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A Novel Electrochemical Quantification Method for Trans/Cis Interconversion of Azo Compounds in a Solid Monolayer Film

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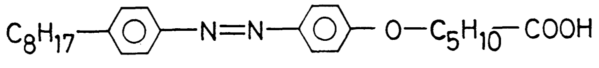
A direct electrochemical quantification method for the trans/cis interconversion reaction of some azobenzene derivatives in a solid monolayer film was developed, on the basis of the photoelectrochemical hybrid phenomenon that we found.

An "in situ" quantitative analysis for the trans/cis interconversion reaction of azo compounds is quite of importance for kinetic studies, since the direct separation of trans/cis mixture is a troublesome and time-consuming work. Although an approximate "difference-spectra" method has been proposed by Brode et al. in their earlier study,1) a large uncertainty of the result will be inevitable for the case that the trans/cis absorption spectra are not well-separated, especially for the solid phase reactions. As is known, there are two typical reversible reactions, i.e., the photochemical trans/cis isomerization2) and the electrochemical reduction/oxidation,3) in the azobenzene system. In the previous studies4) we found a novel hybrid phenomenon concerning these reactions. Based upon this hybrid phenomenon, we have proposed a novel "photon-mode" information storage technique5) and a highly-sensitive photon-counting method.6) Here we present the other unique application, i.e., "in situ" and electrochemically quantifying the trans/cis interconversion process of azobenzene derivative in the solid monolayer films.

The azobenzene derivative used was 4-octyl-4'-(5-carboxyl-pentamethylene-oxy)-azobenzene (ABD, whose molecular structure is shown in Fig. 1), the monolayer film of which was deposited onto a transparent SnO_2 glass substrate, the working electrode, by the Langmuir-Blodgett method. The surface pressure and subphase temperature for the film



ABD

Fig. 1. Molecular structure of the azobenzene derivative used.

fabrication were respectively controlled at 25 mN/m and 20 °C. Cyclic voltammetry was used for the electrochemical measurements, with a 0.2M aqueous potassium perchlorate, buffered to pH 7.0 with a Britton-Robinson solution, being used as an electrolyte. The reference electrode was Ag/AgCl, and the counter electrode was a Pt wire. A 500W xenon lamp was used to induce the photochemical trans/cis isomerization of ABD molecules. The xenon lamp's UV output (320-380 nm) was obtained via a glass filter.

The trans ⟶ cis photoisomerization reaction of ABD molecules in the solid monolayer film was taken as a specific example for the present study. For an easy understanding, the hybrid phenomenon[4)] that we found in azobenzene system may be necessarily described at first. Figure 2 shows the cyclic voltammograms of trans- and cis-ABD monolayer films on a SnO_2 glass electrode, with the cis-ABD film being obtained after the xenon lamp irradiated the initial trans-ABD film for one minute. In the applied potential range no reduction and oxidation peaks were observed in the trans-ABD film, whereas in the cis-ABD film significantly large peaks were obtained due to the reduction of cis-ABD to the hydrazobenzene derivative (i.e., the hydra-ABD, -NH-NH-) followed by the oxidation of the hydra-ABD. The difference in reduction potential ($E_{1/2}$) of the trans- and cis-ABD was estimated to be more than 400 mV in a neutral solution. The hydra-ABD, on the other hand, was exclusively oxidized to the energetically stable trans-ABD because no electrochemical activity was observed after its oxidation in the electro-inactive potential range of trans-ABD. Evidently, these behaviors make the trans-, cis-, and hydra-ABD being clockwisely organized to a "one-way" cyclic process via the sequent photoisomerization, reduction and oxidation reactions, leading to the hybrid phenomenon what we called.

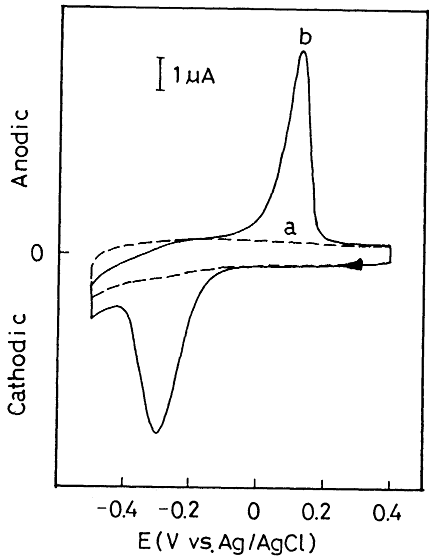


Fig. 2. Cyclic voltammograms of trans (a) and cis (b) ABD monolayer films on an SnO_2 electrode. The cis-ABD was obtained by UV-irradiating the trans-ABD for one minute.

In view of the photoelectrochemical hybrid feature of the present system, the procedure for quantification of the trans⟶cis photoisomerization can be schematically shown in Fig. 3. First of all, the trans-ABD is converted to the cis-ABD by UV-irradiation. Because of the substantially different electrochemical reductivities of trans- and cis-ABD, it is possible to perform a selective reduction of cis-ABD by control of cathodic electrode potential. Consequently, the quantity of cis-ABD (Nc, in mole) in the mixed monolayer film can be calculated from either cathodic or anodic charge(Q, in C) in the reduction-oxidation process, according to

$$Nc = \frac{Q}{F \cdot n} \qquad (1)$$

where, F is the Faraday constant(9.648×10^4 C/mol), and n is the electron number involved in reaction scheme, which takes a value of 2 in the present system.

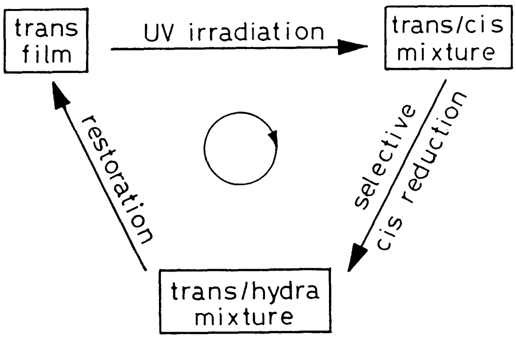


Fig. 3. Experimental procedure for quantification of cis-ABD in the mixed monolayer film.

On the other hand, the total quantity of ABD (N, in mole) in the monolayer film can be calculated by

$$N = \frac{10^{16} A_0 f}{N_0 S_0} \qquad (2)$$

where, A_0 is the apparent area for electrochemical reaction(in cm^2); f is the transfer ratio in the film fabrication process, which is defined as a ratio of the area change in the Langmuir trough associated with the transferring operation to the total substrate area dipped into the subphase solution of the Langmuir trough[7](f = 0.8 in the present case); N_0 is Avogadro's number (6.022×10^{23}/mol); and S_0 is the occupation area per ABD molecule at the film-fabrication condition, which was calculated from the surface pressure-area isotherm of ABD to be 26.1 Å^2/molecule.[8]

The molar percentage of cis-ABD(Φc) in the trans/cis mixed monolayer film is then obtained by

$$\Phi c = \frac{Nc}{N} \, 100\% \qquad (3)$$

The measurement uncertainty of this method mainly arises in the determination process of faradaic charge quantity due to the existence of a non-faradaic charge current. Since a precision of 10^{-8}C in charge quantity is obtainable using an appropriate potential sweep rate, the uncertainty of cis-ABD molar percentage can be limited within 0.05%.

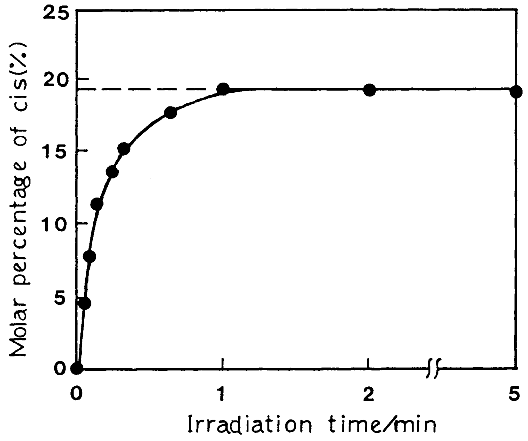


Fig. 4. Relationship between the UV-irradiation time and the molar percentage of cis-ABD in the mixed monolayer film.

Figure 4 shows a series of thus-determined molar percentages of cis-ABD in the mixed film, corresponding to the gradually increased UV-irradiation. Since the hydra-ABD, i.e., the electrochemical reduction product of cis-ABD, is exclusively oxidized to the trans-ABD in the anodic potential sweep, the UV-irradiation experiments were always started from the same trans-ABD state during the "isomerization ⟶reduction⟶ oxidation" repetition. Evidently, the cis-ABD molar percentage in the mixed monolayer film shows a gradual increase, following the increase of irradiation time, and finally becomes constant, indicating that the system has reached to a photostationary state. It was found that only 18.9% of trans-ABD in the monolayer film was converted to the cis-ABD at the photostationary state. This value is comparable with that obtained for the monolayer assemblies at the same condition, in which the cis percentage was roughly estimated to be 30%[9)] by the "difference-spectra" method referred above. Moreover, in the case of a homogeneous chloroform solution, the cis-ABD occupies more than 85%, determined by the "difference-spectra" method, at the same photostationary state. The large difference of the trans to cis conversion percentage between solid monolayer film and homogeneous solution was ascribed to the inhibition effect of a rigid film on the area-increasing trans to cis isomerization.[9)]

The quantification method we proposed is not necessarily limited to the trans ⟶ cis photoconversion reaction, and it can also be used for the cis ⟶ trans photo- or thermal conversion for several azo compounds having the mentioned photoelectrochemical hybrid effect. Since the potential sweep for electrochemical measurement can be made enoughly fast, the quantitative analysis for a system with the cis molecules having a very short life-time, and a system with an extremely small amount of cis component, may also be possible using the present electrochemical method. Finally, the most important feature of the present method may be its "in situ" property which leads to a direct and absolute quantification without necessity of trans/cis separation.

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