

Electrostatically Induced Isomerization of Azobenzene Derivatives in Langmuir–Blodgett Films

Tadashi Enomoto, Hidesato Hagiwara, Donald A. Tryk, Zhong-Fan Liu,[†]
Kazuhiro Hashimoto, and Akira Fujishima*

Department of Applied Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113, Japan

Received: December 12, 1996; In Final Form: April 30, 1997[®]

A novel electrochemically induced *cis*-to-*trans* isomerization process involving amphiphilic azobenzene derivatives in Langmuir–Blodgett monolayer films at electrode/electrolyte interfaces was examined using electrochemical and UV–visible absorption measurements. This isomerization proceeds electrostatically, i.e., with no Faradaic current and no discernible features in the double-layer capacitive charging current, when relatively positive electrode potentials are applied to the monolayer film. This electrostatically induced process is rather slow (first-order rate constants in the 10^{-2} – 10^{-1} s⁻¹ range over the potential range of +0.65 to +0.85 V vs Ag/AgCl, respectively), but the highest rate constant measured (at +0.85 V vs Ag/AgCl) represents an increase of approximately 3 orders of magnitude compared to that of the thermal isomerization process. Surprisingly, the activation energy for the electrostatic process was found to be essentially potential independent and nearly the same as that for thermal isomerization. The rate constants for the *cis*-to-*trans* isomerization obtained at given potentials were also found to depend sensitively on details of the molecular structure, such as the length of the alkyl chain connecting the carboxyl group to the azo group (spacer) and the length of the alkyl tail, which implies that the isomerization reaction involves an interaction between the intrinsic electric field of the molecules in the highly ordered film and the relatively strong electric field associated with the electrical double layer at the electrode surface.

Introduction

Photosensitive molecules are of great interest in terms of their potential applications in molecular devices such as information storage systems¹ and photochemical switching systems.² Azobenzene and its derivatives (ABDs) have been much studied as typical model photoactive compounds owing to their drastic and reversible conformation changes occurring as a result of photoinduced and thermally induced *cis*–*trans* isomerization. Based on these characteristic reactions of azobenzene, molecules that include azobenzene units have attracted much attention as functional compounds over the past 50 years^{3–6} and have been employed, for example, as probes for molecular dynamics,^{7,8} as photochemical switching devices,² and as triggers for photoactive molecular alignment.⁹ In addition, ABDs and their corresponding hydrazobenzene derivatives (HABDs) can be interconverted electrochemically.¹⁰ Thus far, we have focused our attention on the specific photochemical–electrochemical reaction routes that are exhibited in amphiphilic ABD monolayer films.¹ The key feature of these coupled reactions is that *cis*-ABDs produced by UV irradiation in Langmuir–Blodgett (LB) monolayer films are reduced to HABDs at substantially more positive potentials than those for the corresponding *trans*-ABDs. HABDs thus obtained are reoxidized exclusively to the more thermodynamically stable *trans*-ABD form. On the basis of these route-specific reactions, we have proposed several applications of ABD monolayer films, for example, in high-density information storage systems and for electrochemical actinometry.^{1,11} We were also able to sensitively measure the kinetics

of the *cis*–*trans* thermal isomerization process in highly ordered monolayer films using these reactions.¹²

Recently, as part of our photochemical–electrochemical studies on ABD LB monolayer films, we found that *cis*-to-*trans* isomerization proceeds in these films without the passage of any apparent Faradaic current and also without any discernible features in the double-layer capacitive charging current when the potential of the film-covered electrode is swept to positive potential values.¹³ This novel isomerization process may provide not only a new means by which to control the properties of LB films but may also provide new information concerning the isomerization mechanism. Although much progress has been made in the understanding of the thermal isomerization process,^{14–24} the mechanism has not been completely clarified. Two different mechanisms have been proposed: the in-plane inversion mechanism, in which *sp*-hybridization is maintained throughout the reaction, and the rotation mechanism, which involves the loss of π -conjugation. In the present work, we have examined the electrostatic *cis*-to-*trans* isomerization phenomenon in much greater detail, confirming its existence using electrochemical and spectroscopic measurements. This reaction proceeds only as a result of positive potentials applied to the ABD monolayer film-covered electrode, increasing in rate with increasing potential, and is thus distinguishable from the conventional photoinduced¹¹ and thermally induced *cis*-to-*trans* isomerization reactions.

Experimental Section

Reagents. The ABD compounds used were as follows: 4-octyl-4'-(5-carboxypentamethyleneoxy)azobenzene, 4-octyl-4'-(3-carboxypentamethyleneoxy)azobenzene, and 4-dodecyl-4'-(3-carboxypentamethyleneoxy)azobenzene (C₈AzoC₅, C₈-AzoC₃, and C₁₂AzoC₃, respectively), whose molecular structures are shown in Figure 1. These were purchased from Dojindo

[†] Present address: Center for Intelligent Materials Research (CIMR), College of Chemistry and Molecular Engineering, Beijing University, Beijing 100871, People's Republic of China.

* To whom correspondence should be addressed. Phone: +81-3-3812-9276. Fax: +81-3-3812-6227. E-mail: akira-fu@fchem.t.u-tokyo.ac.jp.

[®] Abstract published in *Advance ACS Abstracts*, August 15, 1997.

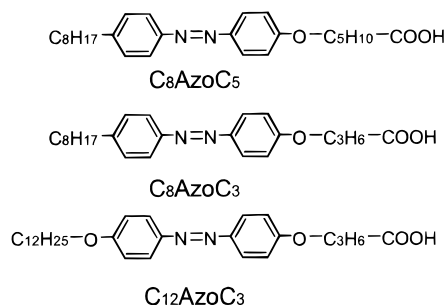


Figure 1. Molecular structures of the amphiphilic azobenzene derivatives used in the present work.

Laboratory. All of the chemicals used were of reagent grade and were used without further purification.

Fabrication of ABD Monolayer Films. The *trans*-ABD monolayer films were deposited onto transparent SnO₂ glass substrates in the dark by the conventional LB method using a commercial film balance (Kyowa Kaimen, HBM-AP). A 0.2 mM cadmium chloride aqueous solution was used as the subphase, and no special pH adjustment was made. The ABD monolayers were spread from the ABD chloroform solutions (1.8 mM) onto the 920 cm² subphase surface. After the solvent was allowed to evaporate for 20 min, the ABD monolayers were compressed at a constant rate of 7 cm² min⁻¹ up to a surface pressure of 25.0 mN m⁻¹, at which the monolayer transfer was conducted. SnO₂ glass, with a sheet resistance of 10 Ω/□,²⁵ was purchased from Asahi Glass Co., Ltd. To increase the hydrophilicity of the surface of the SnO₂ glass, it was pretreated by immersing it in an alcohol-KOH solution (1:1 mixture by volume of ethanol and ~50 wt % KOH) for half a day and then rinsing several times with deionized water (>18 MΩ, Millipore Products) before use. The monolayer film at the air/water interface was transferred to the substrate via the standard vertical dipping-raising method at a rate of 5 mm min⁻¹. Because the surface of the SnO₂ substrate was hydrophilic, only a monolayer film of ABD was formed on the SnO₂ substrate during a single dipping-raising cycle, with the hydrophobic alkyl group exposed to the air and the hydrophilic carboxyl acid group attached to the substrate. All of the ABD monolayer films were fabricated at a constant surface pressure of 25 mN m⁻¹ and a subphase temperature of 20 °C, which was controlled by a thermostat (Tokyo Rikakikai, UC-55).

Photochemical and Electrochemical Measurements. Figure 2 shows the experimental setup for the photochemical-electrochemical measurements. The ABD monolayer film deposited on SnO₂ glass substrate was used as a working electrode (WE) and a Pt wire as the counter electrode (CE). The potential of the working electrode was controlled versus an Ag/AgCl (saturated KCl) reference electrode by a potentiostat (Toho Technical Research, PS-07) or a pulse generator (Toho Technical Research, 2320). A 0.1 M sodium perchlorate aqueous solution, which was made up with pH 7.0 buffer (sodium citrate, 0.0178 M; Na₂HPO₄, 0.164 M), was employed as the electrolyte. Before each experiment, the electrolyte was deaerated with high-purity argon for 15 min. The experiments were carried out at room temperature unless noted otherwise, in which case the temperature was varied using a thermostated water bath.

A 500 W xenon lamp (Ushio Electric Co., UI-501C) was employed for inducing the *trans*-to-*cis* photoisomerization by UV irradiation and the *cis*-to-*trans* isomerization by visible illumination of ABD molecules in the monolayer film. For the UV excitation, a notch-filter centered at 362 nm with a band-

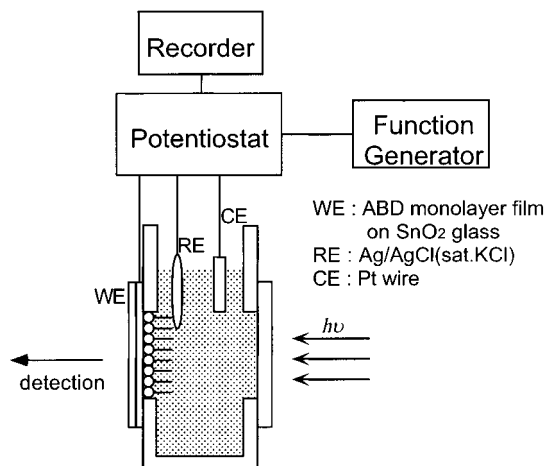


Figure 2. Experimental setup for the photochemical-electrochemical measurements: working electrode (WE), ABD monolayer film deposited on SnO₂ glass electrode; reference electrode (RE), Ag/AgCl (saturated KCl); counter electrode (CE), Pt wire. The hydrophobic head-groups of the ABD molecules are represented by circles attached to the SnO₂ glass surface.

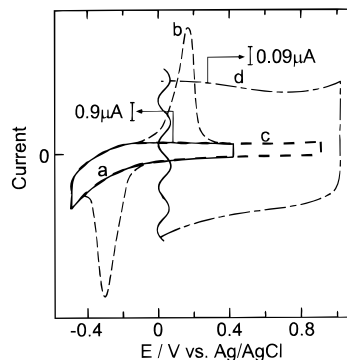


Figure 3. Cyclic voltammograms for the C₈AzoC₅ monolayer film on an SnO₂ glass electrode: (a) *trans* form of ABD monolayer film; (b) after UV illumination for 1 min; (c) after sweeping the potential in the positive direction to 0.9 V; (d) enlarged voltammogram in the positive potential region. The sweep rate was 20 mV s⁻¹.

pass of 60 nm was used. For the visible light excitation, a filter that was transparent to light of wavelength longer than 450 nm was used.

Spectroscopic measurements were also carried out using a UV-visible spectrophotometer (Shimadzu, UV-3101PC) for examination of the ABD-containing monolayer film. In this case, the electrochemical cell was placed in the sample chamber of the spectrophotometer. UV excitation was carried out using light from the xenon lamp, which was supplied to the electrochemical cell using mirrors.

Except during the actual measurement of the cyclic voltammograms, the potential of the ABD monolayer film-modified SnO₂ glass substrate was kept at 0.0 V vs Ag/AgCl, even during illumination and measurement of the absorption spectra.

The potential of zero charge (PZC) of the ABD-modified electrode was determined by conventional capacitance measurements, which were carried out at 100, 500, and 1000 Hz.

Results

The combined photochemical-electrochemical properties of ABD LB monolayer films have been reported in our previous papers.^{26,27} Figure 3 shows typical cyclic voltammograms (CVs) for a C₈AzoC₅ monolayer film on a transparent SnO₂ glass substrate. In curves a and b, the potential sweeps were started at 0.0 V vs Ag/AgCl in the negative direction at a sweep rate

of 20 mV s⁻¹. When the potential was swept in the range -0.5 to +0.4 V, the trans monolayer film did not exhibit a noticeable Faradaic response (curve a). However, when the film was illuminated with UV light for 1 min before the potential scan, a large reduction peak at -0.3 V was observed followed by a reoxidation peak at +0.1 V, as indicated in curve b. This is explained as follows. The UV illumination produces the cis form of a fraction of the ABDs in the monolayer film. Since the cis form is less energetically favored than the trans form in the film, *cis*-ABD is reduced at a substantially more positive potential than *trans*-ABD. The reduction product, HABD, is reoxidized exclusively to the more favored trans form. Therefore, only the cis form is electrochemically active in this potential range. In our previous work, it was found that *trans*-ABDs are typically reduced only at potentials more negative than -0.7 V.^{26,28} In other words, the formation of cis isomers in the monolayer film can be quite reliably confirmed by the presence of the two complementary redox peaks in the potential region positive to -0.5 V.

On the other hand, if the film is subjected to a positive potential, for example, in the +0.5 to +0.9 V range, after UV illumination, the two large redox peaks are not observed, as shown in Figure 3 (curve c). This indicates that the cis-form molecules in the film formed by UV illumination are converted to an electrochemically inactive state, assumed for the moment to be the trans form, at positive potentials. This reaction is apparently not a Faradaic process because no discernible voltammetric features were observed in the potential sweep range shown in curve d, which is shown at a factor of 10 higher current sensitivity in the 0.0 to +1.0 V potential region. After the film was illuminated again with UV light and the CV measured in the -0.5 to +0.4 V potential range, the coupled redox peaks appear again. This series of steps was found to be repeatable typically at least 10 times on the same film, indicating that positive potential treatment at potentials up to +1.0 does negligible damage to the ABD monolayer film.

To examine this phenomenon in more detail, UV-visible absorption spectroscopic measurements were also conducted. Figure 4 shows the changes in the UV-visible absorption spectra for the C₈AzoC₅ monolayer film-covered electrode induced by UV illumination, visible light illumination, and positive electrochemical potentials. The trans-only film has a large absorption peak at 318 nm due to the π - π^* transition (curve a) and a relatively weak peak centered at 450 nm due to the n - π^* transition (curve c).^{4,5} The blue shift of the π - π^* peak in the monolayer film compared with that in chloroform solution (π - π^* peak: 350 nm) has been ascribed to the formation of H-aggregates in the film.^{29,30} After UV illumination for 3 min., the π - π^* peak decreased and the n - π^* peak increased (seen in both curves b and d), indicating partial trans-to-cis photoisomerization. Owing to the steric hindrance, isomerization in the monolayer film was suppressed compared with that in solution so that only ca. 18% of the *trans*-ABD molecules were converted to the cis form.^{30,31} The absorption spectrum of the trans-only film was recovered after visible illumination for 3 min (curve c), demonstrating that the photoisomerization is completely reversible. This cycle can be repeated many times and has been shown unequivocally to involve photoisomerization to the cis form followed by visible light-induced cis-to-trans isomerization back to the trans form.¹¹ In a separate experiment (Figure 4B), the UV-illuminated film was subjected to electrochemical treatment. After a potential of +1.0 V was applied for 60 s to the cis-containing film, the trans-only absorption spectrum was also recovered (curve e). The spectral changes shown in Figure 4B were reasonably well

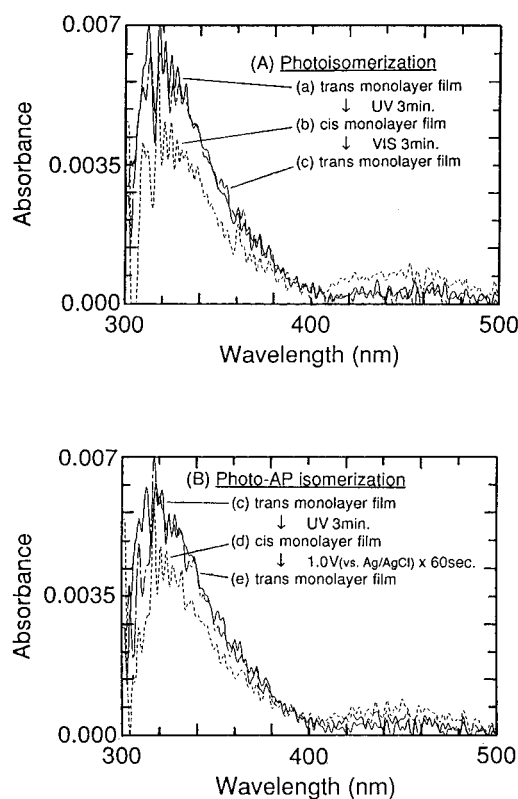


Figure 4. UV-visible absorption spectra for the C₈AzoC₅ monolayer film on an SnO₂ glass electrode: (a) spectral changes due to UV and visible light illumination; (b) spectral changes due to UV illumination and positive potential treatment.

repeatable, suggesting that cis form molecules were also converted back to the trans form by the electrochemical treatment.

Because this phenomenon is apparently electrostatic in nature, it is necessary to determine the potential of zero charge (PZC) of the electrode in order to evaluate the electric field in the electrical double layer. By use of conventional impedance measurements, the PZC of the ABD-LB modified electrode was determined, from the capacitance minimum, to be +0.65 V vs Ag/AgCl.

To measure the kinetics of the electrostatically induced process, the ratio of the surface concentration of the cis form remaining in the film, compared to the initial value, was electrochemically determined as a function of the duration time (*t*) of the applied positive potential. This ratio, $C^*(t) = C(t)/C(0)$, where $C(t)$ and $C(0)$ represent the surface concentrations of cis-form molecules in the film at time *t* and time zero (when the potential was applied), respectively, was determined by integration of the cathodic voltammetry peak (due to reduction of the cis form to DHAB). This ratio is essentially a normalized surface concentration. The results are shown in Figure 5 for the case of an applied potential of +0.80 V vs Ag/AgCl. Figure 5 shows that $C^*(t)$, expressed as a percentage, decreased exponentially with duration time, $C^*(t) = e^{-kt}$, with a time constant of approximately 7.5 s.

We also measured the contribution of the thermal isomerization process. The results (Figure 5, curve a) were obtained at 0.0 V, and the cis-to-trans isomerization rate was assumed to reflect only the thermally activated process. The rate constant for the thermal process at 20 °C was previously reported to be $1.38 \times 10^{-4} \text{ s}^{-1}$.¹² Thus, the electrostatically induced isomerization at +0.85 V vs Ag/AgCl, $1.55 \times 10^{-1} \text{ s}^{-1}$, is approximately 3 orders of magnitude faster than that for the thermally activated process. It should also be noted that the

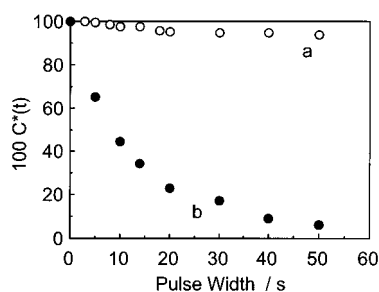


Figure 5. Time dependence of the normalized surface concentration of the *cis* form in the C_8AzoC_5 monolayer film (a) due to thermal isomerization at 20 °C and 0.00 V (○) and (b) due to polarization at 0.80 V (●).

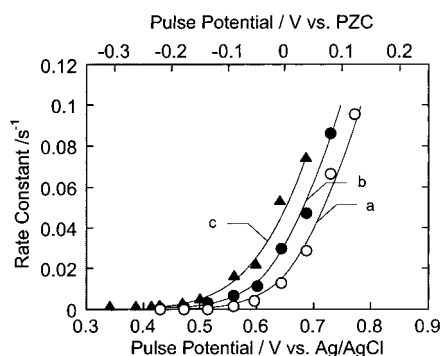


Figure 6. Potential dependence of the rate constants for the *cis*–*trans* isomerization for (a) C_8AzoC_5 (○), (b) C_8AzoC_3 (●), and (c) $C_{12}AzoC_3$ (▲) monolayer films.

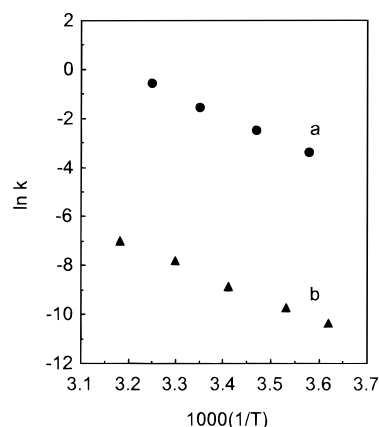


Figure 7. Arrhenius plots (a) for electrostatic isomerization (+0.850 V, ●) and (b) for thermal isomerization (▲) for C_8AzoC_5 molecules in the LB film.

electrostatic measurements were carried out under completely dark conditions so that the contribution of visible light to the isomerization process can be ignored.

Next, the potential dependence of the rate constant k for the *cis*–*trans* isomerization of the C_8AzoC_5 monolayer film is presented. Figure 6 (curve a) shows that the rate constant increases approximately exponentially with potential. The rate constants were found to be almost negligible at potentials negative to +0.65 V but increased rapidly when more positive potentials were applied.

An Arrhenius plot for the electrostatic isomerization process, carried out at +0.850 V vs Ag/AgCl, is shown in Figure 7 (curve a). For comparison, a plot for the thermal isomerization is also shown (curve b). The activation parameters for both cases are listed in Table 1.

To clarify the effect of polarization, similar experiments were also conducted for C_8AzoC_3 and $C_{12}AzoC_3$ monolayer films,

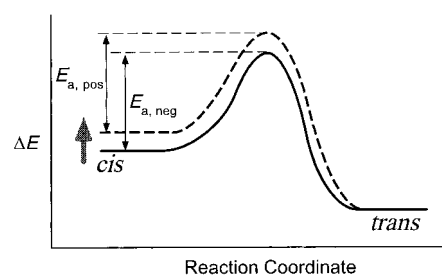


Figure 8. Schematic representation of changes in the reaction energetics due to the presence of an applied electrochemical potential. The dashed curve corresponds to a more positive potential.

TABLE 1: Activation Parameters for the Electrostatic and Thermal Isomerization of *cis*– C_8AzoC_5 in the LB Film

isomerization reaction	$E_a/kJ\ mol^{-1}$	A/s^{-1}	$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger/J\ K^{-1}\ mol^{-1}$
electrostatic	67.3	$10^{10.9}$	65.3	–44.4
thermal	69.0	$10^{8.5}$	66.5	–90.8

as shown in Figure 6 (curves b and c, respectively). These ABDs exhibited similar potential dependences compared to C_8AzoC_5 . However, the rate constants obtained for the C_8AzoC_3 and $C_{12}AzoC_3$ monolayer films at given potentials were larger than those for the C_8AzoC_5 monolayer film. Thus, the electrostatic *cis*–*trans* isomerization process is sensitive to the details of the ABD structure.

Discussion

To understand the electrostatically induced *cis*–*trans* isomerization process, the variation of the potential as a function of distance, from the electrode to the bulk solution, must be considered. This will depend upon the film structure, including the packing of the molecules and the degree of penetration of electrolyte ions between the molecules, and thus, the azobenzene moieties reside in a region that has some hydrocarbon-like character as well as some ionic character. In the solution phase itself, the double-layer properties will depend upon, for example, the ionic strength.

Compared to potentials negative to the PZC, the direction of the electric field in the double layer is reversed at potentials positive to the PZC. Thus, the interaction of the electric field with the electrostatic field of the ABD molecules in the film can be expected to change significantly at more positive potentials. Considering the simple azobenzene molecule itself as an approximate model, the dipole moment of the *cis* form is approximately 3 D compared with approximately 0 D for the *trans* form.³² By use of the simplest possible electrostatic model, the energy corresponding to the orientation of the *cis* form with the positive end of the dipole pointing toward the electrode should become more positive with increasingly positive potential (Figure 8). For the *trans* form, there is a negligible effect of potential. If we assume that the orientation of the *cis* form with the positive end of the dipole pointing toward the electrode is favored at more negative potentials for the azobenzene moiety in the ABD film, then it can be seen that the energy difference between the initial (*cis*) and final (*trans*) states would be approximated by the simple equation

$$\Delta U = -(\Delta\mu)F$$

where $\Delta\mu$ is the difference in dipole moments for the two isomers and F is the field strength. Even if the potential profile next to the electrode was purely solution-like, with a field strength of, for example, $3 \times 10^9\ V\ m^{-1}$ at a potential of 0.3 V vs PZC,³³ this energy difference would only be approximately

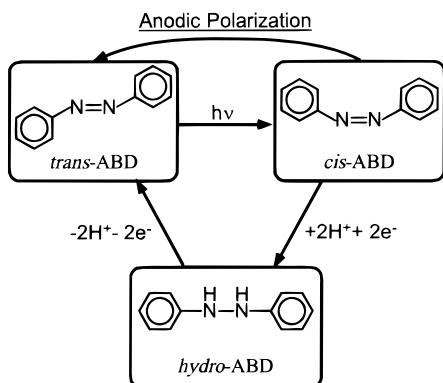


Figure 9. Photochemical-electrochemical reaction routes involving ABD molecules in Langmuir-Blodgett monolayer films.

1.8 kJ mol^{-1} . This value is clearly much less than the activation energy obtained from the Arrhenius plot. In addition, the activation energy obtained for the purely thermal process (69.1 kJ mol^{-1}) is quite comparable to that for the electrostatically induced process. This situation can be schematically represented as shown in Figure 8, with the energy of the initial state raised because of the influence of the electrochemical potential but with the activation energy itself unchanged. Thus, the influence of potential on the *cis*-to-*trans* isomerization rate must operate via the activation entropy. This situation is analogous to that found for the visible light *cis*-*trans* isomerization process for azobenzene moieties trapped within elastomeric matrixes with various degrees of cross-linking.⁷ The potential dependence of the rate constants will be examined in much greater detail in a separate paper.³⁴

In the case of the C_8AzoC_3 monolayer film, the higher rates of electrostatically induced isomerization compared with those for C_8AzoC_5 can be attributed to the shorter alkyl chain (spacer) separating the hydrophilic $-\text{COOH}$ head-group and the azobenzene moiety. In other words, the influence of potential could be accentuated because, since the azobenzene moiety is close to the electrode surface, the electric field strength may be greater (discussed below). Structural characterization studies of C_8AzoC_5 (molecular length, 32.6 \AA) and C_8AzoC_3 (30.0 \AA) multilayer films have been conducted using small-angle X-ray diffraction, UV absorption spectra, and FT-IR absorption spectroscopy, and the azobenzene moiety was found to be $\sim 2.6 \text{ \AA}$ closer to the electrode surface for the latter.³⁵⁻³⁷ The magnitude of the electric field at the azobenzene moiety should be approximately the same for these two molecules if it is assumed that the moiety is largely buried in a hydrocarbon-like layer, with alkyl chains on either side of it, because, to a first approximation, there should be linear potential vs distance profiles whose slopes depend on the dielectric constant of the closely packed hydrocarbon medium.^{38,39} Thus, the interaction of the electric field with the molecular (i.e., *cis*-azobenzene) dipole should be the same for both molecules. However, if there is some ion penetration between the amphiphilic molecules, then there should be a nonlinear, more solution-like potential profile, and some difference should be observed in the kinetics depending on the distance of the azobenzene from the electrode. For the molecule with the shorter spacer chain, C_8AzoC_3 , the magnitude of the potential at the azobenzene group (with respect to the bulk solution) will be larger than that for the longer spacer chain, C_8AzoC_5 , because of the smaller potential drop over the shorter chain, and this difference would be consistent with the larger observed *cis*-to-*trans* isomerization rate constants for the shorter chain molecule. The effect of the potential profile due to the electrolyte in solution could be further examined by varying the Debye length.

An acceleration of the electrostatically induced isomerization process was also observed for LB films formed from an ABD molecule having a longer alkyl chain in the hydrophobic tail, i.e., $\text{C}_{12}\text{AzoC}_3$. An additional influence is that there is an ether linkage connecting the alkyl tail to the azobenzene moiety. Two possible explanations for the larger rate constants can be considered. One possibility is the lateral hindrance effect of the *cis* form of molecules with longer hydrophobic chains in close-packed monolayer films. Generally, the *trans*-to-*cis* isomerization process is quite inhibited for ABDs in LB films owing to the van der Waals attractions between the chains.⁴⁰ In the case of monolayer films at electrode/electrolyte interfaces, the fraction of the *trans* form that underwent isomerization was found to be approximately 18% for both the C_8AzoC_5 and C_8AzoC_3 films and approximately one-twentieth of that (typically, 0.95%) for the $\text{C}_{12}\text{AzoC}_3$ film based on the electrochemical measurements. This result is consistent with the fact that the *cis* form of molecules with longer alkyl tails is less stable in the monolayer film because of a larger free volume required for the V-shaped molecule. Another possibility is that, as in the case of C_8AzoC_5 , the effect is on the activation entropy. Additional results are required in order to clarify this point. In either case, the increased isomerization rates observed for the ABD with a longer hydrophobic chain appear to be associated with closer, more ordered packing in the monolayer film.

An additional contribution may arise because of the presence of the oxygen atom in the ether linkage between the hydrophobic alkyl chain and the azobenzene moiety, which may change the magnitude of the dipole moment of the *cis* form of this molecule. For example, placement of a methoxy group para to the diazo group leads to an increase in dipole moment of approximately 1 D compared to the dipole moment of the simple azobenzene molecule.⁴¹ Further work is also needed to clarify this point.

Further basic research on the electrostatically induced isomerization phenomenon, including its detailed kinetics and thermodynamics, is now in progress. We expect that a better understanding of this new phenomenon occurring in ABD monolayer films will provide fundamental information relevant to the mechanism of *cis*-*trans* isomerization of azobenzene derivatives. In addition, owing to the sensitivity to structural details, this phenomenon could be used as a structural probe for examining a wide variety of azobenzene-containing monolayers. Moreover, this phenomenon may also be applicable to devices employing ABD molecules. For example, Ichimura and co-workers have reported that a polymerized LB monolayer film that possesses azobenzene units can induce alignment changes in a contacting liquid crystal layer as a result of the conformational changes in the azobenzene layer.^{9,42} This system has been termed a "command surface" and is usually controlled via UV and visible illumination, but electrochemical polarization could also conceivably be used to induce the *cis*-to-*trans* isomerization process. Finally, the electrostatic process could also be examined on other types of LB films and self-assembled monolayers not containing azobenzene. Indeed, Abruña and co-workers have reported interesting electrostatically induced effects in LB films that involve orientational changes.⁴³ In that case, however, current peaks were observed that were due to changes in capacitance.

Summary and Conclusions

In the present work, we report a novel electrochemically induced *cis*-*trans* isomerization phenomenon occurring in ABD LB monolayer films at electrode/electrolyte interfaces, shown schematically in Figure 9, based on both electrochemical and spectroscopic measurements. This process occurs electrostatically.

cally at potentials positive to the PZC, with a time constant of 7.5 s at +0.80 V, for example, which is approximately 2 orders of magnitude faster than the thermal process. Based on the kinetic results, which yielded first-order behavior for the C₈-AzoC₅, C₈AzoC₃, and C₁₂AzoC₃ films, the isomerization process is considered to involve electrostatic interactions between the ABD molecules and the high electric field originating from the electrical double layer. In the case of the C₈AzoC₅ film, since the activation energy is virtually the same as that for the thermal process, the difference in rates is due to differences in the activation entropies, which must also involve a response to the electric field.

Acknowledgment. The authors gratefully acknowledge support by the Heiwa Nakajima Foundation and the Ministry of Education, Science and Culture of Japan.

References and Notes

- (1) Liu, Z.-F.; Hashimoto, K.; Fujishima, A. *Nature* **1990**, *347*, 658–660.
- (2) Tachibana, H.; Azumi, R.; Nakamura, T.; Matsumoto, M.; Kawabata, Y. *Chem. Lett.* **1992**, 173–176.
- (3) Hartley, G. S. *J. Chem. Soc.* **1938**, 633–642.
- (4) Griffiths, J. *Chem. Soc. Rev.* **1972**, *1*, 481–493.
- (5) Rau, H. In *Photochromism*; Durr, H., Laurent, H. B., Eds.; Elsevier: New York, 1990; pp 165–192.
- (6) Kumar, G. S.; Neckers, D. C. *Chem. Rev. (Washington, D.C.)* **1989**, *89*, 1915–1925.
- (7) Stadler, R.; Weber, M. *Polymer* **1986**, *27*, 1254–1260.
- (8) Sekkat, Z.; Morichère, D.; Dumont, M.; Loucif-Saï, R.; Declaire, J. A. *J. Appl. Phys.* **1992**, *71*, 1543–1545.
- (9) Ichimura, K.; Suzuki, Y.; Seki, T.; Hosoki, A.; Aoki, K. *Langmuir* **1988**, *4*, 1214–1216.
- (10) Laviron, E.; Mugnier, Y. *J. Electroanal. Chem.* **1980**, *111*, 337–344.
- (11) Liu, Z.-F.; Morigaki, Y.; Hashimoto, K.; Fujishima, A. *Anal. Chem.* **1992**, *64*, 134–137.
- (12) Liu, Z.-F.; Morigaki, Y.; Enomoto, T.; Hashimoto, K.; Fujishima, A. *J. Phys. Chem.* **1992**, *96*, 1875–1880.
- (13) Liu, Z.-F.; Hashimoto, K.; Fujishima, A. *Faraday Discuss.* **1992**, *94*, 221–228.
- (14) Nishimura, M.; Sueyoshi, T.; Yamanaka, H.; Imai, E.; Yamamoto, S.; Hasegawa, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1381–1387.
- (15) Marcandalli, B.; Liddo, L. P.; Fede, C. D.; Bellobono, I. R. *J. Chem. Soc., Perkin Trans. 2* **1984**, 589–593.
- (16) Haberfield, P.; Block, P. M.; Lux, M. S. *J. Am. Chem. Soc.* **1975**, *97*, 5804–5806.
- (17) Asano, T.; Okada, T.; Shinkai, S.; Shigematsu, S.; Kusano, Y.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 5161–5165.
- (18) Asano, T.; Yana, T.; Okada, T. *J. Am. Chem. Soc.* **1982**, *104*, 4900–4904.
- (19) Nishimura, N.; Tanaka, T.; Asano, M.; Sueishi, Y. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1839–1845.
- (20) Brown, E. V.; Granneman, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 621–627.
- (21) Otruba, J. P., III; Weiss, R. G. *J. Org. Chem.* **1983**, *48*, 3448–3453.
- (22) Wolf, E.; Cammenga, H. K. *Z. Phys. Chem., Neue Folge* **1977**, *107*, S21–S38.
- (23) Le Fevre, R. J. W.; Northcott, J. J. *J. Chem. Soc.* **1953**, 867–870.
- (24) Wildes, P. D.; Pacifici, J. G.; Irick, G., Jr.; Whitten, D. G. *J. Am. Chem. Soc.* **1971**, *93*, 2004–2008.
- (25) The sheet resistance is reported in units of Ω per square (\square); see, for example, Streetman, B. G. *Solid State Electronic Devices*; Prentice-Hall: Englewood Cliffs, NJ, 1995; p 354).
- (26) Liu, Z.-F.; Loo, B. H.; Hashimoto, K.; Fujishima, A. *J. Electroanal. Chem.* **1991**, *297*, 133–144.
- (27) Liu, Z.-F.; Hashimoto, K.; Fujishima, A. *J. Electroanal. Chem.* **1992**, *324*, 259–267.
- (28) Morigaki, K.; Liu, Z.-F.; Hashimoto, K.; Fujishima, A. *J. Phys. Chem.* **1995**, *99*, 14771–14777.
- (29) Nakahara, H.; Fukuda, K.; Shimomura, S.; Kunitake, T. *Nippon Kagaku Kaishi* **1988**, 1001–1010.
- (30) Liu, Z.-F.; Loo, B. H.; Baba, R.; Fujishima, A. *Chem. Lett.* **1990**, 1023–1026.
- (31) Liu, Z.-F.; Hashimoto, K.; Fujishima, A. *Chem. Lett.* **1990**, 2177–2180.
- (32) Bard, A. J.; Lund, H. *Encyclopedia of Electrochemistry of the Elements*; Marcel Dekker: New York, 1979; Organic Section, Vol. XIII, p 177.
- (33) Delahay, P. *Double Layer and Electrode Kinetics*; John Wiley & Sons: New York, 1965.
- (34) Hagiwara, H.; Tryk, D. A.; Hashimoto, K.; Fujishima, A. Manuscript in preparation.
- (35) Kawai, T.; Umemura, J.; Takenaka, T. *Langmuir* **1989**, *5*, 1378–1383.
- (36) Kawai, T.; Umemura, J.; Takenaka, T. *Langmuir* **1990**, *6*, 672–676.
- (37) Xu, X.; Kawamura, S.; Era, M.; Tsutsui, T.; Saito, S. *Nippon Kagaku Kaishi* **1987**, *11*, 2083–2089.
- (38) Smith, C. P.; White, H. S. *Anal. Chem.* **1992**, *64*, 2398–2405.
- (39) Smith, C. P.; White, H. S. *Langmuir* **1993**, *9*, 1–3.
- (40) Wang, R.; Jiang, L.; Iyoda, T.; Tryk, D. A.; Hashimoto, K.; Fujishima, A. *Langmuir* **1996**, *12*, 2052–2057.
- (41) Iyoda, T. Personal communication.
- (42) Seki, T.; Sakuragi, M.; Kawanishi, Y.; Suzuki, Y.; Tamaki, T.; Fukuda, R.; Ichimura, K. *Langmuir* **1993**, *9*, 211–218.
- (43) Gao, X.; White, H. S.; Chen, S.; Abruña, H. D. *Langmuir* **1995**, *11*, 4554–4563.