

PHOTOCHEMICAL REACTION SENSITIZED BY DYES IN HETEROGENEOUS PHASE

Kazuhiro MARUYAMA and Noritsugu NARITA

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

A photosensitized reaction of 2-acyl-1,4-benzoquinone 1 by rose bengal in a homogeneous system afforded the dimer 2 in a good yield. Even in the reactions in heterogeneous systems using rose bengal bound on the surface of silica gel particles, the same dimer was obtained in the comparable yields with those in a homogeneous system, but at a slower rate.

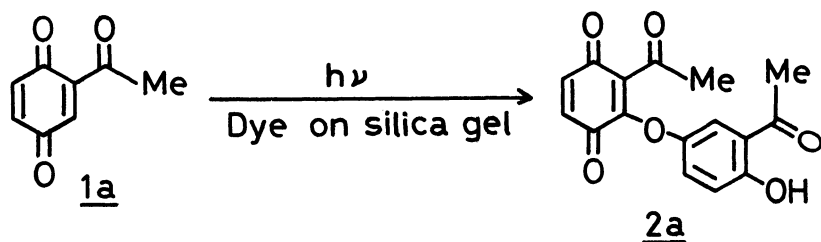
It has been reported that irradiation of 2-acyl-1,4-benzoquinone 1 in the presence of rose bengal in acetonitrile or acetone afforded the quinone dimer 2-acyl-3-(3-acyl-4-hydroxyphenoxy)-1,4-benzoquinone 2 in good yields.¹⁾ In this photodimerization reaction, the excited state of rose bengal played a very important role.

Mechanistic and synthetic studies of this type of photodimerization reaction of quinones encountered difficulties because of the insolubility of the sensitizer, rose bengal. Many of the standard photosensitizing dyes, for example, rose bengal or methylene blue, cannot be used in the non-polar solvents required for certain mechanistic studies or for low temperature photoreaction. These problems may be partially overcome by use of the appropriate heterogeneous system.

In our experiments, sensitizing dyes were deposited on the surface of silica gel particles and the dye-coated particles were then suspended in a solution containing acyl quinone to react. Even though the dye remained completely bound to the solid support, we found that an efficient photodimerization reaction of acyl quinone in solution was achieved.³⁾

The dye phase was prepared according to the method of R.Nilsson and D.R.Kearns.²⁾ In the case of 2-acetyl-1,4-benzoquinone 1a,⁴⁾ an exciting light was passed through glass filters which cut off all light below 500 nm to prevent direct light absorption by the quinone. Photodimerization of 1a was followed by means of ¹H-NMR spectroscopy. With a 0.1 M solution of 2-acetyl-1,4-benzoquinone 1a in benzene, we obtained 20% conversion to the dimer 2a from 1a in 8 h under the irradiation conditions, using 4 g of rose bengal-coated silica gel per liter. Under the comparable conditions but using the dye dissolved homogeneously in acetonitrile, 60% conversion to 2a was obtained for the same period of irradiation. On the other hand, under the same conditions except using methylene blue-coated silica gel, we obtained 15% conversion to 2a after irradiation for 16 h. Methylene chloride was used also as the solvent in this reaction. The yields of the dimer 2a were shown in Table 1.

After stirring for 8 h in C₆H₆ or CH₂Cl₂, only less than 0.1% of dye bound on the surface of silica gel was dissolved in the filtrate. Irradiation of a solution of 1a

Table 1. Yields of the dimer 2a(%)

Solvent	Sensitizing system	Rose bengal-coated SiO ₂ , irradi. for 8 h.	Methylene blue-coated SiO ₂ , irradi. for 16 h.
C ₆ H ₆	heterogeneous	20	18
CH ₂ Cl ₂	heterogeneous	15	15
CH ₃ CN	homogeneous	60	55

in the filtrate obtained above using the same light ($\lambda > 500$ nm) hardly gave 2a within a practical experimental time (10 h).

In the heterogeneous system, the dimer was obtained in lower yields than in a homogeneous system. Such a feature of the reaction is highly suggestive that the initial reactive intermediate of this type of dimerization is the formation of an excited complex between quinone and dye, in which the quinone moiety is of anion radical in its nature. Addition of the excited complex to another molecule of quinone in a ground state with coincident release of the bounded dye molecule will result in the formation of dimer 2. The lower yield in the heterogeneous system may be caused by the smaller equilibrating concentration of the complex between the quinone and the dye.

REFERENCES and NOTES

- 1) K. Maruyama, N. Narita, and Y. Miyagi, Chem. Lett., 1978, 1033.
- 2) R. Nilsson and D. R. Kearns, Photochem. Photobiol., 19, 181 (1974).
- 3) The photodimerization of acylquinone proceeds also in a solution containing the suspended sensitizing dye particles, but the rate of the dimerization is considerably slow (about 1/8 compared with that of the present case).
- 4) 2-Acetyl-5-methyl- and 2-carbomethoxy- substituted 1,4-benzoquinone were confirmed to give the photodimer under the similar conditions.

(Received July 12, 1979)