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Photovoltaic Effect of Aromatic Diamine in Solution

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Photovoltaic behaviors are described of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine dissolved in various polar solvents. Positive photovoltage is observed on the illuminated electrode in highly polar solvents such as methanol and acetonitrile, and none in moderately polar ones such as ethanol and acetone. The influence of a few electrode metals on photovoltage has been examined. The electromotive force increases with the work function of metals from tantalum to platinum. Conditions for the appearance of photovoltage are discussed and the photo-ionization process of the aromatic diamine is considered.

Photovoltaic effects are sometimes observed when an electrode immersed in some organic solution is irradiated with light. This phenomenon has been utilized by a few researchers for studying photochemical or photobiological reactions where ionic species play an important role. Methanol solutions of chlorophyll containing benzoquinone were shown to produce photovoltages which depend upon the pH of the solutions.[1,2] Photovoltage measurements were also carried out in tetracyanoethylene dissolved in tetrahydrofuran by exciting the charge-transfer band.[3] The first problem was to identify the active species inducing electromotive force, identification being carried out by means of ESR, flash photolysis and other spectroscopic techniques. The active species are generally the anions or cations which are generated in solutions by photo-ionization, and held on the electrode by adsorption.

The present work deals with the photovoltaic behaviors of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) in polar solvents. This system seems to be the best for general and exhaustive investigation of photoelectric phenomena in organic fluid solutions, since a number of detailed studies have clarified the primary products and processes which take place on the photo-ionization of TMPD.[4–14]

When TMPD is photo-ionized in solution, a fairly large photocurrent is observed,[4,8,10–13] suggesting the generation of voltaic effect. Although the photovoltaic effect is a phenomenon taking place on the interface between liquid solvent and solid metal, detailed information is scarce as regards the properties and reactions of the active species which produces photo-emf on the interface. It was thought desirable to carry out experiments from the viewpoint of surface phenomenon. In this paper discussions are given on the influence of electrode metals and solvents upon the photovoltaic effect of TMPD solutions.

Experimental

Materials. TMPD was obtained as described.[4] Ethanol for spectroscopy (Nakarai Chemicals), spectrosol-grade acetone and methanol (Dotite), and luminasol-grade dimethylformamide (Dotite) were used without purification for the preparation of solutions. Acetonitrile was refluxed, fractionally distilled twice over phosphorus pentoxide, and finally distilled over potassium carbonate.

Apparatus and procedure. The cell for photovoltaic measurement is shown in Fig. 1. It is made from a quartz tube, the top of the cell being a ground joint fitted to the upper cover, from which 5 mm × 50 mm electrodes are suspended with two tungsten rods.

The electrode metals were cleaned as follows. Platinum and tantalum were washed successively with a solution of a surfactant (R.B.S. 25, Chemical-Products R. Borghgraef), deionized water and distilled methanol, and were then dried. Copper was treated with dilute hydrochloric acid, washed with deionized water and distilled methanol, and then dried.

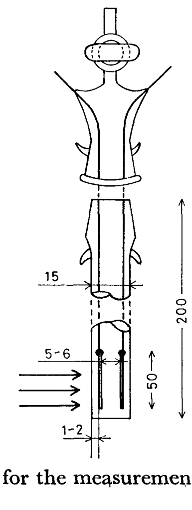

Fig. 1. Cell for the measurement of photo-emf.

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TABLE 1. EFFECT OF POLARITY AND VISCOSITY OF SOLVENT[15) ON THE PHOTO-emf OF TMPD SOLUTION (5×10^{-3} M)

	Dielectric constant (25 °C)	Dipole moment (D)	Viscosity (cp, 25 °C)	Photo-emf (mV)	TMPD$^+$ spectrum	Appearance[4) of phto-current
Acetone	20.7	2.90	0.304	—	—	…
Ethanol	24.3	1.69	1.078	—	+	—
Methanol	32.6	1.69	0.545	10.2(±15%)	+	…
Dimethylformamide	36.7	3.86	0.802	8.6(±10%)	+	+
Acetonitrile	37.5	3.92	0.325 (30 °C)	40.5(±15%)	+	+

The sample solution was introduced into the cell, the electrodes inserted, and high-purity nitrogen (more than 99.999%) was bubbled into the solution for a few minutes through a fine Teflon tube to remove dissolved oxygen. The tube was then pulled out, the upper ground stopper being closed before each experiment.

Only the front electrode was illuminated by light from a high-pressure mercury lamp (250 W, Ushio) with quartz lenses and a glass filter (UV-D1C, Toshiba) which passes only light having energy 3.1—4.1 eV. The distance between the lamp and the cell was fixed at about 400 mm. The lower part of the front electrode was illuminated over a 20 mm× 2—3 mm area.

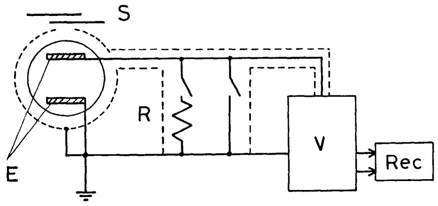

Fig. 2. Schematic diagram of measureing circuit.
S: Shutter, E: Electrodes, R: 100 kΩ resistor, V: Vibrating-reed electrometer, Rec: Recorder.

The apparatus for measurement of photovoltage is shown in Fig. 2. The entire cell was put in a brass pipe to be protected from electrical noise. A vibrating-reed electrometer (TR-84 M Takeda Riken) was used to read photo-induced voltage. Photovoltage was recorded with values across a shunt resistor of 100 kΩ. This helped improve the reproducibility of measurement and produce the stable value of voltage, though the magnitude of the observed voltage became smaller. The resistance of the sample solutions were in the range 4×10^5—$5 \times 10^6\ \Omega$, differing with solvent. The lower limit of the detection of photovoltage was down to 0.05 mV.

Results

The photovoltage responses are shown in Table 1 for 5×10^{-3} M solutions of TMPD in various polar solvents. Positive photovoltages were observed on the illuminated electrode in methanol, dimethylformamide, and acetonitrile. Experiments in dimethylformamide were repeated several times for each sample, the deviation from the mean value being within ±10%. In the other solvents the error, partly due to the optical system, was estimated to be within ±15%.

No photo-emf was detected in moderately polar solvents, acetone or ethanol. The positive sign in the column of TMPD$^+$ spectrum in Table 1 indicates that the sample solution turns bluish after the irradiation for measurement of the photo-voltage, *viz.*, TMPD$^+$ is photo-generated and exists either in the form of the free or paired ion in the solution. Appearance of the photocurrent indicates the existence of photo-generated free ions, not paired, in the solution.[4)

The effect of electrode metal on the photovoltage response is shown in Table 2 for 5×10^{-4} M solutions of TMPD in dimethylformamide. The electromotive force shows a tendency to increase with the work function of the metal.

TABLE 2. EFFECT OF WORK FUNCTIONS OF ELECTRODE METALS ON THE PHOTO-emf OF TMPD SOLUTIONS (5× 10 M) IN DIMETHYLFORMAMIDE

	Work function[16) (eV)	Photo-emf (mV) (±15%)
Pt	5.4	10.2
Cu	4.5	4.7
Ta	4.1	0.5

The maximum quantity of the photo-emf was obtained over the concentration range 10^{-3}—10^{-4} M. The phtovoltage decreased remarkably when the solution was diluted to 10^{-5} M or less. In concentrated solution ($\geqq 10^{-2}$ M) photovoltage response became small due to the diminution in intensity of the exciting light on the surface of the electrode caused by the inner filter effect in the front portion of the sample solution. The molar extinction coefficient was determined to be $(2.6 \pm 0.1) \times 10^3$ M^{-1} cm^{-1} for the first absorption maximum of TMPD at 3.8 eV in dimethylformamide.

No photovoltage (more than 0.05 mV) was generated by irradiating the system containing no TMPD and composed of only solvent and electrodes.

Discussion

Cationic and anionic species should be photo-generated in equal concentration. However, the photovoltage appeared positively on the illuminated electrode. The concentration gradient of charged species in the vicinity of the electrode can be induced from the difference in the diffusion velocity between TMPD$^+$ and anionic species. The latter might have a larger

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15) J. A. Riddick and W. B. Bunger, "Techniques of Chemistry," ed. A. Weissberger, Vol. 2, "Organic Solvent," third ed., John Wiley & Sons, Inc., N. Y. (1970).

16) A. J. Dekker, "Solid State Physics," Asian ed., Maruzen Co., Ltd., Tokyo (1960), p. 223.

diffusion velocity since the electron is to react easily with the solvent molecules and to be transferred successively. On the contrary, stable TMPD$^+$ has ordinary diffusion velocity of the solvated ion. It is well-known that either cation or anion is adsorbed preferentially from electrolyte solution onto the metal surface. TMPD$^+$ might be adsorbed preferably onto the surface of the illuminated electrode.

No response of photo-emf was detected in acetone (Table 1). Ultraviolet excitation of TMPD in acetone produced no absorption of TMPD$^+$. Thus the cation, active species, does not seem to be generated in the solution. In ethanol the photo-generation of TMPD$^+$ surely occurs (Table 1), but neither photocurrent nor photovoltage was detected. This implies that TMPD$^+$ observed spectroscopically in ethanol is to be present in the form of ion-pair which gives rise to absorption but cannot contribute to photoelectric effect. The particular situation in ethanolic solution was discussed in other papers.4,7) The polarization energy seems to be somewhat short in acetone or ethanol for the photo-generation of ion-pair or dissociation into free ions.

Methanol, dimethylformamide, and acetonitrile, in which the photoelectric effects could be observed are highly polar. The fall in the ionization level by polarization energy or the ease for photo-ionization should be in the order of polarity of the solvents. The magnitude of the photovoltage, however, was not in the order of polarity, and seems to depend on the viscosity of solvents as well (Table 1). Actually, the photo-emf was hardly observed in *N*-methylpropionamide which has a high dielectric constant (ε=172$^{14)}$ at 25 °C) and high viscosity (5.2 cp$^{14)}$ at 25 °C) due to the hydrogen-bonded aggregation. A lower viscosity may accelerate the formation of the concentration gradient of the active ionic species. Higher viscosity of dimethylformamide in spite of its large polarity, would prevent the generation of a larger photo-emf than in methanol. Photoelectric responses were especially large in acetonitrile. A possible explanation might be that the anionic species in acetonitrile is very mobile and diffuses away rapidly.

The cation present in the adjacent neighborhood of the electrode was supposed to be the active species to produce electromotive force. The cation will pull out the electron from electrode metal if the metal had a small work function, and will be changed to neutral TMPD which cannot produce electromotive force. The electron-transfer process between TMPD$^+$ and metal or the oxidation-reduction reaction on the metal surface can take place more easily as the work function of the metal decreases. Thus the photovoltage obtained gets smaller, as the work function of electrode metal becomes smaller (Table 2). If the work function is smaller than the energy of the state of TMPD$^+$, no photovoltage response would be detectable, because of the instant reduction of cation to neutral molecule.

It is concluded that photo-generation of dissociated TMPD$^+$ is necessary for the appearance of photovoltage in the solution. The magnitude of photo-emf seems to be determined by the quantity of TMPD$^+$ in the vicinity of the electrode.