CHEMISTRY LETTERS, pp. 665-668, 1976. Published by the Chemical Society of Japan

EFFECT OF p-BENZOQUINONE ON SPECTRAL SENSITIZATION OF SILVER CHLORIDE

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The spectral sensitization of silver chloride has been studied electrochemically. The fact that the effect of p-benzoquinone on the dye-sensitized photocurrent depends on the kinds of dye and electrolyte suggests the existence of two electron transfer channels in the sensitization process.

Oxidizing agents such as p-benzoquinone may be able to take electrons away from electronically excited dye molecules. If this process occurs and competes with the electron transfer process from the excited dye molecules to a semiconductor electrode, the decrease in the sensitized photocurrent may be observed. From the above standpoint, we investigated the effect of p-benzoquinone in the electrolyte solution containing dye on the spectral sensitization of a silver chloride membrane electrode.

The silver chloride crystal obtained from Oyo Koken Ind. was a thin plate with the dimension of 8x8x0.5 (mm^3), and it was used after etching with a potassium cyanide or sodium thiosulfate aqueous solution. Photocurrent was measured by using the experimental setup described previously.[1] The following electrochemical cell which was essentially the same as that reported by Mulder,[2] and Gerischer and Selzle[3] was constructed: Pt(I)/electrolyte(I), dye/AgCl/electrolyte(II)/Pt(II). The dyes used as spectral sensitizers were rhodamine B and 1,1'-diethyl-2,2'-quinocyanine chloride.

In the measurement of the photocurrent, the d.c. voltage of 3 V was applied between the two platinum electrodes, and interference filters of 10 nm in half width were used to illuminate the dye-containing electrolyte solution. Under this condition, the dark current due to ionic conduction and the photocurrent flowed by about 10^{-6} A and about 10^{-12}—10^{-9} A, respectively. In order to determine the photocurrent selectively, a light chopper and a lock-in-amplifier were used. The frequency of the chopping was 125 Hz.

p-Benzoquinone was added to the electrolyte solution (I) just prior to the measurement of the sensitized photocurrent. Fluorescence and absorption spectra of the dyes were measured with a HITACHI MPF-2A fluorescence spectrophotometer and a SHIMAZU MPS-5000 spectrophotometer, respectively.

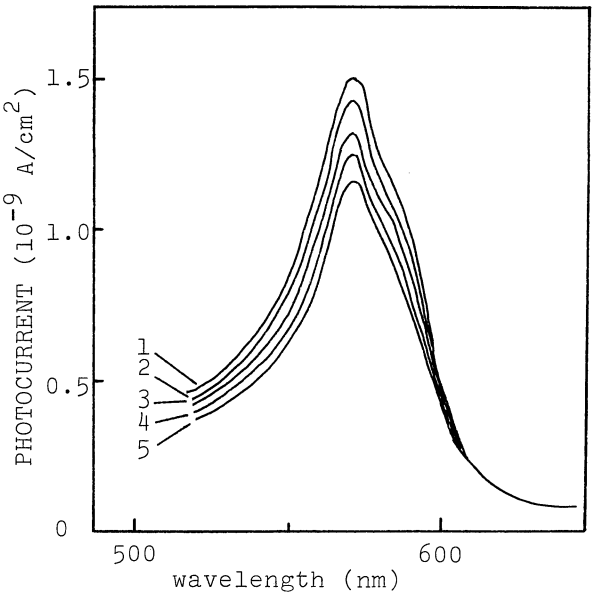

Fig.1. Effect of p-benzoquinone on the sensitized photocurrent by rhodamine B (2×10^{-5} mol/l). Concentration of p-benzoquinone: 1) 0, 2) 2×10^{-6}, 3) 5×10^{-6}, 4) 2×10^{-5}, 5) 4×10^{-5} mol/l.

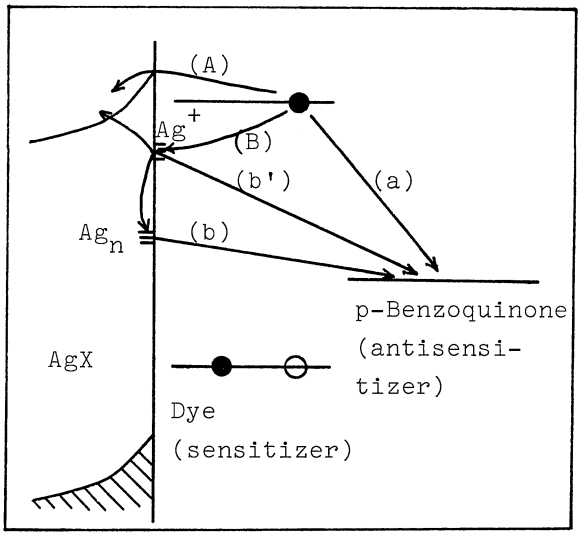

Fig.2. Schematic diagram of electron transfer process in the presence of p-benzoquinone.

Spectral Sensitization by Rhodamine B

The sensitized photocurrent by rhodamine B in a $AgNO_3$ electrolyte solution decreased with increasing the concentration of p-benzoquinone as shown in Fig. 1. The fluorescence and the absorption intensities of the rhodamine B solution in the visible region were decreased with illumination period if the solution contained p-benzoquinone. This fact indicates that the reaction of p-benzoquinone with excited rhodamine B occured. According to James,[4] p-benzoquinone can oxidize silver atoms on the surface of silver halides, i.e., electrons can be transferred from a silver speck to p-benzoquinone. This fact suggests the existence of paths (b) and/or (b') for electron transfer processes as shown in Fig. 2. The path (a) in Fig.2 will correspond to the photochemical reaction of rhodamine B with p-benzoquinone. Electron transfer from the electronically excited rhodamine B molecules to p-benzoquinone via the paths (a), (b), and/or (b') will result in the decrease in the sensitized photocurrent by the addition of p-benzoquinone into the electrolyte solution (I).

Spectral Sensitization by 1,1'-Diethyl-2,2'-quinocyanine chloride

The effect of p-benzoquinone on the sensitized photocurrent by 1,1'-diethyl-2,2'-quinocyanine chloride was also investigated. In this case, the steady state photocurrent was increased by the addition of p-benzoquinone into the electrolyte solution (I) as shown in Fig. 3. The increase in the sensitized photocurrent with the concentration of p-benzoquinone was usually observed whenever a KCl, KNO_3, or

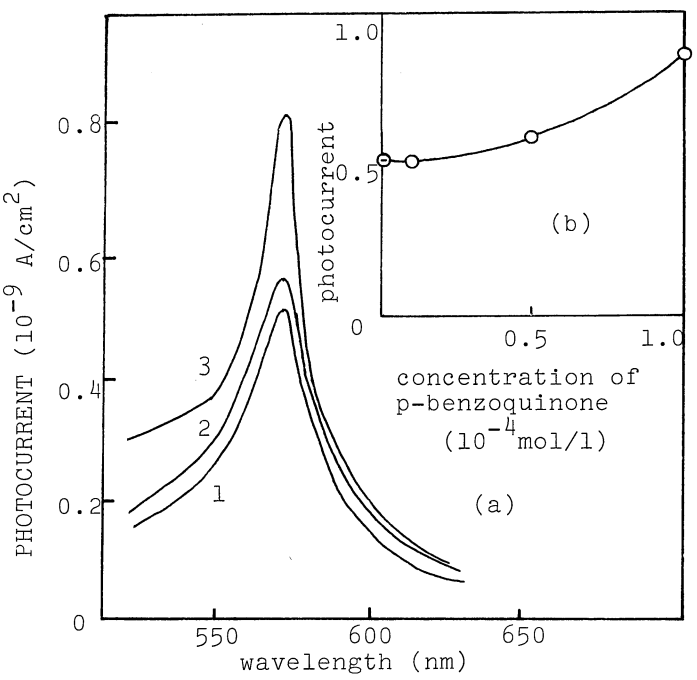

Fig.3. Effect of p-benzoquinone on the sensitized photocurrent by 1,1'-diethyl-2,2'-quinocyanine chloride ($1x10^{-4}$ mol/l).
(a) Action spectra. Concentration of p-benzoquinone: 1) 0, 2) $5x10^{-5}$, 3) $1x10^{-4}$ mol/l.
(b) Relation between sensitized photocurrent at 570 nm and concentration of p-benzoquinone.

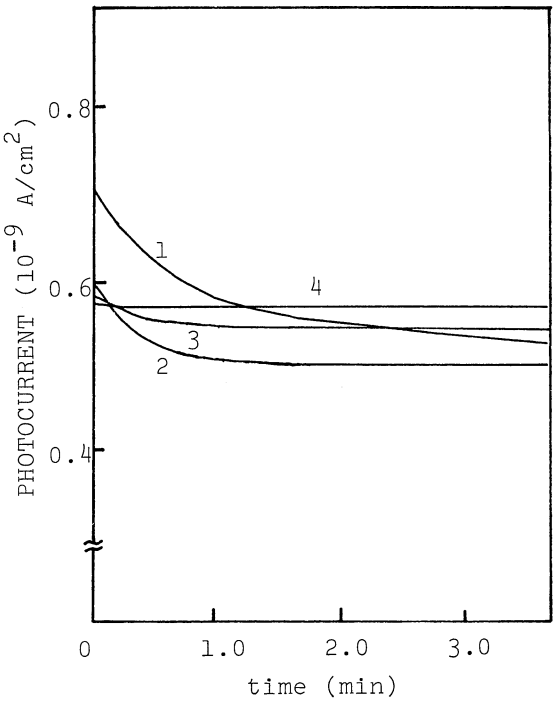

Fig.4. Change in the sensitized photocurrent by 1,1'-diethyl-2,2'-quinocyanine chloride ($1x10^{-4}$ mol/l) with irradiation time.
Illumination wavelength: 570 nm.
Concentration of p-benzoquinone: 1) 0.0, 2) $1x10^{-5}$, 3) $2x10^{-5}$, 4) $5x10^{-5}$ mol/l.

$AgNO_3$ aqueous solution was used for the electrolyte solution (I). However, the degree of the increase in the sensitized photocurrent by the dye in a $AgNO_3$ electrolyte solution was lower than that in the cases of the other electrolyte solutions.

Fig. 4 shows the effect of p-benzoquinone on the decay characteristics of the sensitized photocurrent by the dye at 570 nm. Figs. 3 and 4 show that the addition of p-benzoquinone has the same effect as that of supersensitizers for the spectral sensitization by the dye. It should be noted, however, that the sensitized photocurrent showed a tendency to decay at t=0 when the concentration of p-benzoquinone is not so high. This fact is opposite to the usual supersensitization with a reducing agent[5] such as potassium ferrocyanide which raises the sensitized photocurrent even at t=0. In fact, we found that the sensitized photocurrent was raised at t=0 by the addition of potassium ferrocyanide of a similar concentration to that in the case of p-benzoquinone.

We only suggest at the present stage that, in the spectral sensitization by 1,1'-diethyl-2,2'-quinocyanine chloride, the electron transfer via the path (A) in Fig. 2 might be predominant, and that a small amount of reduced form of p-benzoquinone in the electrolyte solution (I) might effectively act as a supersensitizer.

The above results clearly show that the effect of p-benzoquinone on the sensitized photocurrent varies depending on the kind of dye used as a sensitizer. The kind of the electrolyte solution also influences the effect of p-benzoquinone on the sensitized photocurrent since the increase in the sensitized photocurrent by 1,1'-diethyl-2,2'-quinocyanine chloride in the KCl electrolyte solution is more remarkable than that in the case of $AgNO_3$. These facts suggest the existence of at least two channels for the electron transfer from the excited dye molecules to silver chloride: electron transfer via surface levels formed of silver ions, i.e., the process (B) in Fig. 2, and electron transfer to the conduction band of silver chloride, i.e., the process (A) in Fig. 2. Recognition of the existence of different kind of electron transfer channels depending on the sort of sensitizing dyes and electrolyte might be of great help in understanding the spectral sensitization of the photographic process.

The authors wish to thank Dr. T.Tani and Dr. A.Fujishima for their valuable comments. They also wish to express their appreciation to Mr. M.Kawaguchi for his help in the experiments.

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(Received May 15, 1976)