Communications to the Editor

Control of Reaction Kinetics by Manipulation of Micellar Size and Shape

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Although a great many studies have been performed regarding the possibility of kinetic and geometric control of reaction pathways in micellar[1-3] and vesicular media,[4,5] relatively little is known about reactions in "extended" micelles or lyotropic liquid crystals. These phases are not uncommon at higher concentrations of typical micelle-forming reagents in aqueous solutions.[2,6] There exists a wide variation in the structure of such phases, analogous to the polymorphism in thermotropic liquid crystals. In this work, the focus is on nematic lyotropic liquid crystals in which the organic aggregates are either rodlike or disklike in shape and which have appropriate viscoelastic properties to respond to external torques such as magnetic fields or surface alignment to influence their orientational order.

In a recent study by Ueoka et al.[7] of the hydrolytic cleavage of peptide ester substrates, it was found that kinetic selectivity was sensitively coupled to the sphere–rod transition of micellar aggregates. This was ascertained by determining the hydrodynamic parameters and enantioselectivities and showing a striking similarity in their mutual dependences on surfactant compositions. In the case of a liquid-crystal system, sphere–rod–disk phase transitions can be determined both optically and thermodynamically and are well-defined critical phenomena. One might therefore anticipate marked changes in reaction characteristics at these transitions.

There is a small region of the ternary phase diagram of sodium decyl sulfate (SDS), 1-decanol, and water in which, as a sensitive function of either concentration or temperature, transitions occur between three phases: N_L, N_C, and I. These symbols represent, respectively, an aggregate having a bilayer structure, a cylindrical structure, and an isotropic phase of spherical micelles.[8] The N_C and N_L aggregates are substantially larger than the conventional micelle.[6] It is the strategy of this study to investigate the kinetics of a bimolecular reaction through these phase transitions in order to ascertain the effects of environment on the reactivity. The reaction chosen is the bromination of trans-stilbene, since there already exists a careful study of this system in aqueous micelles and vesicles.[9] It is shown that the N_C phase provides an environment in which the rate of reaction drops significantly as compared to the N_L phase and that this decrease occurs when one enters N_C by either raising the temperature at fixed concentration or raising the sodium decyl sulfate concentration at fixed temperature.

A 10^{-4} M solution in the liquid crystalline solvent (sodium decyl sulfate/1-decanol/water) was prepared by dissolving weighed amounts of trans-stilbene in 1-decanol, adding the appropriate
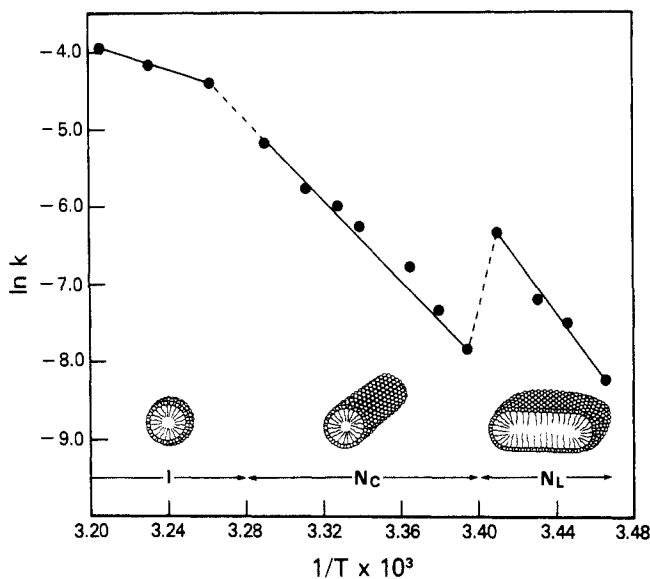

Figure 1. Arrhenius plot of the bromination of trans-stilbene in the N_L, N_C, and I phases of SDS/water/1-decanol, 35/58/7 wt %.
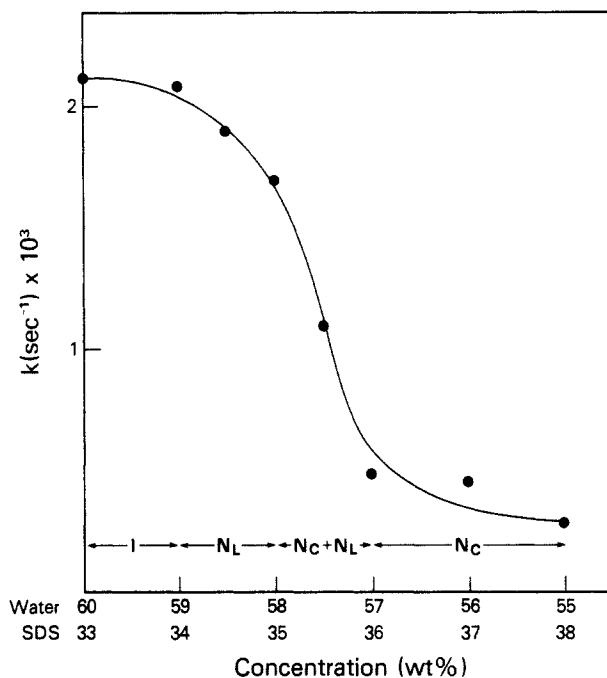

Figure 2. Pseudo-first-order rate constants k (s^{-1}) for the bromination of trans-stilbene as a function of SDS/water concentration at 20 °C and constant 1-decanol concentration (7 wt %).

quantities of sodium decyl sulfate and water, and stirring for 24 h. The N_L–N_C and N_C–I transitions were depressed by ~1 deg in these solutions. Solution, 0.5 g, was placed in a 1 mm path length UV cuvette and thermostated for 20 min at the appropriate temperature in the range 15.5–39 °C. Bromination was initiated by injecting 20 μL of 0.027 M aqueous bromine and stirring vigorously. Utilizing a Perkin-Elmer 330 spectrophotometer interfaced with a Model 3600 data station, the disappearance of stilbene absorption at 314 nm was monitored for at least 2 half-lives. No phase separation was detected by optical microscopy during the entire course of the reaction. The pseudo-first-order rate constant was evaluated from a plot of ln [stilbene] vs. time.

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At least three independent experiments were conducted at each temperature. The estimated error in the rate constants is 15%.

Pseudo-first-order rate constants are plotted as a function of temperature (Figure 1) and as a function of concentration (Figure 2) through the N_C, N_L, and I phases. On each plot, the experimental values for the phase-transition temperatures determined optically are indicated. The rates of bromination are significantly lower in the N_C phase. Activation energies, enthalpies, and entropies all show pronounced changes through the phase transitions; for example, $\Delta H^{\ast} = 63, 39$, and 12 kcal mol^{-1} for N_L, N_C, and I phases, respectively. However, because of the small temperature ranges accessible, these values are inherently inaccurate. It is clear from these observations that changes in the shape of the aggregate alter the solubilization, orientation, or local motions of guest molecules leading to substantial reactivity changes.

Earlier studies of reactions in lyotropic liquid crystals have reported changes in rate at the liquid crystal–isotropic phase transition.[10-12] Micellar reactions frequently show pronounced changes at the critical micelle concentration.[1,2] The rate control observed in this work is quite different, in that it is specifically associated with changes in shape of the micellar aggregates themselves. Suggested by this work is the intriguing possibility of using micellar shape as a tool in controlling reaction rates and reaction products.

Registry No. H$_3$C(CH$_2$)$_9$SO$_4$Na, 142-87-0; H$_3$C(CH$_2$)$_9$OH, 112-30-1; H$_2$O, 7732-18-5; (E)-C$_6$H$_5$CH=CHC$_6$H$_5$, 103-30-0.

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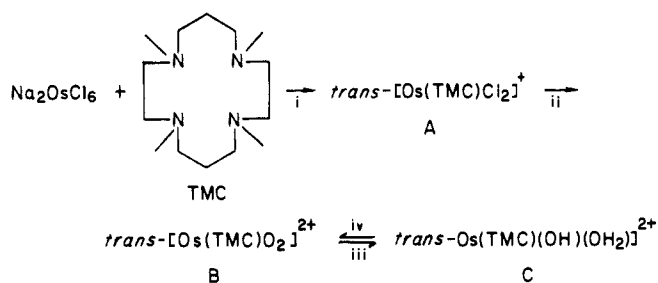
Novel UV–Vis Spectral Feature and Electrochemical Behavior of High-Valent Osmium(VI) Dioxo Complex of 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC). Reversible Three-Electron Redox Couple and Vibronic Structured UV–Vis Absorption Bands Involving trans-[Os^{VI}(TMC)O$_2$]$^{2+}$

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High-valent macrocyclic tertiary amine complexes of Os(VI) have attracted our interests in connection with our work on trans-[Ru^{VI}(TMC)O$_2$]$^{2+}$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane).[1] Meyer and co-workers[2] recently reported that a reversible three-electron redox couple of Os(VI) to Os(III) was observed with Os(trpy)(O)$_2$(OH)$^+$ (trpy = 2,2′,2″-terpyridine), using an "activated glassy carbon electrode". This would be a general property of trans Os(VI) dioxo complexes provided that the intermediate Os(V) and Os(IV) species are stable enough with regard to ligand dissociation and μ-oxodimerization

(Os—O—Os) processes. We describe here some novel spectroscopic and electrochemical properties of a macrocyclic tertiary amine Os(VI) dioxo complex, trans-[Os^{VI}(TMC)O$_2$]$^{2+}$ (B), that exhibits

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Scheme I^a
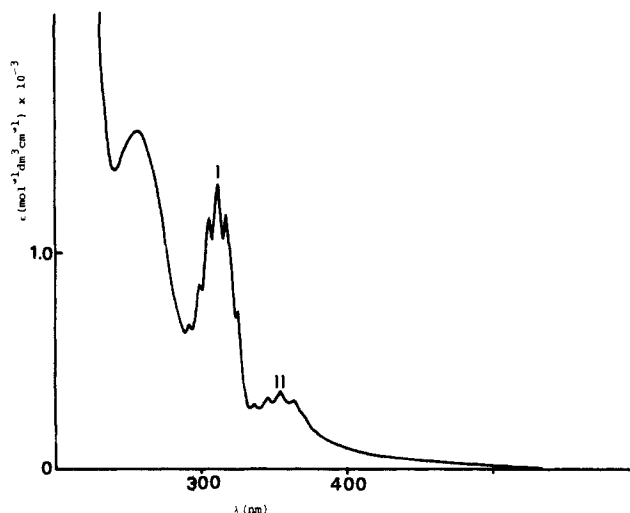
Figure 1. UV–vis absorption spectrum of trans-[Os^{VI}(TMC)O$_2$]$^{2+}$ in CH$_3$CN.

a *reversible three-electron redox couple at a pyrolytic graphite or glassy carbon electrode.*

The synthesis of osmium macrocyclic tertiary amine complexes is outlined in Scheme I (Satisfactory elemental analysis have been obtained for complex A and B). As expected, complex A exhibits an intense UV–vis absorption band at 305 nm characteristic of the P$_\pi$(Cl) → d$_\pi$(Os(III)) charge-transfer transition of trans-dichlorotetrammine osmium(III) species.[3] Formulation of the yellow solid B as trans-[Os^{VI}(TMC)O$_2$](ClO$_4$)$_2$ also comes from its observed diamagnetism ($\mu_{eff} \sim 0$ μ_B) and intense IR band at 870 cm^{-1} which is typical of ν_{as}(Os=O) stretch of the ^{1}A$_{1g}$ [(d$_{xy}$)^2] ground state of the trans Os(VI) dioxo species.[4] The UV–vis absorption spectrum of B (Figure 1) in CH$_3$CN is spectacular, exhibiting two distinct vibronic structured bands, I and II. Simple ligand field analysis[5] shows that the lowest energy ligand-field transition from the ^{1}A$_{1g}$ [(d$_{xy}$)^2] ground state to the doubly degenerate d$_\pi$ (d$_{xy}$, d$_{yz}$) level produces ^{3}E$_g$ [(d$_{xy}$)^1(d$_\pi$)^1] and ^{1}E$_g$ [(d$_{xy}$)^1(d$_\pi$)^1] excited states. Transitions to both excited states are Laporte forbidden and may acquire intensity by vibronic coupling to the A$_{2u}$ [ν(Os=O)] vibrational stretching mode and in the case of a triplet, spin–orbit coupling mechanism. As the spin-allowed transition is more intense than the spin-forbidden one, band I is assigned to the ^{1}A$_{1g}$ → ^{1}E$_g$ transition. With the works of Winkler and Gray,[5] strong spin–orbit coupling perturbation will decompose the ^{3}E$_g$ state into six states of (A$_{1g}$, A$_{2g}$), E$_g$, and (B$_{1g}$, B$_{2g}$) symmetries in order of decreasing energy in the D_{4h} double group.

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(4) See, for example: Griffith, W. P.; Pawson, D. J. Chem. Soc., Dalton Trans. 1973, 1315–1320.
(5) Winkler, J. R.; Gray, H. B. Inorg. Chem. 1985, 24, 346–355.