J. Org. Chem. **1996,** *61,* 9417−9421

Modification of Photochemical Reactivity by Nafion. Photocyclization and Photochemical *Cis*−*Trans* Isomerization of Azobenzene

Chen-Ho Tung* and Jing-Qu Guan

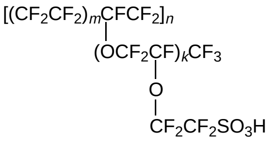
Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, China

Received May 22, 1996[⊗]

The photophysical and photochemical behavior of azobenzene (AB) incorporated into solvent-swollen acid form Nafion (Nafion-H$^+$) membranes were examined. In water-swollen Nafion-H$^+$ membrane AB exhibits strong fluorescence at room temperature, which has never been observed in isotropic solvents. Photolysis of AB adsorbed in water-swollen Nafion-H$^+$ results in its cyclization to give benzo[*c*]cinnoline (BC) and benzidine (BZ) in quantitative yield. The product distribution is very dependent upon the number of AB molecules in each water cluster of the Nafion membrane (occupancy number). In the case of the occupancy number greater than 2, BC and BZ are formed equimolarly, while when only one AB molecule exists in each water cluster, BC is exclusively produced. The AB molecules incorporated into methanol-swollen Nafion-H$^+$ membrane do not emit fluorescence and only undergo *cis*−*trans* isomerization when they are photoirradiated. These observations suggest that in water-swollen Nafion-H$^+$ AB molecules are solublized in the fluorocarbon/water interface, and the protons of the Nafion-H$^+$ participate in the photochemical and photophysical processes of AB. On the other hand, in methanol-swollen Nafion-H$^+$ membrane AB molecules are located in the methanol pools, and their photochemical and photophysical behaviors are not intervened by the Nafion protons.

Introduction

Selectivity in organic phototransformations continues to be one of the main topics of current interest.[1] Of the various approaches use of constrained and ordered media had shown considerable promise.[1,2] Nafion represents a novel and unique family of polymers which consists of a perfluorinated backbone and short pendant chains terminated by sulfonic groups.



$$[(CF_2CF_2)_mCFCF_2]_n \quad \text{with } (OCF_2CF)_kCF_3 \text{ on CF, and } O\text{–}CF_2CF_2SO_3H \text{ on that CF}$$

$m = 5–15.3$

$n =$ ca. 1000

$k = 1, 2, 3$

When swollen in water, the structure of Nafion is believed to resemble that of a reverse micelle (Figure 1).[3−5] It is suggested that the hydrated SO_3^- head groups are clustered together in a water-containing pocket of ca. 50 Å in diameter, which are interconnected by short channels (ca. 10 Å in diameter) within the perfluorocarbon matrix (Figure 1). The polymer backbone of Nafion provides exceptional chemical, thermal, and mechanical stability while the sulfonic acid groups provide ion-exchange and swelling abilities. It has been established[6−8] that water-swollen Nafion can incorporate high concentrations of aromatic hydrocarbons and organic dyes, thus raising the possibility of obtaining high local concentration of organic molecules and inorganic cations. These optically transparent membrane systems are readily amenable to spectroscopic investigations. Because of these attractive properties, this polymer has been utilized as a medium for photophysical and photochemical studies in recent years.[9−12] Up to now, the majority of the photochemical studies within the water-swollen Nafion have made use of this material just as a heterogeneous and micellelike medium to gain control of the pathways undergone by the substrate excited states. However, this polymer in its protonated form is a superacid.[13] The acid groups can act as active sites and directly intervene in the chemical process occurring in the water-containing pockets of the polymer.

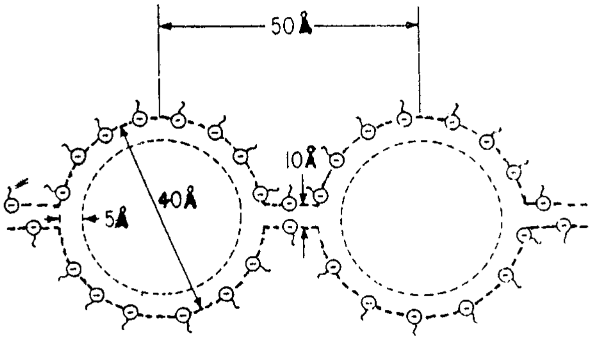


Figure 1. Schematic representation of the two-phase cluster-network model for Nafion membranes.

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1996.

(1) Ramamurthy, V., Ed. *Photochemistry in Organized and Constrained Media*; VCH: New York, 1991.

(2) Fox, M. A., Ed. *Organic Phototransformations in Non-homogeous Media*; American Chemical Society: Washington D. C., 1985.

(3) Komoroski, R. A.; Mauritz, K. A. *J. Am. Chem. Soc.* **1978**, *100,* 7487.

(4) Lee, P. C.; Meisel, D. *J. Am. Chem. Soc.* **1980**, *102,* 5477.

(5) Sondheimer, S. J.; Bunce, N. J.; Fyfe, C. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1986**, *C26,* 353.

(6) Lee, P. C.; Meisel, D. *Photochem. Photobiol.* **1985**, *41,* 21.

(7) Szentirmay, M. N.; Prieto, N. E.; Martin, C. R. *J. Phys. Chem.* **1985**, *89,* 3017.

(8) Niu, E.-P.; Ghihhino, K. P.,;Smith, T. A.; Mau, A. W.-H. *J. Lumin.* **1990**, *46,* 191.

(9) Niu, Er-Ping; Mau, A. W.-H. *Aust. J. Chem.* **1991**, *44,* 695.

(10) Mohan, H.; Iyer, R. M. *J. Chem. Soc., Faraday Trans.* **1992**, *88,* 41.

(11) Mika, A. M.; Lorenz, K.; Azczuek, A. *J. Memb. Sci.* **1989**, *41,* 163.

(12) Priydarsini, K. I.; Mohan, H.; Mittall, J. P. *J. Photochem. Photobiol. A. Chem.* **1993**, *69,* 345.

(13) Sondheimer, S. T.; Bunce, N. J.; Lemke, M. E.; Fyfe, C. A. *Macromolecules* **1986**, *19,* 339.

S0022-3263(96)00946-2 CCC: $12.00

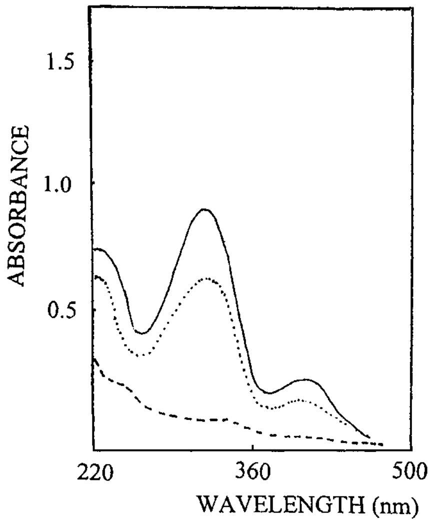


Figure 2. Absorption spectra of azobenzene: incorporated into water-swollen Nafion membrane (—); in aqueous solution (····); background absorption of Nafion membrane (----).

In the present paper we illustrate the influence of the chemical environment of Nafion host on the photochemistry of azobenzene (AB) adsorbed in water- and methanol-swollen acid form Nafion (Nafion-H$^+$) and provide an example that a cooperative contribution of the acid sites of the Nafion-H$^+$ is required in the course of photochemical reaction performed within swollen Nafion. The azobenzene system follows two different reaction pathways depending on the photolysis condition.[14] Thus, upon irradiation in neutral medium *cis*−*trans* isomerization occurs and photostationary mixtures of both stereoisomers are obtained. However, when the photolysis is performed in the presence of acids, azobenzene undergoes the photochemical cyclization to benzo[*c*]cinnoline (BC), and variable amounts of benzidine (BZ) are produced. In this case, the conjugated acid of azobenzene (not the neutral molecule) is the species which undergoes ring closure. We demonstrate that by including the azobenzene molecules in solvent-swollen Nafion one can control the reaction pathways. Furthermore, we observed the fluorescence of azobenzene at room temperature for the first time.

Results and Discussion

Incorporation and Absorption Spectrum of Azobenzene (AB) in Nafion Membrane. Azobenzene normally exits in the stable *trans*-form, and the *cis*-isomer easily thermally reverted to the *trans*-isomer.[14] Thus, in the present study we only investigate *trans*-azobenzene. We could successfully incorporate AB into water-swollen Nafion membrane by soaking the membrane in an AB aqueous solution. Figure 2 shows the absorption spectrum of the Nafion membrane after equilibrating with a 2 × 10^{-5} M solution of AB in water. Undoubtedly, this absorption spectrum is mainly originated from the AB incorporated into the Nafion. The background absorption of the membrane itself is also shown in Figure 2, and is rather low in the near UV region. Substraction of the background absorption from the total absorption spectrum of the sample yielded the absorption spectrum of AB in Nafion, the maxima of which are at ca. 418, 315, and 228 nm, corresponding to the $n_s \rightarrow \pi_1^*$, $\pi_1 \rightarrow \pi_1^*$ and $\Phi_1 \rightarrow \Phi_1^*$ transitions respectively.[14] The $n_s \rightarrow \pi_1^*$ transition is slightly red-shifted while that of the $\pi_1 \rightarrow \pi_1^*$ slighly blue-shifted compared to those in water (415, 318, and 228 nm in water). This observation suggests that the environment around AB molecules in Nafion is slightly less polar than that in water. It has been established that AB can undergo protonation in acidic aqueous solution.[14] Thus, it might be expected that AB exists as its protonated form (ABH$^+$) when it is incorporated into Nafion-H$^+$ membrane. However, this suggestion cannot be substantiated only by UV absorption, since the absorption spectra for the protonated and neutral AB are identical.[15] Considering the hydrophobicity and the positive charge of ABH$^+$, it is likely that the cationic ABH$^+$ molecules are located close to the sulfonate head groups in the fluorocarbon/water interface of the membrane.

Table 1. Occupancy Number of AB in Water-Swollen Nafion Membrane with Various Amount of AB and Water

water contents (wt %)	concentration of AB in Nafion (¥10^3 M)				
	3.8	19.0	22.0	30.8	40.0
23	0.34	1.82	2.00	2.77	3.56
17	0.30	1.49	1.73	2.40	3.14
12	0.25	1.26	1.48	2.05	2.66
10	0.236	1.18	1.37	1.92	2.49
6	0.204	1.02	1.18	1.65	2.01

The solubility of AB in water-swollen Nafion membrane is rather high (4 × 10^{-2} M, calculated in its swollen form). We have prepared the Nafion-H$^+$ membrane samples adsorbing various amount of water and AB. By using the parameters reported in the literature,[5,16] we could calculate the occupancy numbers (the number of AB molecules contained in each water cluster of Nafion, n_{AB}/cluster) of the samples, which are listed in Table 1. Results show that each cluster can hold 3.5 AB molecules.

In order to obtain information about the adsorption process, we analyzed the concentration of AB incorporated into the Nafion membrane as a funcion of soaking time. The following eqution was employed for the study of the adsorption kinetics of AB into the membrane.[17]

$$C_t/C_\infty = 4\sqrt{DT}/T\sqrt{\pi} \tag{1}$$

C_t and C_∞ represent the concentrations of AB in the membrane at time t and after equilibration, respectively. D is the diffusion coefficient in cm^2 s^{-1}, and T is the thickness in cm. The plot of C_t vs $\sqrt{t}$ is linear. From the plot, the diffusion coefficient was determined to be 7.6 × 10^{-10} cm^2 s^{-1}. This confirms the applicability of eq 1 and shows that the sorption is diffusion-controlled, like the sorption process of Rhodamine 6G in Nafion membrane.[10]

The adsorption behavior of AB into methanol-swollen Nafion-H$^+$ membrane is completely different from that for the water-swollen one. The enhancement of UV absorption of AB in methanol-swollen Nafion membrane fails to occur. When the membrane sample is immersed in the desired methanol solution of AB and reaches equilibration, the concentration of AB in the membrane is almost the same as that in the bulk solution. This observation suggests that in methanol-swollen Nafion AB

---

(14) Griffiths, J. *Chem. Soc. Rev.* **1972**, *1*, 481.

(15) Sadtler Research Laboratories, Sadtler Ultra Violet Spctra, 136UV.

(16) Gierke, T. D.; Munn, G. E.; Wilson, F. C. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1687.

(17) Helfferich, F. *Ion Exchange*; McGraw Hill: New York, 1962.

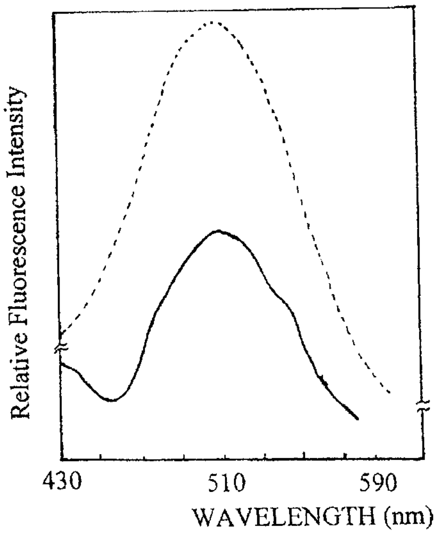
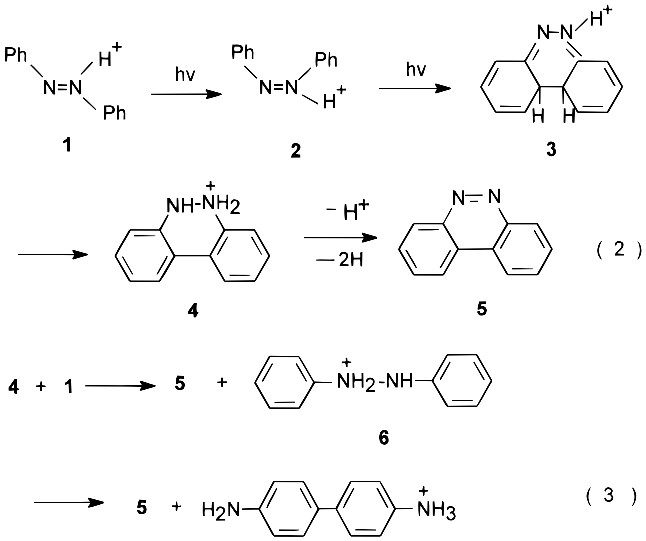


Figure 3. Fluorescence spectra of azobenzene incorporated into water-swollen Nafion-H$^+$ membrane: water content of 23 wt% (—); water content of 6 wt % (····). All of the spectra were obtained at azobenzene concentration of 3.8×10^{-3} M, excitation at 410 nm.

molecules are located in the methanol pool, as evidenced by fluorescence and photochemical studies (see below).

Fluorescence of AB in Nafion Membrane. It has been established that AB does not exhibit fluorescence.[18] The reason for this is that the first singlet excited state of this compound is of ^{1}(nπ*) character. Moreover, a ^{3}($\pi\pi$*) state lies below but close to the ^{1}(nπ*) state. Thus, radiationless decay of the ^{1}(nπ*) via efficient intersystem crossing to the ^{3}($\pi\pi$*) shortens the lifetime of the ^{1}(nπ*) state. On the other hand, Rau[18] could detect the fluorescence from the protonated AB (ABH$^+$) at 77 K. This observation was attributed to the fact that protonation of the azo-group results in the inversion of the nπ* and $\pi\pi$* singlet states, and the radiation transition from the latter lower energy state to the ground state is orbital overlap allowed. However, this fluorescence can only be observed at 77 K, since in fluid solution the twisting of the molecule about the N=N bond makes the ^{1}($\pi\pi$*) state mix with the ^{3}(nπ*) state, thus enhancing the intersystem crossing to the triplet state. By incorporating AB molecules into water-swollen Nafion-H$^+$ membrane, we could successfully detect the strong fluorescence of AB at room temperature for the first time. Figure 3 shows the fluorescence spectra of AB incorporated into water-swollen Nafion-H$^+$ membrane. The general feature of this spestrum is identical to that reported in the literature.[18] Obviously, AB is protonated. By reference to the UV absorption we propose that the molecules of AB are located in the fluorocarbon/water interface in the membrane, and the constrained environment surrounding the AB molecule restricts its twisting. Furthermore, for the sample soaking less amounts of water, the environment surrounding AB becomes more constrained. Thus, the fluorescence emission is enhanced. To ascertain the fact that the acid groups of the Nafion play a role in AB fluorescence emission, we investigated the photophysical property of AB incorporated into water-swollen Nafion membrane in sodium form (Nafion-Na$^+$). No fluorescence was detected in this case. This suggests that the cooperative contribution of the acid sites is a requirement for the fluorescence of AB.

Scheme 1. Mechanism of the Formation of Benzo[*c*]cinnoline (5) and Benzidine (7)



We could not detect any fluorescence emission from AB incorporated into methanol-swollen Nafion-H$^+$ membrane. This observation again suggests that AB is solublized in the methanol pool, and the protons of the Nafion-H$^+$ do not intervene in the photochemical process of AB.

Photocyclization of AB Incorporated into Water-Swollen Nafion Membrane. Photoirradiation of water-swollen Nafion-H$^+$ membrane soaking AB results in the cyclization of AB to give benzo[*c*]cinnoline (BC). Variable amounts of benzidine (BZ) is also produced if the occupancy number of AB in the water cluster of the Nafion is large, as shown in Scheme 1. This reaction could be followed by the UV absorption of the sample. In general, after 1 h irradiation with a 150-W Hanovia high-pressure mercury lamp the absorption of AB completely disappears. Instead, an absorption spectrum with maxima at 248 and 354 nm is detected, which is assignable to the absorption spectrum of BC in protonated form (BCH$^+$).[19] The products can be easily isolated and purified by the following procedure. Extraction of the irradiated membrane with methanol gives BC. Since BZ is also protonated and may strongly interact with the sulfonate groups of the Nafion-H$^+$, this compound cannot be extracted from the Nafion membrane by methanol. However, after the residual membrane is neutralized with 1 N NaOH aqueous solution, extraction with diethyl ether readily gives BZ. The yield of the sum of BC and BZ was close to 100% based on the consumption of the starting material. The assignments of the products relies on their UV absorptions, ^{1}H NMR, and MS spectroscopies which are given in the Experimental Section.

The product distribution was found to be dependent on the occupancy number of AB in the water cluster of the Nafion sample, as shown in Table 2. Photolysis of the sample with an occupancy number greater than 2 leads to the formation of BZ and BC with a ratio of ca. 50:50. However, for the sample with an occupancy number less than 0.4, we could only isolate the photocyclization product BC in a quantitative yield and no BZ was detected.

---

(18) Rau, H. *Ber. Bunsenges. Phys. Chem.* **1967**, *71*, 48.

(19) Sadtler Research Laboratories, Sadtler Ultra Violet Spectra, 23847 UV. The UV absorption spectrum of protonated BC in this handbook also exhibits a maximum at 308 nm in methanol. We found that this band should be assigned to the absorption of the unprotonated BC.

Table 2. Molar Ratio of BZ to BC in the Products of Photocyclization as a Function of the Occupancy Number of AB Incorporated into Water-Swollen Nafion

n_{AB}/cluster	3.56	2.40	1.82	1.49	1.18	0.34	0.25	0.016
m_{BC}/m_{BZ}	0.96	0.96	0.77	0.48	0.12	0	0	0

We have measured the quantum yield for the photocyclization of AB incorporated into the Nafion-H$^+$ membrane and found that the plot of the quantum yield as a function of the square of the light intensity is linear. This suggests that the photocyclization is a two-photon process. We demonstrated by experiment that photoirradiation of AB incorporated into water-swollen Nafion-Na$^+$ membrane could not yield any cyclization product. All of the observations mentioned above can be rationalized by the well-established mechanism[14,20] for the photocyclization which is given by eqs 2 and 3 in Scheme 1.

The conjugated acid of azobenzene, not the neutral molecule, is the species which undergoes photocyclization. The first photon converts the protonated trans-isomer of AB (**1**) into the cis-isomer (**2**), and the second photon results in the cyclization of the cis-isomer to the intermediate **3**. Rapid conversion of **3** into the more stable **4** can occur by two prototropic shifts. BC (**5**) is then formed by dehydrogenation of **4**. The nature of the latter oxidation step is dependent on the reaction condition. When the occupancy number of AB in the water cluster of the Nafion membrane is greater than 2, the probability of a water cluster to contain two AB molecules would be high. The dehydrogenation of **4** is caused by ABH$^+$ according to the disproportionation mechanism as shown by eq 3 in Scheme 1. Thus, for one BC molecule formed, one molecule of hydrozobenzene (**6**) is produced. Under the acidic condition in the water cluster of Nafion-H$^+$, **6** is efficiently rearranged to benzidine (BZ, **7**). Consequently, the ratio of BZ to BC in the products is close to 1:1 (Table 2). On the other hand, in the case of the occupancy mumber less than 0.4 (Table 2), the probability of one water cluster to host two AB molecules would be rather low. The dehydrogenation of **4** might be caused either by oxygen presented in the water cluster of Nafion or by the -SO_3H groups of the Nafion. It has been well documented[21] that *cis*-stilbenes, like *cis*-azobenzene, can undergo photocyclization to give phenanthrene in the presence of oxygen. The first step of this photocyclization yields dihydrophenanthrene, which then is oxidized to phenanthrene by oxygen. By reference to this oxidization, **4** might be dehydrogenated by oxygen. On the other hand, it has been established[22] that photoirradiation of azobenzene in 98% sulfuric acid results in BC in high yield. In this case, the solvent is the effective dehydrogenating agents for **4**, being reduced during the reaction to sulfur dioxide. We found that the Nafion-H$^+$ membrane as the medium of the photochemical reaction can be recycled, but the efficiency for the catalysis of the photocyclization of azobenzene decreased slightly after many cycles. Thus, we infer that the SO_3H groups of the Nafion also might be the dehydrogenating agents for **4**. The above two mechanisms for the dehydrogenation of **4** (oxygen vs. SO_3H group) cannot be substantiated without further information. In any case, BC is the unique product in the photocyclization when the occupancy number is less than 0.4.

The results mentioned above illustrates that in the photocyclization reaction of AB the Nafion is more than just a passive medium. The acid sites of the Nafion also play an essential role in the reaction.

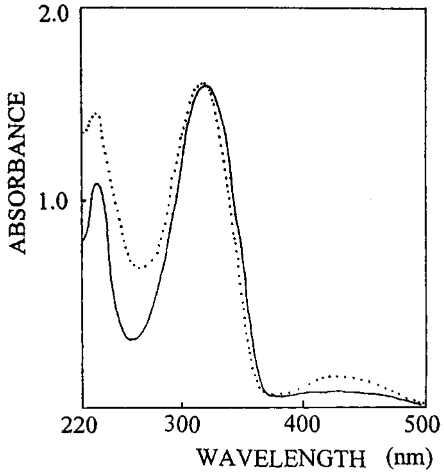


Figure 4. Absorption spectra of AB incorporated into methanol-swollen Nafion-H$^+$ membrane before (—) and after (····) irradiation.

Photochemical *Trans*–*Cis* Isomerization of AB Incorporated into Methanol-Swollen Nafion Membrane. *cis*-Azobenzene absorbs at shorter wavelength than the *trans*-isomer.[14] Furthermore, the extinction coefficient of the $ns \rightarrow \pi^*$ transition for the *cis*-isomer is greater than that for the *trans*-isomer.[14] Thus, the *trans*–*cis* isomerization of AB is easily detected by UV absorption spectra. By this technique, we successfully observed the *trans*–*cis* isomerization of AB incorporated into methanol-swollen Nafion-H$^+$ membrane. Figure 4 shows the UV absorption spectra of the samples before and after photoirradiation. We could obtain a photostationary mixture of the *cis*- and *trans*-isomers but could not detect any photocyclization product, neither BC nor BZ. This observation is consistent with the proposal that in methanol-swollen Nafion-H$^+$ the AB molecules are solublized in the methanol pool. Thus AB is not protonated and the photocyclization cannot occur.

Conclusions

This work illustrates that solvent-swollen Nafion can play an important role in the selective phototransformations of azobenzene. In water-swollen Nafion-H$^+$, azobenzene molecules are most likely located in the fluorocarbon/water inteface and exist as their protonated form. In this constrained medium the protonated azobenzene exhibits strong fluorescence at room temperature. Photoirradiation of these samples results in cyclization of AB to give BC and BZ in quantitative yield. Great influence of the occupancy number of AB in the water cluster of Nafion on the product distribution was observed. In the case of one water cluster containing two AB molecules, the reaction intemediate **4** was dehydrogenated by disproportionation mechanism. Consequently BC and BZ were formed equimolarly. When one water cluster only hosts one AB molecule, **4** was probably oxidized by -SO_3H groups of Nafion and/or by oxygen presented in the water cluster exclusively to yield BC. On the other hand, in methanol-swollen Nafion AB molecules are solublized in the methanol pool and cannot be protonated. No fluo-

---

(20) Badger, G. M.; Drewer, R. J.; Lewis, G. E. *Aust. J. Chem.* **1966**, *19*, 643.

(21) Muszkat, K. A. *Top. Curr. Chem.* **1980**, *88*, 89.

(22) Badger, G. M.; Joshua, C. P.; Lewis, G. E. *Autr. J. Chem.* **1965**, *18*, 1639.

rescence emission from AB could be detected. Photoirradiation of these samples leads to the *cis*−*trans* isomerization of AB.

Experimental Section

Materials. Nafion membrane 117 in acid form (Nafion-H$^+$) with an equivalent weight of 1100 and thickness of 0.0175 cm was a product of Du Pont and was kindly donated by Dr. A. W.-H. Mau of CSIRO, Division of Chemicals and Polymers. Prior to use, the membrane was cleaned by boiling in concentrated nitric acid for 4 h, and then throughly washed with distilled water and finally immersed in water for 24 h. The membrane in sodium form (Nafion-Na$^+$) was obtained by immersing the pretreated Nafion-H$^+$ membrane in 1 N NaOH aqueous solution. Excess base was then removed by stirring the sample in water. Azobenzene (AB) was recrystallized three times from ethanol before use. Doubly-distilled water was used throughout this work.

Preparation of Nafion Samples. The weighed Nafion membrane samples were immersed in a solution of AB in water or in methanol (2.5×10^{-5} M), and the solution was kept continuously stirred. At certain intervals the samples were taken out from the solution, thus samples adsorbing various amount of AB were prepared. To reach equilibration, the samples were kept in the solution for at least one day. The amount of uptake of AB by the membrane was determined by the difference in the absorbance of the solution before and after the addition of the Nafion membrane. The amount of the solvent (water or methanol) adsorbed into the membrane was determined by the difference of the sample weights before and after soaking.

Photoirradiation and Product Analysis. Photoirradiation was carried out in a quartz reactor. A 150-W high-pressure mercury lamp was used as the excitation source, and $K_2Cr_2O_4$ aqueous solution as the filter. The *cis*−*trans* isomerization of AB incorporated into methanol-swollen Nafion membrane was detected by UV absorption spectra. For the water-swollen samples, after irradiation the membrane was extracted with methanol, and BC was obtained. The residual membrane was neutralized with 1 N NaOH aqueous solution and then extracted with diethyl ether to give BZ. BC and BZ were identified by ^{1}H NMR and MS spestroscopies. BC: *m*/*z*: 180 (M$^+$); ^{1}H NMR ($CDCl_3$, ppm): 8.9 (2H, d), 8.6 (2H, d), 8.0 (4H, m). BZ: ^{1}H NMR (CD_3COCD_3, ppm): 7.3 (4H, d), 6.7 (4H, d), 4.4 (4H, s).

Acknowledgment. We thank the National Science Foundation of China for financial support. We also thank Dr. A. W.-H. Mau of CSIRO, Division of Chemical and Polymers, Australia for donation of Nafion 117 membrane and for encouraging discussion.

JO960946K