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Experimental Test for Micelle Porosity

F. M. Menger* and J. M. Bonicamp

Department of Chemistry, Emory University
Atlanta, Georgia 30322

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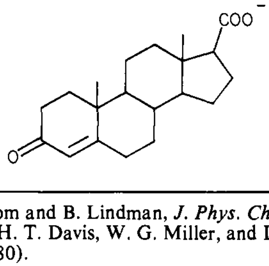
The Hartley model portrays a micelle as a hydrocarbon droplet surrounded by an ionic coat. For decades the model has been the central dogma in micellar chemistry, and today chemists still accept it literally. For example, Wennerstrom and Lindman call "simplistic" claims by others that water penetrates the oil droplet.[1] Franses et al. define a micelle as "closed" (meaning that a closed connected surface can be constructed such that all head groups lie on the same side of the surface and all hydrocarbon tails lie on the other side).[2] It is as if departures from the Hartley model can be summarily dismissed. The fact of the matter is that there is substantial doubt as to the validity of the oil droplet picture. Neither ^{13}C NMR spectra,[3] ORD data,[4] kinetic experiments,[5] gas solubility measurements[6] nor molecular model studies[7] support the Hartley concept. Instead, our results strongly suggest a porous micelle with a rough surface and deep water-filled cavities; monomers are far more disorganized than implied in the conventional structure. A recent statistical theory developed in the Flory laboratory is also at variance with the oil droplet construct.[8] The distinction between the Hartley micelle and the "Menger micelle" (so dubbed for the sake of brevity and alliteration) is not trivial. Consider the most important property of micellar systems: solubilization. If the Hartley micelle is correct, then lipophilic materials enter the micelle core by dissolution much like partitioning between a hexane/water mixture. If the Menger micelle is correct, then binding would take place in water-filled cavities and be accompanied by an entropically favorable release of micellar solvent; in other words, "hydrophobic binding" would be a major factor in micelle–guest association. Since an increasing number of papers on micelles are appearing in this journal and elsewhere, results bearing on the controversy seemed worth communicating.

Micelles are transient and elusive species, and experiments designed to define their structure necessarily entail assumptions and limitations which preclude "proof" in the usual sense of the word. For example, an early attempt by Muller[9] to test the water content of micelle interiors involved a ^{19}F NMR study of micellar $CF_3(CH_2)_{10}CO_2^-$. Chemical shift data pointed to CF_3/water contact, but water penetration into the micelle could be deduced only under the assumption that the CF_3 groups do not loop back to the aqueous micelle surface. Mukerjee and Mysels did not accept this assumption.[10] It thus became clear that rigid systems are required if looping effects are to be avoided, and for this reason we selected steroidal probes for our work. Most of the steroids were bifunctional in character (e.g., 4-androsten-3-one-17β-carboxylic acid). The carboxylate served to anchor the steroid at cationic micellar surfaces. An α,β-unsaturated carbonyl (the probe group) was separated from the carboxylate by a rigid steroidal framework. In a Hartley micelle, the probe group would dip into an oil droplet. In a Menger micelle, the probe group would reside in a region where water is present and perhaps plentiful. A test for micelle porosity was based on this difference.



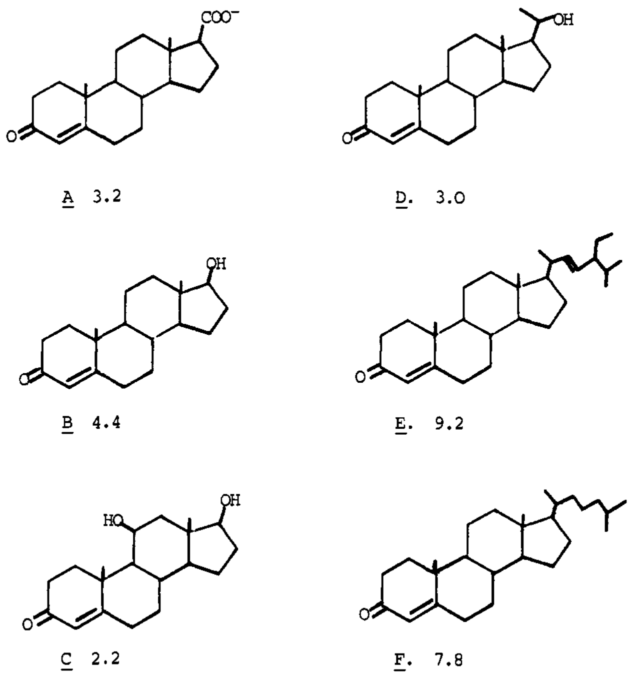


Figure 1. Rates of reduction of steroids adsorbed in HTAB micelles by borohydride relative to the corresponding bulk-water reduction rate of 3-methyl-2-cyclohexen-1-one at 25.0 °C. See text for experimental details.

Steroids were reduced at the carbonyl in 0.020 M aqueous hexadecyltrimethylammonium bromide (HTAB) solutions containing 0.016 M sodium borohydride. The anionic reducing agent can enter a micelle cavity but not an oil droplet; thus rate data on the reactions provide information about the environment of the probe moiety. By following the reaction spectrophotometrically (λ 242.5 nm) with a 0–0.1 absorbance scale, it was possible to use a low steroid concentration (5.4×10^{-6} M) to minimize perturbation of the micelles. Pseudo-first-order rate constants at 25.0 °C were secured with satisfactory reproducibility (± 10%), provided (1) 0.10 M NaOH was used to stabilize the aqueous borohydride, (2) borohydride solutions were freshly prepared and titrated, (3) HTAB was purified by repeated crystallizations from acetone, and (4) data from four repeat runs were averaged. In the absence of borohydride, no steroid reaction was observed under the reaction conditions. Rate constants were the same whether a reaction was initiated by adding steroid to HTAB/BH_4^- or by adding BH_4^- to HTAB/steroid (showing that association phenomena are not rate determining). Binding experiments proved that above the CMC of the surfactant, where we operated exclusively, micelle–steroid complexation is complete.

Rates of borohydride reduction for several micellar steroids are given beneath their structures in Figure 1. These rates are relative to the second-order rate constant for borohydride reduction of 3-methyl-2-cyclohexen-1-one in bulk water at 25 °C ($k_2 = 0.048$ m^{-1}/s^{-1}). Micellization of the steroids is seen to induce small rate increases over the corresponding bulk water reaction. This result precludes binding of the carbonyls in water-free oil droplets. Nor can the carbonyls loop out of an oil droplet onto the micelle surface where anchor groups such as the D-ring carboxylate are undoubtedly located. One might postulate, perhaps, that the carbonyl drags water and borohydride into a normally nonaqueous oil droplet, but a rapid carbonyl reduction under such unlikely circumstances seems farfetched. Only one viable explanation for the observed rates remains. Steroids must bind in micellar pores or on hydrophobic patches near the micelle surface where water

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and borohydride are accessible. The small observed catalysis has literature precedent and can be ascribed to a favorable accumulation of borohydride at the cationic Stern region. This is confirmed by a 4- and 2--fold rate decrease with steroids A and F, respectively, when the 0.020 M HTAB is replaced with an anionic surfactant, 0.010 M laurate.

Reduction rates for the micellar steroids in Figure 1 vary only slightly when the D-ring substituent is changed from ionic to polar (compare A with F). These trivial kinetic variations imply that even extremely water-insoluble steroids bind where water and borohydride are available. The obvious preference for surface adsorption over internal dissolution has two explanations. (1) Surface binding is far less disruptive to the micelle structure than solubilization in an already crowded core. (2) Water surrounds those chain segments that happen to reside outside the core, because water must fill the spaces that necessarily exist between the chains. When a hydrophobic guest encounters a micelle, the guest enters and displaces micellar water (an entropically favorable process). Thus, suggestions not to the contrary, micelle–guest association takes places in pores and on "fatty patches" where water meets a disorganized assembly of surfactant tails.

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Homogeneous Catalysis of the Photoreduction of Water by Visible Light. 2. Mediation by a Tris(2,2′-bipyridine)ruthenium(II)–Cobalt(II) Bipyridine System[1]

C. V. Krishnan and Norman Sutin*

Chemistry Department, Brookhaven National Laboratory
Upton, New York 11973

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The visible-light-induced formation of hydrogen from water is a subject of much current interest.[2] Many of the systems that have been studied are based on the use of tris(2,2′-bipyridine)ruthenium(II) [$Ru(bpy)_3^{2+}$] as a photosensitizer and require the presence of heterogeneous catalysts such as Pt or Au.[2-9] Very few homogeneous systems have been reported.[1,7,9] Our approach to the homogeneous generation of hydrogen is to convert the luminescent excited state of tris(2,2′-bipyridine)ruthenium(II) [$^*Ru(bpy)_3^{2+}$] to the more strongly reducing (and longer lived) ion $Ru(bpy)_3^+$.[1] The $Ru(bpy)_3^+$ reduces a metal complex which reacts with H_3O^+ or H_2O to form an unstable hydride. The hydride in turn decomposes to yield hydrogen. The blue cobalt(I) bipyridine complexes produced by Na(Hg)[10] or electrochemical[11] reduction of cobalt(II) bipyridine complexes are very powerful reducing agents ($E^0 \sim -1$ V vs. NHE) and are not likely to form stable hydrides in solution. Cobalt(I) bipyridine complexes are thus excellent candidates for mediating the homogeneous formation of hydrogen.[12] This expectation has been confirmed: visible-light irradiation of solutions containing $Ru(bpy)_3^{2+}$, ascorbate, Co^{2+}, and bpy or substituted bpy and phen derivatives produces hydrogen with a quantum yield of up to 0.13 mol einstein^{-1}. Low yields of H_2 are also produced in the absence of Co^{2+}. The latter system is discussed first.

Table I. Quantum Yields for Hydrogen Formation at 450 ± 20 nm and 25 °C[a,b]

pH	10^3[bpy], M	10^3[Co(II)], M	Φ_{H_2},[c] mol einstein^{-1}
3.5			3×10^{-4} [d]
4.1			2×10^{-4} [d]
5.0			0.7×10^{-4} [d]
6.0			0.4×10^{-4} [d]
3.5	4.0		$\sim 0.4 \times 10^{-6}$
5.0	4.0		$\sim 0.4 \times 10^{-6}$
5.0	0.0	2.0	0.5×10^{-2} [e]
5.0	0.2	2.0	1.0×10^{-2}
5.0	0.4	2.0	1.8×10^{-2}
5.0	0.7	2.0	1.5×10^{-2}
5.0	2.0	2.0	0.6×10^{-2}
5.0	0.0	10.0	0.6×10^{-2} [e]
5.0	0.2	10.0	1.3×10^{-2}
5.0	0.4	10.0	2.4×10^{-2}
5.0	0.7	10.0	2.7×10^{-2}
5.0	2.0	10.0	2.0×10^{-2}
5.0	2.2[f]	10.0	13×10^{-2}

[a] The $Ru(bpy)_3^{2+}$ and total ascorbate concentrations were 5×10^{-4} and 0.7 M, respectively, and the light intensity was (3–5) × 10^{-7} einstein s^{-1}. Photolysis times were typically 1–3 h. [b] The observed quantum yields were corrected for the fraction of $^*Ru(bpy)_3^{2+}$ quenched by HA^- ($K_{SV} = 12$ M^{-1}) and the fraction of light absorbed by $Ru(bpy)_3^{2+}$. The hydrogen was determined by gas chromatography and also volumetrically.[9] [c] Unless otherwise noted, the quantum yields were calculated from the rates of hydrogen evolution immediately after the end of an induction period which was 2–5 min in the presence of added bpy and Co^{2+}. [d] These quantum yields were calculated by dividing the total number of moles of H_2 produced by the number of photons absorbed during the photolysis time (~2.5 h) minus the induction period (~0.5 h). [e] In contrast to the solutions that contained both added bpy and Co^{2+}, the induction period for these systems was ~45 min. [f] In this case 4,4′-$(CH_3)_2$bpy was added instead of bpy. When the photolysis was performed in D_2O the gas formed was more than 90% D_2.

Previous studies[13,14] have shown that the main reactions occurring in the $Ru(bpy)_3^{2+}$–ascorbate system under flash-photolysis conditions are

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} {}^*Ru(bpy)_3^{2+}$$

$$^*Ru(bpy)_3^{2+} + HA^- \xrightarrow{k_q} Ru(bpy)_3^{+} + HA\cdot$$

$$HA\cdot \rightarrow H^+ + A^{-}\cdot$$

$$Ru(bpy)_3^{+} + A^{-}\cdot \xrightarrow{k_t} Ru(bpy)_3^{2+} + A^{2-}$$

$$H^+ + A^{2-} \rightarrow HA^-$$

where HA^- is the ascorbate ion, HA· is the protonated ascorbate

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