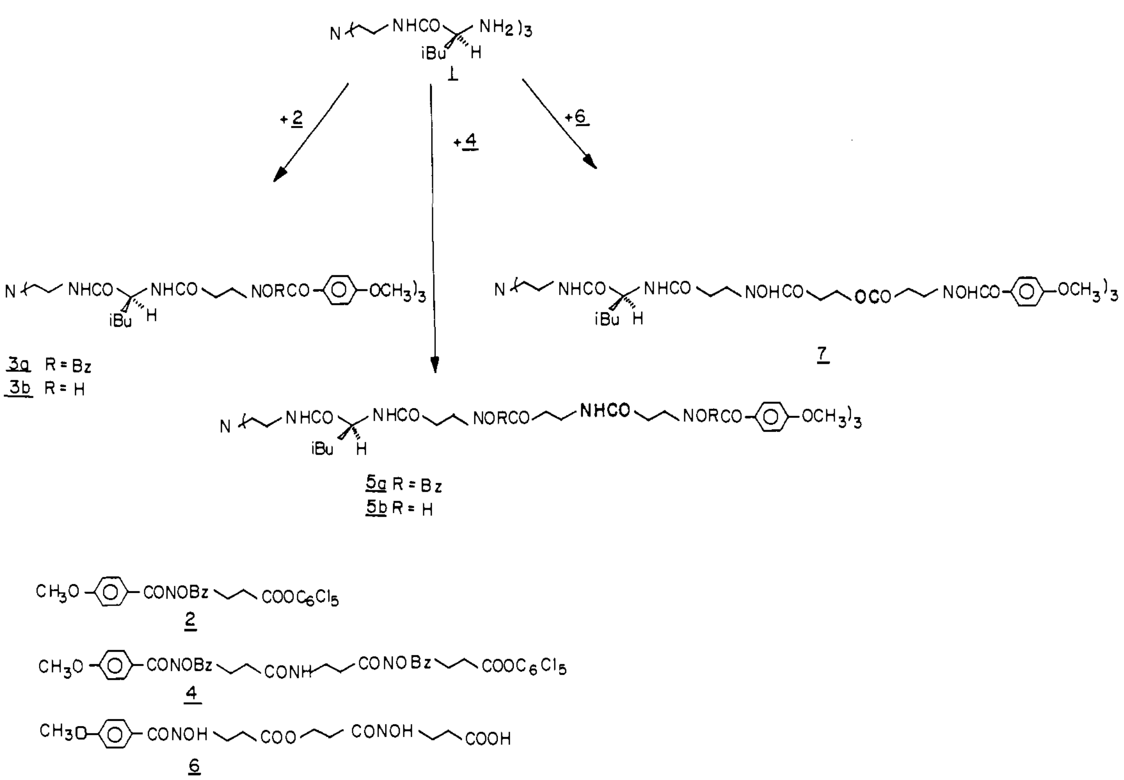
Scheme I



and its CD (0.29 mM in CDCl$_3$) reveals Cotton effects at 450 nm ($\Delta\epsilon = +2.4$) and at 345 nm ($\Delta\epsilon = -3.64$). This indicates predominance of the Λ-cis configuration[10] which is stabilized by H bonds.

Extension of **3** with a second set of alternating amide and hydroxamate groups yielded **5a** which also has interchain H bonds according to its IR (NH absorptions around 3300 cm^{-1}, 1.6 mM CDCl$_3$) and NMR spectra ($\Delta\delta = 0.39$ ppm in CDCl$_3$ and $\Delta\delta = 0.15$ ppm in CD$_3$OD for the diastereotopic NCH$_2$*CH$_2$* protons). The absolute signs of the Cotton effects of the diferric complex **5b-2Fe** are identical with those of the monoferric complex **5b-Fe** but almost fourfold in intensity (Figure 1). This establishes identical configuration around each guest ion, Δ-cis according to the aboslute signs, and ultimately implies the presence of a right-handed helical structure. The configurations of the Fe^{3+} complexes of **5b** are thus opposite to those of the Fe^{3+} complex of **3b**. Molecular models of **5b-2Fe** point toward H bonds between the peripheral amide–NH of one strand and the central amide–CO of the adjacent strand that inverts the directionality of the remaining H bonds and thereby the preferred handedness of the Fe^{3+} complexes. The bonded NH frequencies of the isolated **5b-Fe** (3285 cm^{-1} in 1.2 mM CDCl$_3$) and **5b-2Fe** (3310 cm^{-1} in 1.2 mM CDCl$_3$) and their diminished Cotton effects in protic MeOH ($\Delta\epsilon = +0.60$ at 374 nm for **5b-Fe**, and $\Delta\epsilon = -0.60$ at 470 nm and $\Delta\epsilon = +1.90$ at 390 nm for **5b-2Fe**) relative to aprotic CDCl$_3$ (Figure 1) strongly support this possibility.

In order to obtain further evidence for the role of the peripheral H bonds ditopic binder **7**, where the peripheral amides had been replaced by ester groups, was synthesized and examined. Binder **7** has its remaining amides H bonded in CDCl$_3$, as shown by its low NH frequencies (around 3275 cm^{-1} in 5 mM CDCl$_3$) and its NMR pattern. The signs of the Cotton effects of the diferric complex **7-2Fe** are identical with those of the monoferric complex **7-Fe** but twice in intensity (Figure 1). This demonstrates identical configuration for both complexes, Λ-cis according to the absolute signs, and the formation of a left-handed helix. The complexes of ester **7** thus adopt a configuration opposite to those of amide **5b** but identical with that of the monotopic binder 3b, indicating restoration of the original H bond pattern in **3**.

The generation of diastereomeric helical metal complexes of either right- or left-handedness by using the very same amino acid as a chiral constituent demonstrates the governing role of H bonds in shaping these arrangements. To which extent the nature of these H bonds may modulate the height of the pitch and thereby the proximity of the metal ions is under current investigation, as is the expansion of these systems to generate artificial ion channels.

Acknowledgment. We thank Prof. S. Lifson for fruitful discussions, R. Lazar for her devoted technical assistance, and the Minerva Foundation for support of this project.

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[10] Raymond, K. N.; Muller, G.; Matzanke, B. F. *Top. Curr. Chem.* **1984**, *123*, 49-102.

Electrochemical Formation of an Organic Thin Film by Disruption of Micelles

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The preparation of organic thin films has attracted considerable interest in recent years in view of their potential applications to microelectronics, optics, etc.[1] Various methods for preparing organic thin films have been presented.[2-4]

Recently, we demonstrated that a micelle formed by surfactants having a ferrocenyl moiety can be broken up into monomers when the surfactants are oxidized chemically or electrochemically and that a solubilizate is released from the micelles as the micelles

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[1] For a review, see: Vincett, P. S.; Roberts, G. G. *Thin Solid Films* **1980**, *68*, 135.

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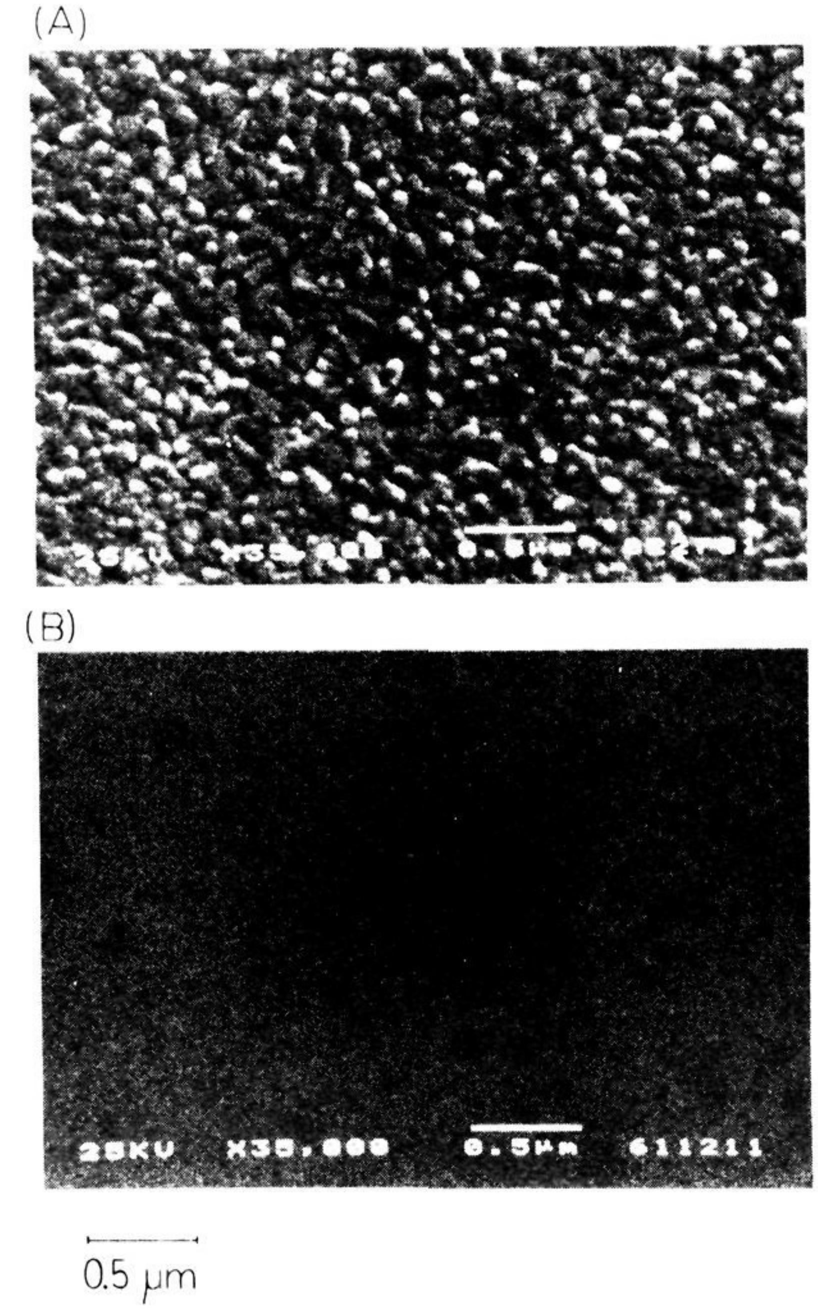

Figure 1. Scanning electron micrographs of (A) the film coated on the ITO (Q = 0.074 coulombs/cm^2) and (B) a bare ITO surface. The calibration mark at the bottom of the micrographs corresponds to 0.5 μm.

are broken up.[5,6] We report here a novel method for preparing an organic thin film by using this property of these surfactants, which demonstrates a new film-forming technique.

The solubilizate used was the dye, 1-phenylazo-2-naphthol (**1**), which is sparingly soluble in water and does not form aggregate itself. The surfactant used was (11-ferrocenylundecyl)trimethylammonium bromide (**2**$^+$).[6] Electrochemical measurements were carried out at 25 °C under a nitrogen atmosphere. Indium tin oxide electrodes (ITO) were obtained from Matsuzaki Shinku Co. (10Ω/square). The test solution consists of 2.0 mM **2**$^+$, 39 μM **1**, and 0.2 M Li_2SO_4. Most of **2**$^+$ may exist in the form of micelles because critical micelle concentration of **2**$^+$ in 0.2 M Li_2SO_4 aqueous solution is negligibly small (below 0.1 mM[6]). Under these conditions, the concentration of the **2**$^+$ micelle in the test solution was estimated to be 8.7 μM by using the aggregation number of **2**$^+$ in the presence of 0.2 M Li_2SO_4, 230.[6] On the basis of Poisson statics,[7] one micelle may solubilize 4.5 molecules of **1** on the average.

The cyclic voltammogram of this solution showed a reversible one-electron oxidation step with a half-wave potential of +0.15 V versus a saturated calomel electrode (SCE).[8] This step may be assigned to the redox system, **2**$^+$/**2**$^{2+}$.[6] No redox process of **1** was observed up to the potential of ultimate current rise.

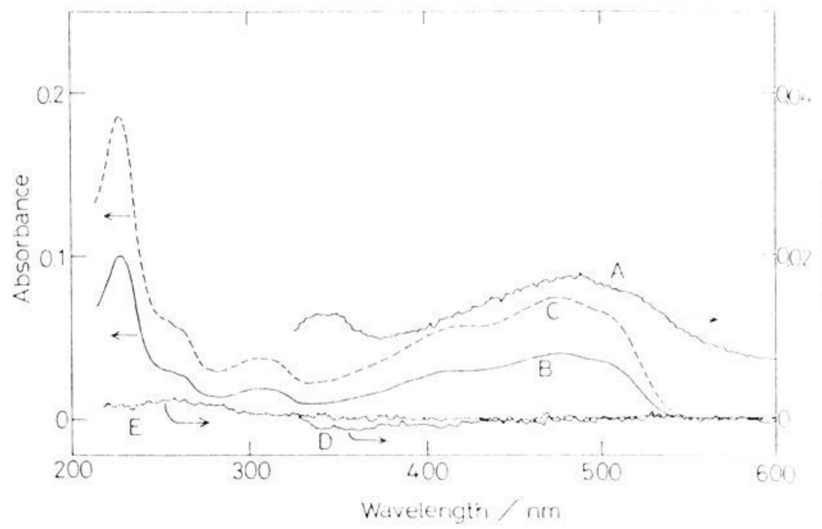

Figure 2. Electronic absorption spectra[10] of the ITO obtained by the electrolysis of the **2**$^+$ solution containing **1** (A) and not containing **1** (D). B and E show the spectra of the ethanol solutions prepared by washing the surfaces A and D, respectively, as well as the spectrum of the ethanol solution of 4.5 μM **1** (C).

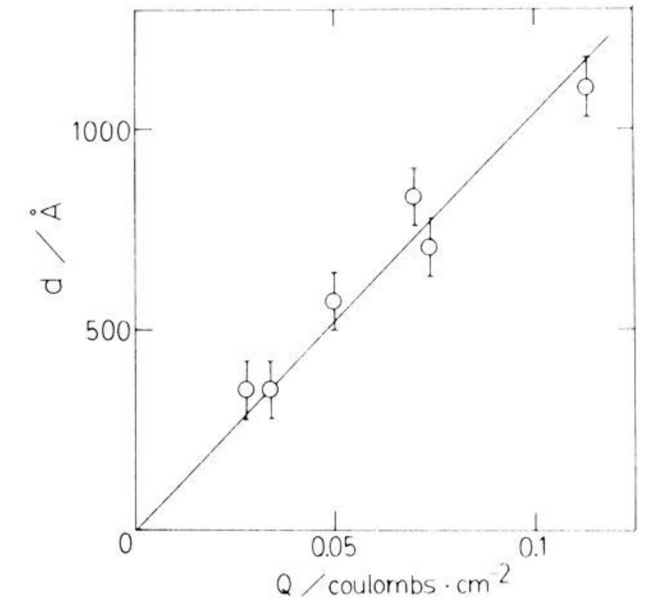

Figure 3. The dependence of the film thickness, d, on the amount of electricity passed through the ITO, Q.

Controlled-potential electrolysis of this solution at the ITO, which was maintained at +0.30 V, was done while stirring the solution. After a definite amout of electricity, Q (coulombs/cm^2), passed through the ITO, the ITO was rinsed with distilled water and dried in the air.

Figure 1 shows the electron micrographs of (A) the film on the ITO obtained by controlled-potential electrolysis for 20 min (Q = 0.074 coulombs/cm^2) and (B) a bare ITO. Nuclei with diameters of 600–900 Å are observed in the film. The film thickness was determined to be 700 Å by the usual interference technique.[9]

Figure 2 shows the absorption spectra of (A) the film on the ITO (Q = 0.074 coulombs/cm^2),[10] (B) the ethanol solution prepared by washing this film, and (C) 4.5 μM **1** in ethanol. The absorption peaks in spectrum B were the same as those in spectrum C and were different from those of **2**$^+$ under identical conditions. No absorption peak was observed either on the ITO obtained by the electrolysis of a **2**$^+$ solution devoid of **1** (D)[10] or in an ethanol solution prepared by washing this ITO (E). These results support the hypothesis that the thin film formed on the ITO is made of **1**.

1 (51%) released from the **2**$^+$ micelles by electrolysis was deposited on the ITO. This percentage is based on the amount of electricity passed through the ITO and the number of moles of **1** deposited on the ITO. The latter value was determined by spectrum B.

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(6) Saji, T.; Hoshino, K.; Aoyagui, S. *J. Chem. Soc., Chem. Commun.* **1985**, 865.

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(8) The value of the half-wave potential and the number of electrons involved in the electrode process were determined by the same method as described in ref 5.

(9) Tolansky, S. *Multiple-Beam Interferometry of Surfaces and Films*; Oxford University Press: London, 1948.

(10) For all the spectra, the corrections for backgrounds are made by subtracting the absorption of the ITO or absorption cell. At wavelengths shorter than 330 nm, the absorption spectra of the film on the ITO could not be measured due to the high absorbance of the ITO itself.

Such a film formation may be explained by the following processes: (1) The 2^+ micelles solubilizing **1** diffuse to the ITO surface. (2) 2^+ forming micelles are oxidized to 2^{2+}. (3) The 2^+ micelles break up into 2^{2+} monomers, owing to the enhancement in the electrostatic repulsion among positively charged tail groups and in their hydrophilic character as well. (4) **1** molecules are released from the micelles as a result of the disappearance of the micelles. (5) **1** molecules are supersaturated and finally deposited on the ITO.

Figure 3 shows a plot of the film thickness, d, versus Q. It shows that the value of d increases linearly with Q. This result indicates the possibility of precise control of the film thickness.

Present experiments show that such an electrochemical method serves as a novel tool for preparing thin films of materials which are soluble in a micellar solution. Furthermore, this method may enable a large surface to be coated with a uniform thin film without using organic solvents.

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Dynamics of the Wolff Rearrangement: Spectroscopic Evidence of Oxirene Intermediate

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The Wolff rearrangement, involving the decomposition of an α-diazoketone to yield a ketene, is of great interest and importance in chemistry. Although it has been studied for many years by various techniques,[1-3] the dynamics of this reaction from excitation of a diazoketone to the formation of the final product(s) have eluded direct observation. Only the last intermediate ketene has been observed to react with solvents to yield stable products.[4-6] Ketene is postulated to be formed from other precursors, ketocarbene and/or oxirene. Ketocarbenes were finally detected by Chapman and his co-workers, very recently, in solid matrices at 15 K by using strained diazoketones.[3] Here we report the direct observation of the dynamics of the Wolff rearrangement for an unstrained diazoketone in water at 298 K. The precursor to ketene is observed and assigned to be an oxirine, an important chemical species that had yet to be unambiguously detected.[2,3] Both spectral and dynamic features are presented.

The first compound chosen for this study is the common sodium 1-oxo-2-diazonaphthoquinone-5-sulfonate. Its absorbance spectrum in water (1×10^{-4} M) is shown in Figure 1 a (solid curve). After continuous photolysis,[1,7] the diazoketone yields mainly indene carboxylic acid (reaction 5 in Figure 2) whose spectrum is shown in Figure 1a (dashed curve). The diazoketone exhibited very weak fluorescence from S_1 to S_0. Careful single photon counting measurements indicate that the S_1 lifetime is at most 1 ns.

Wishing to observe and determine the nature of the possible ketene precursors ketocarbene and/or oxirene, as shown in the

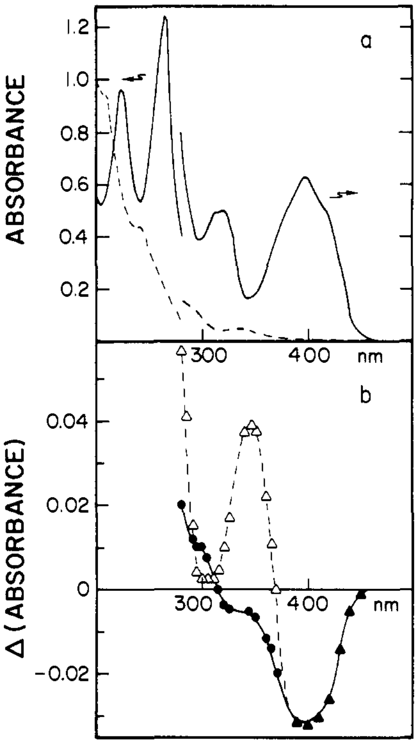

Figure 1. (a) Absorbance spectra of sodium 1-oxo-2-diazonaphthoquinone-5-sulfonate (solid curve) and the final photolytic product in water, indene carboxylic acid (dashed curve). (b) Transient spectra observed upon laser excitation of the diazoketone at 337 nm, immediately after laser pulse (solid curve) and 3 μs later (dashed curve).

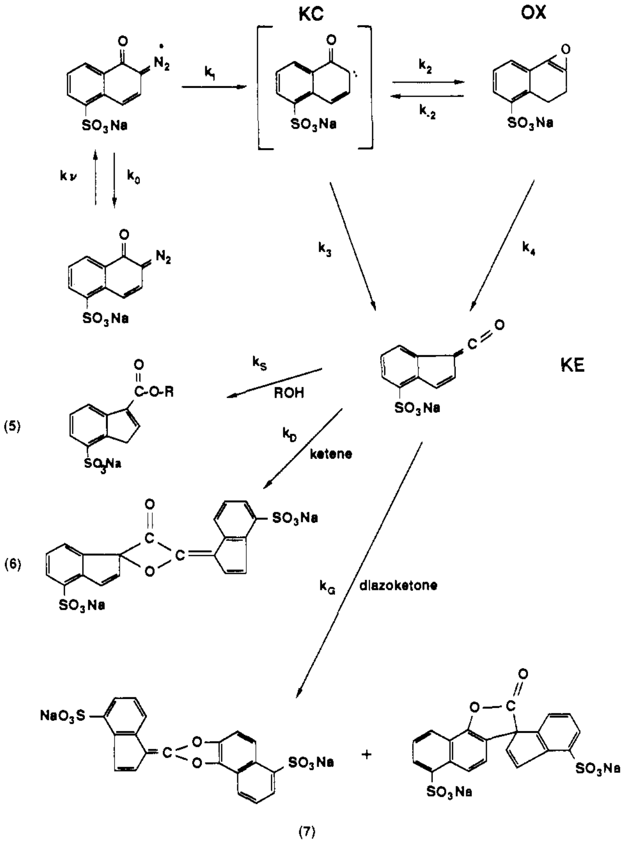

Figure 2. Reaction scheme after excitation of sodium 1-oxo-2-diazonaphthoquinone-5-sulfonate: KC, ketocarbene; OX, oxirene; and KE, ketene.

reaction scheme (Figure 2), we undertook a ns laser flash photolysis study. The diazoketone in water (4×10^{-4} M) was excited with an N_2 laser (Molectron UV 400, pulse width 8 ns, excitation

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