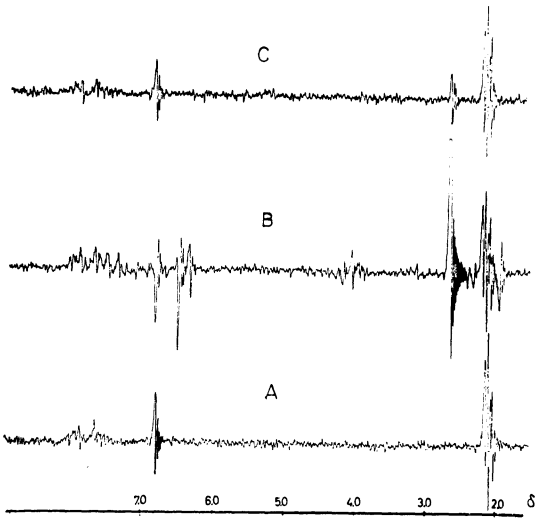


Fig. 1 a. Polarized PMR signals observed in the photochemical reaction of 1,4-naphthoquinone and acetaldehyde.
A: Before irradiation, B: During irradiation, C: After irradiation.

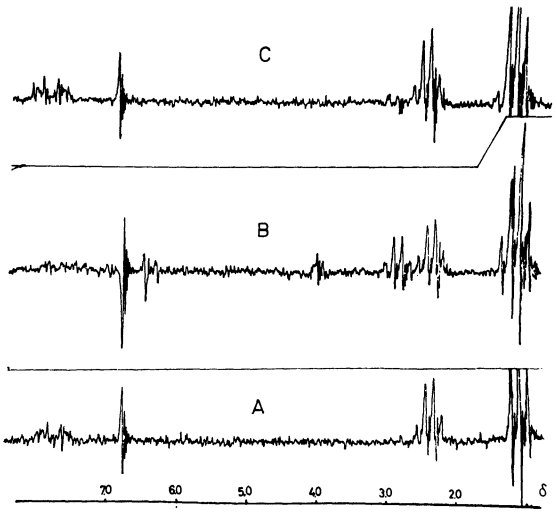


Fig. 1b. Polarized PMR signals observed in the photochemical reaction of 1,4-naphthoquinone and propanal.
A: Before irradiation, B: During irradiation, C: After irradiation.

References

1) J. M. Bruce and E. Cutts, *J. Chem. Soc., C*, **1966**, 449.
2) No 2-acylated hydroquinone was obtained in the photochemical reaction of *p*-quinone with *p*-nitrobenzaldehyde, the so-called 1,4-addition compound, hydroquinone monoester, being the sole product (*cf.* 1)).
3) In the photochemical reaction between *p*-quinones and *p*-nitrobenzaldehyde no polarized PMR signal could be observed in the region δ=3.50—6.0.
4) K. Maruyama, T. Otsuki, A. Takuwa, and S. Arakawa, This Bulletin, **46**, 2470 (1973).