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NEGATIVE PHOTOCONDUCTION IN SOLUTION DUE TO PHOTOEJECTION OF ELECTRON FROM *p*-BENZOQUINONE ANION TO TETRAMETHYL-*p*-PHENYLENEDIAMINE CATION

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Photolysis of a solution of a strong electron donor and acceptor in tetrahydrofuran caused decrease of the electric conductivity of the solution. The negative photoconduction was presumably due to photoionization of the anion which exists slightly on dissociation equilibrium, and to subsequent trapping of the solvated electron by the cation of the donor.

Photoejection of electrons from aromatic anions takes place easily in ethers.1) Trapping of the ejected electron to a suitable acceptor has been observed in tetrahydrofuran(THF).2) When the acceptor is positively charged, the whole process will bring about decrease of the electric charge in the solution. We observed the negative photoconductivity in solutions of *p*-benzoquinones(BQ's) and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine(TMPD) in THF. It is recognized spectroscopically and electrically that the following equilibrium is present in the solution by the charge-transfer interaction, and that BQ^- and $TMPD^+$ are slightly present.

$$BQ + TMPD \xrightleftharpoons{K_1} BQ\cdot TMPD \xrightleftharpoons{K_2} BQ^- + TMPD^+. \qquad (1)$$

<u>Experimental</u> Solvents were carefully purified and checked by electric resistivity. THF and 1,2-dimethoxyethane were dried with KOH, then fractionally distilled twice over $LiAlH_4$ (both 2×10^9 Ω cm). Acetone(Nakarai, for Electronics) was used without further purification (5×10^6 Ω cm). 1,2-Dichloroethane was washed with KOH solution, distilled over P_2O_5 and fractionally distilled once more over K_2CO_3 (3×10^6 Ω cm).

Filtrated light from a high-pressure mercury lamp (250 W) or 488 nm light of an Ar^+ laser (10 mW) was chopped by a shutter. The measuring cell and procedures were essentially the same as described before.3) Photocurrent was measured directly by means of a synchroscope or a recorder as the voltage change across 100 kΩ resister which was connected in series with the sample cell.

<u>Results and Discussion</u> A typical response of the negative photoeffect is shown in Fig. 1. The conductivity of the solution decreased as long as the duration of the excitation was sufficiently short. If a longer light pulse was illuminated, the decrease of the photocurrent became dull and at last the current began to increase to show positive photoconduction. The conductivity after a light pulse recovered exponentially. When a solution containing only BQ was excited, not negative but pos-

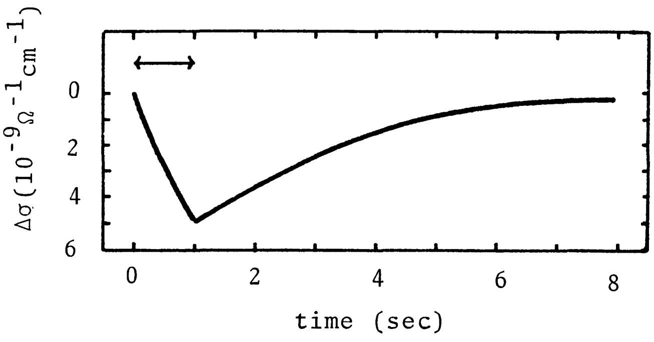

Fig. 1. Negative photoconductivity in THF solution containing chloro-BQ (1.0×10^{-2} M) and TMPD (5.1×10^{-3} M).
The symbol ⟷ indicates a duration of illumination.

itive photocurrent was observed to increase slowly.

The negatively photoconductive response was observed only in the wavelength range between about 400 and 500 nm, where the semiquinone anion radical that is present in the solution according to eq. (1) has the absorption bands. No photoconductive signal was detected on irradiation of light longer than 520 nm where the charge-transfer band is present. Ordinary positive photocurrent was merely observed when the solution was excited by light shorter than 390 nm.

The equilibrium constant, K_1, and the extinction coefficient of the charge-transfer band (max. 680 nm) were spectroscopically determined to be 12 M^{-1}(±10%) and 59 M^{-1} cm^{-1} for the THF solution of chloro-BQ and TMPD at room temperature. K_2 was determined to be about 10^{-10} M from the conductivity of the solution (2.3×10^{-8} Ω^{-1} cm^{-1}) by assuming that the mobilities of cation and anion are both 3×10^{-4} cm^2 V^{-1} sec^{-1}. If 10^{-2} M of chloro-BQ and TMPD were dissolved in THF, the concentration of charge-transfer complex and each ion would become to be some 10^{-3} M and 10^{-7} M, respectively.

The anion will be photo-ionized, $BQ^- + h\nu \longrightarrow BQ + e_s$. The solvated electron then will be trapped by $TMPD^+$ within its lifetime, $e_s + TMPD^+ \longrightarrow TMPD$. The facility of these processes may be due to the ease of photoejection from BQ^- and to the relatively long lifetimes of e_s in ethers.

Negative photocurrents were observed similarly in combinations with TMPD and different quinones (BQ, chloro-BQ and 2,5-dichloro-BQ), but chloranil was not found to contribute to the negative photoeffect.

Effect of solvents was examined to test the dependence of the process on the lifetimes of e_s. In 1,2-dimethoxyethane (dielectric constant: ε=7.2) negative photoeffect was observed, but no negative effect could be detected in 1,2-dichloroethane (ε=10.4) and acetone (ε=20.7). These results imply that the lifetime of e_s must be sufficiently long for the appearance of the negative photoeffect. The lifetime of e_s could be estimated to be some 100 μsec in moderately polar ethers.[1,2] Dissolved oxygen made it very hard for the negative photoeffect to appear.

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