NOTES

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Negative Photoconduction in Solution of Aromatic Amine and Benzoquinone by Flash Excitation

Jun-ichi NAKATA, Takeshi IMURA, and Kazuo KAWABE
Electrophysics Laboratory, Department of Electrical Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565

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Synopsis. The conductivity of a solution of benzoquinone and TMPD decreased after being subjected to flash excitation. This is attributed to the decrease of free ions due to the equilibrium shift produced by photo-induced disappearence of the ion pair.

When the absorption of light causes a decrease in the electrical conductivity of a material, the phenomenon is called negative photoconduction. It occurs occasionally in some inorganic solids.$^{1)}$

A new type of negative photoconduction (on continuous excitation) was observed$^{2)}$ in organic solution containing both *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) and *p*-benzoquinones under the following conditions: (I) In the wavelength range of exciting light 400—500 nm, where *p*-benzoquinone or its chloro-derivatives and small amounts of their semiquinone anion radicals have characteristic absorption bands, the anion radicals are slightly present in the solution due to equilibrated ionic dissociation. (II) For solvents, the negative photoconduction was observed only in appropriately polar ethers such as THF and 1,2-dimethoxyethane, but not in dioxane, a non-polar ether, nor in other moderately polar solvents such as acetone, benzotrifluoride and 1,2-dichloroethane.

We have studied the transient change in the conductivity of a solution after being subjected to flash irradiation for a few μs and the origin of the phenomenon.

Materials,$^{2)}$ the apparatus and procedure$^{3)}$ are the same as described. The input energy of discharge to obtain a light pulse was 180 J. Two glass filters (Toshiba VY-42 and VB-46) were used. Current signal was read through 10 kΩ resistor; the time constant of the circuit is estimated to be about 1 μs. High purity nitrogen (more than 99.999%) was substituted for dissolved oxygen in the solution. All the experiment were carried out at room temperature.

The conductivity of a THF solution containing both TMPD and chloro-*p*-benzoquinone of the same concentration 1.0×10^{-2} M momentarily increased for *ca.* 15 μs, before the subsequent negative photoconduction was slowly initiated (Fig. 1(a)). Conductivity reached the minimum value at 1.5—2.0 ms, and then recovered exponentially to the original value in the dark within a few seconds. At minimum the decrease in conductivity was a few percent of the original conductivity ($2.3\times10^{-8}\Omega^{-1}\,\text{cm}^{-1}$).$^{2)}$

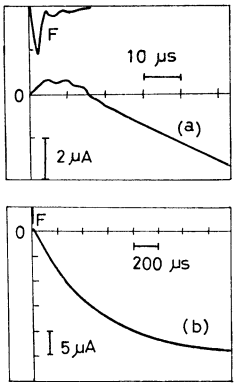

Fig. 1. Photocurrent of THF solution containing both TMPD and chloro-*p*-benzoquinone with the same concentrations of 1.0×10^{-2} M.
Negative photoconduction is shown to begin slowly after the light pulse(F) is over (a), and the minimum value is reached at about 1.5—2.0 ms (b).

The following equilibrium was reached in the solution:

$$A + D \rightleftarrows A\cdot D \rightleftarrows A^-\cdot D^+ \rightleftarrows A^- + D^+. \qquad \text{(a)}$$

Concentration of the ion pair was estimated to be more than 10^{-6} M from the absorption spectra assuming the molar extinction coefficient of D^+ (mainly in the ion pair) to be $10^4\,\text{M}^{-1}\,\text{cm}^{-1}$; the concentration of free A^- was evaluated to be 10^{-7} M.$^{2)}$

By optical excitation of $A^-\cdot D^+$, an electron will be ejected and subsequently trapped by $A\cdot D^+$:

$$A^-\cdot D^+ + h\nu \rightarrow e_s^- + A\cdot D^+ \rightarrow A\cdot D \text{ or } A + D. \qquad \text{(b)}$$

This brings about reduction in the concentration of the ion pair $A^-\cdot D^+$ with subsequent recovery of equilibrium:

$$A^- + D^+ \xrightarrow{k_c} A^-\cdot D^+ \longleftarrow A\cdot D. \qquad \text{(c)}$$

According to the left-hand side of (c), the conductivity of the solution decreases. This was verified from the second-order plot of Fig. 1(b). The rate constant k_c was estimated to be of the same order as diffusion limited.

The positive conductivity change appearing within *ca.* 15 μs at the first portion of the responce (Fig. 1(a)) is attributed to the formation of charge carriers according to the left-hand side of (b).

Free anion is also photo-ionized and ejects an electron:

$$A^- + h\nu \rightarrow e_s^- + A. \qquad \text{(d)}$$

This is a minor reaction as compared with (b). The electron in (d) will be scavenged by A in a moment. Thus, (d) takes no part in negative photoconduction. We proposed²⁾ that the origin of the negative photoconduction is attributed to (d) and the subsequent trapping of electron by D^+:

$$e_s^- + D^+ \rightarrow D. \qquad (e)$$

However, the solvated electron is to be scavenged by A in competition with (e):

$$e_s^- + A \rightarrow A^-. \qquad (f)$$

These reactions yields no conductivity change.

Slow recovery from the negative photoconduction was expressed by first order kinetics, and corresponds to ionic dissociation of A·D *via* $A^-\cdot D^+$. The right hand side of (c) might be slow. Slow ionization of quinones by interaction with aliphatic amines was reported⁴⁾ by the rapid scan spectrophotometric method.

No solvated electron could be detected spectroscopically with our flash apparatus. The concentration of solvated electron should be 10^{-6} M or less since all A^- is not photo-ionized. Optical path-length of about 100 cm is required if the molar extinction coefficient of solvated electron in THF is about $10^4\ M^{-1}\ cm^{-1}$.

References

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4) T. Yamaoka and S. Nagakura, *ibid.*, **44**, 1780 (1971).