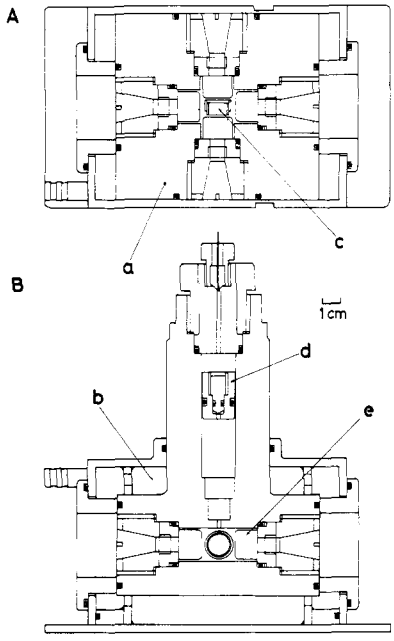

Figure 4. Cross sections of the high-pressure vessel: (A) top view; (B) side view; (a) pressure vessel; (b) water-circulating jacket; (c) inner sample cell; (d) liquid separation plunger; (e) quartz disk.

(benzene–hexane) and column chromatography (silica gel/benzene–hexane); mp 162.2–163 °C (lit.[30] mp 162 °C). MeO-NO_2-AB was prepared by methylation of OH-NO_2-AB with methyl iodide and purified by column chromatography (silica gel/benzene) and recyrstallization (ethanol); mp 157.9–159 °C (lit.[31] mp 157.5–158 °C). The solvents used for the measurements were spectrophotometric grade, or reagent grade purified by distillations.

High-Pressure Kinetics. The reaction of azobenzene was followed by means of a high-pressure sampling technique.[32] In the push–pull substituted azobenzenes, a pressure vessel with four optical windows, illustrated in Figure 4, was used. It is made of 17-4PH stainless steel and equipped with a water-circulating jacket. The diameter of the windows is 8 mm. The sample solution was contained in the inner cell, which was similar to the one described by le Noble and Schlott.[33] The same solvent as the reaction mixture was used as the pressurizing fluid inside the optical vessel, and it was separated from the pressure-transmitting fluid, hexane, by a plunger in the upper cylinder. The pressure drop because of the friction was shown to be negligible (<0.7%) by the direct pressure measurement with a manganin coil in the sample room. The slower reactions were followed by means of a Shimadzu UV-180 double-beam spectrophotometer, and a tungsten projection lamp was the excitation light source. The experimental detail was described previously.[34] Fast decay times were measured by a flash spectroscopic technique. A xenon flash tube, a Jarrel-Ash grating monochromator, and a photomultiplier were attached to the windows of the pressure vessel. The monitoring light source was a stabilized halogen lamp. The light passed through the monochromator was introduced to the high-pressure cell. A two-cavity Ditric Optics interference filter was installed between the cell and the photomultiplier in order to eliminate the scattered flash light. The absorption maximum of the *E* isomer was monitored. The transient signals were recorded by a transient memory TM-1410 of Kawasaki Electronica Co. A high-speed signal averager, TMC-300 (Kawasaki Electronica), was used when S/N ratio improvement was necessary. The reproducibility of the rate constant was ±1–1.5%. In chlorinated hydrocarbons, the reaction was sometimes accelerated by adventitious acid. This undesired catalysis was prevented by adding small amounts of piperidine (ca. 10^{-3} M) to the reaction mixture. The addition of the base in other solvents did not produce any measurable change in the rate constant, except for PhNH-NO_2-AB; in this compound, it was found that piperidine catalyzed the reaction, and all of the measurements were done in the absence of the base.

Acknowledgment. We express our appreciation to Drs. Masami Okamoto (Kyoto Institute of Technology) and Yasunori Okamoto (Oita University) for thier advice on the flash experiment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan (No. 56540263).

Registry No. (*Z*)-**1** (X = NMe_2; Y = NO_2), 73815-07-3; (*Z*)-**1** (X = anilino; Y = NO_2), 82248-50-8; (*Z*)-**1** (X = MeO; Y = NO_2), 20488-63-5; (*Z*)-**1** (X, Y = H), 1080-16-6.

(30) Patterson, D.; Sheldon, R. P. *J. Soc. Dyers Colour.* **1960**, *76*, 178.
(31) Schmidt, O. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 3201.
(32) Asano, T.; Okada, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3585.
(33) le Noble, W. J.; Schlott, R. *Rev. Sci. Instrum.* **1976**, *47*, 770.
(34) Asano, T. *Oita Daigaku Kogakubu Kenkyu Hokoku* **1980**, *6*, 95.

Rate Control by Restricting Mobility of Substrate in Specific Reaction Field. Negative Photochromism of Water-Soluble Spiropyran in AOT Reversed Micelles

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Abstract: The thermocoloration of a water-soluble spiropyran, 1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline]-6-sulfonic acid (**1**), which has been newly synthesized in this work, in the anionic AOT reversed micelles has been investigated in order to evaluate the effect of the reversed micelles in controlling the reaction rates or pathways by restricting the mobility of the substrates being situated in a specific reaction field. The probe **1** showed a negative photochromism in polar solvents such as water, MeOH, and EtOH as well as in the AOT reversed micelles. The thermocoloration rates of **1** were retarded by about 20 times in the 0.2 M AOT/0.6 M H_2O/hexane micelles compared with those in MeOH in which microscopic polarity was comparable to that in the interior core of the reversed micelles adopted. This was explicable in terms of the restriction in the internal rotation of the 2,3 σ bond of **1** during the thermocoloration accompanied by the cis–trans isomerization in a largely restricted field as provided by the reversed micelles. The extent of deceleration in the thermocoloration in the AOT reversed micelles was decreased by increasing the R ([H_2O]/[AOT]) value. The results obtained suggested a possibility that in the specific reaction field as provided by the reversed micelles, it may be possible to hold the labile substrate at the higher energy level by restricting the freedom of molecular motion.

Reversed micelles provide a unique field to solubilize ionic or polar solutes in apolar media and can control the reaction rate or pathway occurring in the interior core of micelles.[1] The system is roughly classified into two distinct categories:[2] (1) the catalysis

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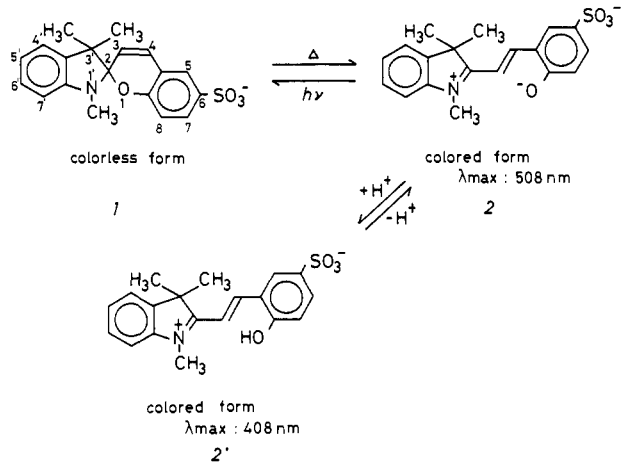
by the detergent itself in the reversed micelles provided by the functional detergents and (2) the assistance of the restricted field produced in the interior core of micelles. The former has been exemplified in numerous studies[1,2] in which the general acid–base catalysis with detergents is examined. On the other hand, few examples of the latter case have been published so far.[3-7] In an extension of our recent studies,[2-5] we have particularly focused on the specific effect of the restricted field, which is formed in the reversed micellar core, on the mobility of solubilized substrates. The intramolecular (unimolecular) reaction seems most convenient[3] for the investigation of the effect of restricted field on the reaction rate or pathway. In this work, hence, we synthesized a spiropyran (1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline]-6-sulfonic acid) (**1**) with a sulfonate group on the phenyl ring to alter the solubility as desired[8] and studied the photochromism of the water-soluble spiropyran **1** in the anionic AOT reversed micelles. The spiropyran **1** and its open-ring form **2** (eq 1) are soluble in water, less soluble in alcohol and Me_2SO_2, and



insoluble in apolar solvents. In order to completely encapsulate the substrate in the water pool of micelles and prohibit the direct interaction with detergents, we employed the anionic AOT/hexane micelle in this work.

Experimental Section

Materials. 1′,3′,3′-Trimethylspiro[2*H*-1-benzopyran-2,2′-indoline]-6-sulfonic acid (**1**) was synthesized as follows. *N*-(2-Hydroxybenzylidene)aniline-5-sulfonic acid was synthesized by sulfonation of *N*-(2-hydroxybenzylidene)aniline prepared from salicylaldehyde and aniline according to a reported method.[9] To 34 g (0.176 mol) of *N*-(2-hydroxybenzylidene)aniline in a reaction vessel was added 175 g (0.880 mol) of concentrated sulfuric acid. The mixture was vigorously stirred for 90 min at 70–80 °C on a water bath and then poured onto 200 mL of ice water under stirring to give a yellow crystalline mass. The crude products were isolated by vacuum filtration, washed with cold water, and dried in an oven at 130 °C for 8 h. The IR spectra of the crude product (KBr disk) showed characteristic bands at 1600 (C=N), 1400 (SO_2 (as)), and 1200 cm^{-1} (SO_2 (s)). A mixture of the above sulfonated product (49 g, 0.176 mol), barium hydroxide octahydrate (120 g, 0.370 mol), and water (300 mL) was steam-distilled until the distillate was aniline free. The residue was cooled to give solid materials. The pale yellow solid obtained was dried in a vacuum oven and dissolved in 500 mL of absolute ethanol. Dry gaseous hydrogen chloride was passed through the ethanolic solution until barium chloride precipitated out. After the inorganic salts were filtered off, the filtrates were evaporated with a small amount of water to give redish brown syrup containing salicylaldehyde-3-sulfonic acid polyhydrate. The syrupy material (15 g, 0.077 mol) and 1,3,3-trimethyl-2-methyleneindoline (Eastman Kodak, Rochester, NY[10] (13.5 g, 0.078 mol) were dissolved in 160 mL of methanol and refluxed for 90 min on a steam bath. After the solution was cooled to room temperature, the redish brown precipitate was filterted off and washed with cold methanol. After recrystallization from methanol and drying at 140 °C for 8 h in an Abderhalden apparatus, pure **1** was obtained in the open-ring form in 50% yield (13.8 g): Mp ~240 °c dec; IR (KBr) 1600 (C=N^+), 1400 and 1360 (SO_2 (as)), 1300 (C—N (ar)), 1220 (SO_2 (s)), and 1020 cm^{-1} (C—O—C). Anal. Calcd for $C_{19}H_{19}NO_4S$: C, 63.85; H, 5.36; N, 3.92. Found: C, 63.43; H, 5.37; N, 3.87.

AOT was prepared according to the procedures previously described[3] and purified by preparative silica gel liquid chromatography. Purity of the surfactant was inspected by IR, TLC, and elemental analysis; mp 186–190 °C. Anal. Calcd for $C_{20}H_{37}O_7SNa$: C, 54.03; H, 8.39. Found: C, 53.76; H, 8.91.

Solvents employed were carefully purified, dried, and stored under moisture-free conditions.

Miscellaneous Measurements. The water content in reversed micelles was determined on a Karl Fischer moisture automatic titration apparatus Model MK-A III, Kyoto Electronics MFG Co., Ltd., Kyoto. All visible and ultraviolet spectra were measured on a Hitachi 124 recording spectrophotometer equipped with a thermoregulated cell compartment. Homogeneity of **1** or its open-ring form **2** in solutions was very carefully inspected by using TLC developed with hexane ethanol (9:1) and detected by exposing the plates to I_2 vapor. Detection of the closed-ring form (**1**, R_f 0.3) on TLC was carried out under continuous irradiation with visible light during the development, while the open-ring species (**2**, R_f 0) was developed in the dark.

In order to estimate the microscopic viscosity of the interior core of the AOT/hexane reversed micelles, we determined the depolarization fluorescence (p) as a function of water content by using a water-soluble fluorescent probe, pyranine (1-hydroxy-3,6,8-pyrenetrisulfonic acid, Sigma), on a Union Giken Model FS-501S fluorescence polarization spectrophotometer.[11]

Kinetics. Photoirradiation was carried out in a thermoregulated water bath connected to a Komatsu-Yamato Coolnics Model CTR-120 Thermostat with a Toshiba Model SHL-100 UV-2 mercury lamp. Visible light (400–450 nm) was isolated by employing a liquid filter (1 cm thick) of 10% (v/v) aqueous $CuCl_2$ solution. The distance from the light source to the sample cuvette was 22 cm. The rates for the thermocoloration of **1** to **2** were followed by monitoring an increase in the intensity of the absorption maxima around 400–430 nm. The absorption maximum of species **2** was due to the solvent polarity: 408 nm in an aqueous buffered solution (pH 5), 425 nm in MeOH, 430 nm in EtOH, and 425 nm in the 0.2 M AOT/0.6 M H_2O/hexane reversed micelles. The rate constants k_1 for the thermocoloration were obtained by analysis of the first-order kinetics for the appearance of species **2** in solutions.

Results and Discussion

Photochromism between 1 and 2. The reaction of spiropyran **1** can be written as in eq 1 and is now generally believed to be responsible for photochromism.[12] An obvious assumption to explain the photochromism is to assign the closed spiro structure **1** to the colorless form and the open structure **2** to the colored form. There exists an equilibrium between colorless and colored forms of spiropyrans, and the reaction in either direction can occur both photochemically and thermally. Similar to several spiropyrans bearing free hydroxy, carboxy, or amino groups on either ring,[13,14] the present compound **1** was found to exhibit negative or reversed photochromism in polar media (eq 1). Compound **2** gives a red or reddish-orange color in polar solvents depending on pH and solvent polarity at a given temperature. If the visible light corresponding to the absorption maximum is irradiated onto the solution, the color of the solution fades accompanied by the formation of **1**. After the colorless solution was kept in the dark

(1) (a) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems;" Academic Press: New York, 1975. (b) Fendler, J. H. *Acc. Chem. Res.* **1976**, *9*, 153. (c) Sunamoto, J.; Kondo, H. *Yukagaku* **1977**, *26*, 389.
(2) Kondo, H.; Fujiki, K.; Sunamoto, J. *J. Org. Chem.* **1978**, *43*, 3584.
(3) Sunamoto, J.; Horiguchi, D. *Nippon Kagaku Kaishi* **1980**, 475.
(4) Sunamoto, J.; Hamada, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3130.
(5) Sunamoto, J.; Kondo, H.; Hamada, T.; Yamamoto, S.; Matsuda, Y.; Murakami, Y. *Inorg. Chem.* **1980**, *19*, 3668.
(6) Seno, M.; Araki, K.; Shiraishi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 899.
(7) O'Connor, C. J.; Fendler, E. J.; Fendler, J. H. *J. Chem. Soc., Dalton Trans.* **1974**, 625.
(8) Taylor, L. C. U.S. Patent 3 320 067, 1967.
(9) Bigelow, L. A.; Eatouch, H. "Organic Synthesis"; Wiley: New York, 1967; Collect. Vol. I, p 80.
(10) This was a kind gift of Professor R. A. Moss, Rutgers, The State University of New Jersey.
(11) Sunamoto, J.; Kondo, H.; Miwa, I. *J. Phys. Chem.*, in press.
(12) Bertelson, R. C. "Photochromism;" Brown, G. H., Ed.; Wiley: New York, 1971; Chapter 3.
(13) Shimizu, I.; Kokado, H.; Inoue, E. *Kogyo Kagaku Zasshi* **1969**, *72*, 171.
(14) Shimizu, I.; Kokado, H.; Inoue, E. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1730.

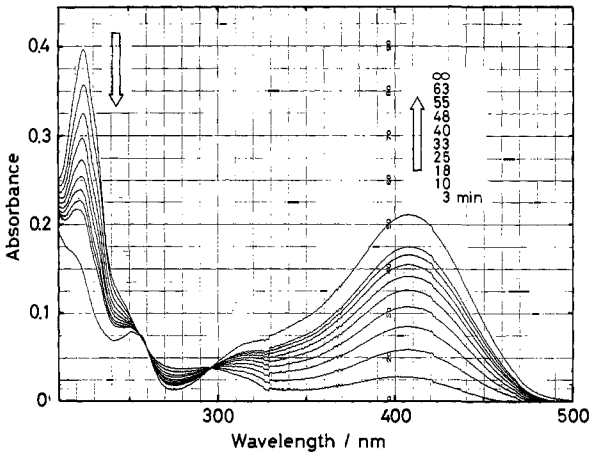


Figure 1. Visible spectral change of the photobleached **2** (**1**, 1.0×10^{-5} M) as a function of time for the thermocoloration in the dark in an aqueous buffered solution (pH 5) at 25.0 °C.

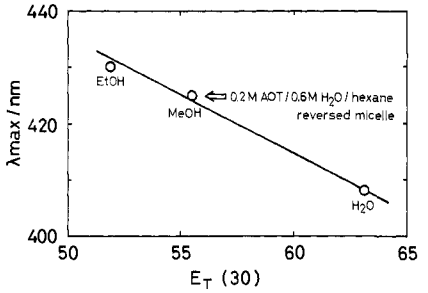


Figure 2. Absorption maxima of **2** in several polar solvents as a function of the Dimroth's solvent-polarity parameter, $E_T(30)$ at 25.0 °C. Blank arrow shows the absorption maximum in the AOT/hexane micelle.

at a given temperature, the solution turns red again (Figure 1). Namely, the present system shows a typical thermocoloration–photobleaching cycle.[12] This also means that the colored open-ring species **2** is thermodynamically more stable than the colorless form of closed-ring **1**. This was also true for anionic AOT/hexane reversed micelles case.

Figure 2 shows the change in the absorption maximum of species **2** as a function of Dimroth's parameter for solvent polarity, $E_T(30)$.[15] The absorption maximum shows a blue shift with an increase in the polarity of the solvents employed, which is ascribed to the stabilization of the ionic excited state upon solvation with polar solvents.[16] The absorption maximum of species **2** in the AOT micelles was 425 nm, close to that in methanol (Figure 2), which suggests the polarity of the microenvironment around **2** in the AOT reversed micelles is simply considered to correspond to that of methanol.

In an aqueous solution, an increase in pH brings about a decrease in the intensity of the absorption band at 408 nm, accompanied by a simultaneous increase in that at 508 nm, with an isosbestic point at 452 nm. This is caused by the acid-dissociation process (eq 1). From the pH–intensity profile for the two absorption bands, the pK_a of the hydroxy group of species **2** was estimated to be 6.2. Judging from the spectroscopic characteristics, the species must be in a free form with regard to the hydroxy group (**2'**) in the 0.2 M AOT/0.6–1.0 M H_2O/hexane reversed micelles.

Thermocoloration. The first-order rate constants for the thermocoloration of **1** under various conditions are summarized in Table I. In a homogeneous system, the rate of thermocoloration decreases with a decrease in solvent polarity. This may be interpreted in terms of stabilization in the ground state of the neutral closed-ring species **1** and/or unstabilization of the polar transition

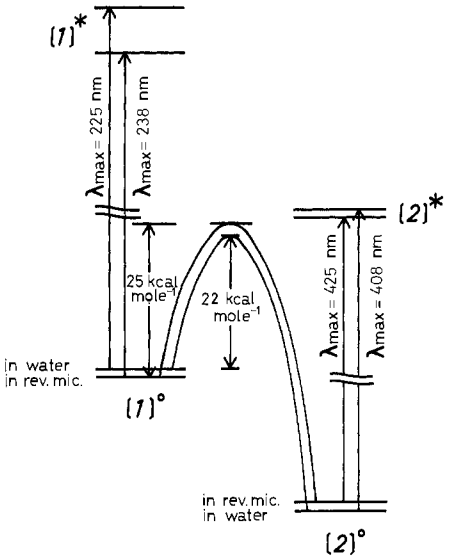


Figure 3. Energy diagram that indicates the correlations and differences, in the energies of excitation for the unstable colorless form **1** and stable colored form **2** and energies of activation for the thermocoloration of **1** between the aqueous buffered solution (pH 5) and the 0.2 M AOT/0.6 M H_2O/hexane reversed micelle.

Table I. Kinetic Parameters of the Thermocoloration of 1 under Different Microenvironments at 25.0 °C[a]

environment	rate × 10^6, s^{-1}	relative-rate ratio	half-life, min.
aq soln (pH 5)	317	1	36
aq soln (pH 8)	983	3.1	12
HeOH	158	0.5	72
EtOH	114	0.36	100
0.2 M AOT/0.6 M H_2O/hexane	7.6	0.024	1500 (25 h)
0.2 M AOT/1.0 M H_2O/hexane	13.0	0.040	900 (15 h)

[a] $[1] = 1.0 \times 10^{-5}$ M.

state toward the ionic product by solvation with less polar solvents. Nevertheless, the microscopic polarity in the AOT micelles is comparable to that in methanol as described above; the conversion rate from **1** to **2** in the AOT reversed micelles was decelerated by 10–20 times compared with that in methanol. Hence, the observed deceleration must be explained in terms of an effect other than the solvent polarity of the microenvironment. Molecular-model building suggests to us that in order for **1** to open the pyran ring and take a possibly conjugated and planar conformation like the merocyanine dye structure **2**, two σ bonds, which originally clipped to olefinic double bond, must largely rotate with the cis–trans isomerization. Most probably, the rotative movement will be controlled by the rigidity of the field.

The microscopic viscosity of the water pool in the AOT micelles seems to be relatively high compared with that in the bulk aqueous solution, which has been confirmed by fluorescence,[17] ESR,[18] NMR,[19] and laser photolysis[20] studies so far. Hence, another explanation for the rate deceleration in thermocoloration in the reversed micellar system may be possible in terms of the ability of an increase in the microviscosity to restrict the mobility of the substrate in the reversed micellar core. From the fluorescence depolarization measurements of the probe encapsulated in the AOT/hexane micellar core (data not shown),[11] we also observed that the mobility of a fluorescent probe, pyranine, was significantly hindered with a decrease in the water content. This means that a decrease in the R ($[H_2O]/[\text{surfactant}]$) value gives rise to an

(15) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Liebigs Ann. Chem.* **1963**, *661*, 1.
(16) Vandewyer, P. H.; Hoefnagels, J.; Smets, G. *Tetrahedron* **1969**, *25*, 3251.
(17) Zinsli, P. E. *J. Phys. Chem.* **1979**, *83*, 3223.
(18) Menger, F. M.; Saito, G.; Sanzero, G. V.; Dodd, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 909.
(19) Wong, M.; Thomas, J. K.; Nowak, T. *J. Am. Chem. Soc.* **1977**, *99*, 4730.
(20) Calvo-Perez, V.; Bedderd, G. S.; Fendler J. H. *J. Phys. Chem.* **1981**, *85*, 2316.

Table II. Comparison of Thermodynamic Parameters of Activation in Aqueous Buffered Solution and Anionic AOT Reversed Micelle[a]

environment	E_{act}, kcal/mol	$\Delta G^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
aq soln (pH 5)	22.85	22.02	22.26	+0.81
0.2 M AOT/0.6 M H_2O/hexane	22.34	24.95	21.75	−8.75

[a] $[1] = 1.0 \times 10^{-5}$ M.

increase in the viscosity of the micellar core. Increasing the R values in the reversed micellar system, of course, brings about a decrease in the microscopic viscosity[11,17-21] and an increase in the microscopic polarity of the water pool, subsequently resulting in an increase in the thermocoloration rate (Table I). In order to make the point clearer, we determined the thermodynamic parameters of activation for the present reaction from an Arrhenius plot, where the most reliable linear correlations were attained in both the aqueous and reversed micellar systems. Clearly, from the results listed in Table II, the difference in the entropy term in the reaction rate between the two systems is brought about by means of restricting the freedom of molecular motion (Figure 3).

It may be reasonablly concluded, thus, that the rate deceleration of the thermocoloration of **1** in the reversed micellar core must be caused by the restriction of the mobility and internal rotation of **1** in a highly viscous environment. Furthermore, through kinetic studies on the thermocoloration process in various media, it was found that the photobleached species being at a higher energy level has a longer lifetime in the restricted field provided by reversed micelles than in the homogeneous regular solutions. In addition, present results suggest that the photochromism of spiropyran serves as a good kinetic probe for exploring the microenvironmental effect of the reaction field.

Acknowledgment. The support of the Ministry of Education, Science, and Culture (Grants-in-Aid No. 447068 and 56550594) is gratefully acknowledged.

Registry No. 1, 82352-70-3; **2**, 82352-71-4; **2'**, 82352-72-5; *N*-(2-hydroxybenzylidene)aniline, 779-84-0; 1,3,3-trimethyl-2-methyleneindoline, 118-12-7.

(21) Also, from the ^{13}C NMR T_P measurements of glycine encapsulated in the water pool of dodecylammonium propionate reversed micelles, it is confirmed that the microscopic viscosity of the micellar core increases with a decrease in R values; Tsujii, K., Sunamoto, J. and Fendler, J. H., unpublished results.

Hydroboration Kinetics. 4. Kinetics and Mechanism of the Reaction of 9-Borabicyclo[3.3.1]nonane with Representative Haloalkenes. The Effect of Halogen Substitution upon the Rate of Hydroboration[1]

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Contribution from the Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907. *Received October 15, 1981*

Abstract: The rates of hydroboration of several haloalkenes have been investigated. The kinetics parallel those observed for the parent alkenes in that the faster reacting haloalkenes show kinetics which are first order in $(9\text{-BBN})_2$, while the slower reacting ones display kinetics which are three-halves order—first order in haloalkene and one-half-order in $(9\text{-BBN})_2$. Because of these kinetics, the relative reactivities were established by competitive reactions. These studies reveal the effect of the halogen substituent: 1-hexene, 100; allyl iodide, 7.1; allyl bromide, 4.6; allyl chloride, 4.0. Thus, the effect of an allylic chlorine is to reduce the rate of hydroboration at the γ-position by a factor of 25. In the systems in which hydroboration is directed to the β-position, the rate reduction is less: 2-methyl-2-butene, 100; 1-chloro-3-methyl-2-butene, 57; 1-bromo-3-methyl-2-butene, 54. In these latter cases, hydroboration is followed by rapid elimination and rehydroboration. A vinylic chlorine has a much more dramatic effect of forcing the hydroboration to the 2-position as well as greatly reducing the rate of hydroboration: 1-hexene, 100; *cis*-1-chloro-1-butene, 0.0093.

Introduction

The hydroboration reaction is a method of easily obtaining many organoboranes which are very useful in organic synthesis.[2] While many interesting reactions have been discovered and applied in syntheses, details of the mechanism of hydroboration are still not known.[3] An excellent way of obtaining information concerning the mechanism of a reaction is via kinetic studies. However, in the past, a major difficulty in studying the kinetics of hydroboration has been in finding a suitable hydroborating agent whose kinetics can be easily followed.

Recently it was discovered[3] that 9-borabicyclo[3.3.1]nonane, $(9\text{-BBN})_2$, is an excellent candidate for the investigation of the mechanism and kinetics of hydroboration for many reasons. (1) It has high thermal stability and purity.[4] (2) It is easier to handle compared to other boranes because of its lower sensitivity to oxygen and water vapor.[4] (3) With one reaction center per boron, its overall reaction with an alkene involves only one dissociation step and one hydroboration step. This can be contrasted to that of

(1) Presented in part at the 180th National Meeting of the American Chemical Society, Las Vegas, NV, Aug 1980; American Chemical Society, Washington, DC, 1980; ORGN 316.

(2) Negishi, E.; Brown, H. C. *Synthesis* **1974**, 74.

(3) (a) Brown, H. C.; Scouten, C. G.; Wang, K. K. *J. Org. Chem.* **1979**, *44*, 2589–2591. (b) Brown, H. C.; Wang, K. K.; Scouten, C. G. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 698–702. (c) Wang, K. K.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 5303–5306.

(4) (a) Brown, H. C.; Knights, E. F.; Scouten, C. G. *J. Am. Chem. Soc.* **1974**, *96*, 7765–7770. (b) Brown, H. C.; Mandal, A. K.; Kulkarni, S. U. *J. Org. Chem.* **1977**, *42*, 1392–1398.

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