mg, $5.32 \times 10^{-5}$ mol) was diluted to 100 mL in a volumetric flask with dichloromethane, and 0.98 mL ($5.21 \times 10^{-7}$ mol of **11**) of this solution was syringed into the 1.2-cm o.d. perpendicular compartment. The dichloromethane was evaporated with a stream of nitrogen. A 0.30-mL sample of a methanol solution $1.73 \times 10^{-3}$ M in aclacinomycin A ($5.19 \times 10^{-7}$ mol) and $4.0 \times 10^{-2}$ M in Trizma buffer ($2.0 \times 10^{-2}$ M in each Tris and Tris·HCl) was syringed into the second 1.2-cm o.d. compartment. The methanol solution was freeze–thaw degassed and sealed. After temperature equilibration of the methanol solution at 0 °C for 5 min, the solution was mixed at 0 °C with the *dl* dimer **11** by shaking in an ice water bath for 2 min. The sample was then placed in the EPR cavity maintained at 1 °C. The spectrum obtained is shown in Figure 4. Under these conditions the signal persisted for at least an hour.

**Spectroscopic Monitoring of the Reaction of Aclacinomycin A with *dl* Dimer 11.** A two-compartment cell was used consisting of a 1-cm Beckman, Pyrex cuvette fused to a degassing chamber 1.6 cm o.d. × 4.5 cm long and a 0.9-cm o.d. tube for attachment to a vacuum line with an Ultra Torr Union. The angles between the cuvette and the 0.9-cm tube and 1.6-cm chamber were 90° and 120°, respectively. The 120° angle is necessary to prevent concentration changes resulting from solvent distillation in the cell during the course of the reaction. Aclacinomycin A (8.2 mg, $1.01 \times 10^{-5}$ mol), Tris (12.1 mg, $1.0 \times 10^{-4}$ mol), and Tris·HCl (15.8 mg, $1.0 \times 10^{-4}$ mol) were dissolved in 50 mL of methanol in a volumetric flask by magnetic stirring for 2 h. *dl* Dimer **11** (8.8 mg, $3.10 \times 10^{-5}$ mol) was dissolved in 5.0 mL of methylene chloride. A syringe was used to transfer 0.82 mL ($5.08 \times 10^{-6}$ mol) of the methylene chloride solution to the cuvette compartment of the cell. The methylene chloride was evaporated with a stream of nitrogen. An aliquot of the aclacinomycin A solution (2.5 mL, $5.05 \times 10^{-7}$ mol) was added to the 1.6-cm chamber. The methanol solution was freeze–thaw degassed and the apparatus sealed. The cell was then transferred to a thermostated cell holder at 24.6 ± 0.1 °C. The cell holder consisted of an aluminum block milled to accomodate the entire apparatus and connected to a refrigerated circulator. The thermostated cell holder replaced the standard cell holder of the Hewlett Packard 8450A spectrometer. The methanol solution was temperature equilibrated at 24.6 ± 0.1 °C for 20 min by placing the cell holder at 90° to its normal position. The *dl* dimer **11** and the aclacinomycin A solution were then rapidly mixed by shaking the cell holder vigorously. The absorbance of the solution from 330 to 700 nm as a function of time was recorded as shown in Figures 1 and 2. After 24 h the spectrum showed only the anthraquinone chromophore and appeared similar to the spectrum at time 0. An identical reaction solution gave the absorbance change at 600 nm vs. time as shown in Figure 3. The reaction was monitored at 600 nm because only the tautomer of 7-deoxyaklavinone absorbed significantly at this wavelength. The decay in the absorbance at 600 nm over the time period 80–700 s fits perfectly to a combined first- and second-order kinetic expression, using a nonlinear least-squares fitting procedure.

**Yields of 8 and 9 as a Function of Reactant Concentrations.** Two compartment cells were charged and freeze–thaw degassed as described above to give methanol solutions with the concentrations of aclacinomycin A and *dl* dimer **11** indicated in Table I buffered with a 1:1 mixture of Tris and Tris·HCl. Upon mixing, the solutions, except one, were allowed to react at ambient temperature for 24 h. One reaction was terminated after 11 min by opening to oxygen. The solutions were analyzed for **8** and **9** by HPLC with a 0.30 × 0.04 m Alltech RSIL-phenyl column eluting with 3% water–97% methanol at 2.0 mL/min, detecting at 438 nm. The analytical method was calibrated with standard solutions. The yields of **12** and **13** were determined by GLC using a 3.7 m × 0.32 cm SE-30 on 100/120 mesh high-performance Chromosorb W column at 130 °C eluting with helium at 25 mL/min. The concentrations of **12** and **13** from the reaction mixture $2.9 \times 10^{-4}$ M in **7** and $2.9 \times 10^{-3}$ M in **11** were (3.0 ± 0.1) × $10^{-3}$ M and (2.7 ± 0.1) × $10^{-3}$ M, respectively, determined relative to standard solutions. Formation of **12** and **13** was also verified by $^1$H NMR spectroscopy.

7-Deoxyaklavinone (**8**) and bi(7-deoxyaklavinon-7-yl) (**9**) were isolated from two reactions run similarly. The products were separated by flash chromatography[19] on a 1.0-cm o.d. column packed with 15 cm of Merck silica gel 60 (40–63 μm) and eluted at a flow rate of 5 cm/min with 1.8% methanol–98.2% methylene chloride. The products were identified as **8** and **9** by comparison of $^1$H NMR spectral data with data in the literature.[13]

**Reductive Cleavage of Bi(7-deoxyalklavinon-7-yl) (9).** A two-compartment cell was charged and freeze–thaw degassed as described above to give a methanol solution $5.1 \times 10^{-5}$ M in **9**, $1.9 \times 10^{-4}$ M in *dl* dimer **11**, $4.0 \times 10^{-3}$ M in Tris, and $4.0 \times 10^{-3}$ M in Tris·HCl. Upon mixing, the solution was allowed to react at ambient temperature for 24 h. Spectroscopic monitoring showed formation of the hydroquinone chromophore characterized by absorption at 408 nm over the time period 0–180 s. After 24 h the characteristic quinone absorption had reappeared. HPLC analysis as described above indicated that the solution contained $4.1 \times 10^{-5}$ M 7-deoxyaklavinone (**8**) and $3.1 \times 10^{-5}$ M bi(7-deoxyaklavinon-7-yl) (**9**). GLC analysis using the condition described above indicated that the concentration of **12** was $2.9 \times 10^{-4}$ M and the concentration of **13** $0.87 \times 10^{-4}$ M.

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# On the Structure of Micelles

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**Abstract:** Kinetic studies of micellar olefin oxidation by permanganate ion show that a terminal olefin is oxidized 2 orders of magnitude faster than internal olefins. This is interpreted in terms of coiling and disorder which place chain termini in the water-rich Stern region. The results are not consistent with the Dill–Flory and Fromherz models.

Several years ago Breslow et al.[1] reported that the photolysis of benzophenone-4-carboxylate in SDS or CTAB micelles leads predominantly to oxygen insertion at the terminal methylene of the surfactant tails. As much as 27% of the functionalization occurs at C-11 of SDS. We interpret this observation as evidence for micelle looping and disorder which bring into proximity the chain termini and carbonyls near the micelle surface (where the anionic benzophenone certainly resides[2]). The word "disorder" signifies here a nonradial positioning of the chains as would occur, for example, in a "brush-heap" configuration.[3] Unfortunately, the photolysis experiments required large amounts of benzo-

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Table I. Rate Constants for Permanganate Oxidations of Double Bonds in Several Monomeric and Micellar Olefins[a]

| run | olefin | surfactant | structure | $k_2$, $M^{-1}$ $s^{-1}$ |
|---|---|---|---|---|
| | | Monomeric | | |
| 1 | *trans*-3-hexenoic acid | | $CH_3CH_2CH=CHCH_2COOH$ | 490 |
| 2 | *cis*-3-hexenoic acid | | $CH_3CH_2CH=CHCH_2COOH$ | 440 |
| 3 | 4-pentenoic acid | | $CH_2=CHCH_2CH_2COOH$ | 220 |
| 4 | cyclohexene | | | 330 |
| 5 | 4-pentenoic acid (50:50 $CH_3CN/H_2O$) | | $CH_2=CHCH_2CH_2COOH$ | 5.6 |
| | | Micellar | | |
| 6 | *trans*-3-hexenoic acid | SDS | $CH_3CH_2CH=CHCH_2COOH$ | 540 |
| 7 | 11-undecylenic acid | SDS | $CH_2=CH(CH_2)_8COOH$ | 250 |
| | | Myr | | 204 |
| 8 | *cis*-palmitoleic acid | SDS | $CH_3(CH_2)_5CH=CH(CH_2)_7COOH$ | 6.3 |
| 9 | oleic acid | SDS | $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ | 1.6 |
| | | Myr | | 1.5 |
| 10 | *cis*-vaccenic acid | SDS | $CH_3(CH_2)_4CH=CH(CH_2)_7COOH$ | 1.4 |
| 11 | cyclohexene | SDS | | 70 |

[a] Runs with sodium dodecyl sulfate (SDS) as the carrier surfactant were carried out in water at 25.0 °C with 0.01 N NaOH and 0.20 N NaCl. Run 5 contained 50% (v/v) $CH_3CN$. Runs with potassium myristate (Myr) as the carrier surfactant were carried out in water at 25.0 °C with 0.01 N KOH but no NaCl. Surfactant concentrations were 0.040 N in all cases.

phenone (SDS/ketone = 2). As Breslow et al. fully appreciated, this exacerbated the ever-present concern that the probe modifies the environment upon which it is supposed to report.[4]

We have recently investigated coiling, disorder, and water content in micelles using "inoffensive" probes attached directly to the surfactant chains as in the keto-surfactant below:[5]

$$CH_3(CH_2)_7C(=O)(CH_2)_7N(CH_3)_3^+$$

The carbonyl probe is small and relatively nondisruptive; its "primary" position is fixed relative to the other chain atoms. Solvent-sensitive $^{13}C$ chemical shifts indicated that the carbonyl experiences a polar medium within the micelle. Yet even the carbonyl is subject to the criticism that it might "drag" water into a normally dry region or perturb, in some other manner, the micelle structure. Indeed, the possible shortcomings of the carbonyl probe may be easier to articulate than those of modern probes whose elaborate structures defy analysis. For this reason we examined another type of probe, which seemed even less perturbing than the carbonyl: the acetylenic unit.[6] Both ≡CH/≡CD exchange data and solvent-sensitive ≡CH chemical shifts disclosed considerable contact between water and the terminal proton of the surfactants below:

$$HC{\equiv}CCD_2(CH_2)_{10}N(CH_3)_3^+ \qquad HC{\equiv}CCD_2(CH_2)_{10}OSO_3^-$$

The present paper describes an olefinic probe whose behavior confirms the notion that chain termini spend a considerable amount of time in a hydrophilic micellar environment. In addition, the experiments compare the water exposure at various sites along the surfactant tail. These results permit us to discriminate between three divergent theories of micellar structure devised by Dill–Flory,[7] Fromherz,[8] and ourselves.[3]

Micellar olefins were oxidized with potassium permanganate in water at 25.0 °C and pH 12. Several features of this system seemed attractive: (1) Oxidation of olefins to glycols under basic conditions is a high-yield reaction.[9,10] (2) Since permanganate has an intense absorption at 545 nm, only minute levels are required to follow the oxidation spectrophotometrically. Thus, most runs used $2 \times 10^{-5}$ M permanganate along with a 10–500-fold excess of micellar olefin. Reactions were cleanly pseudo first order under these conditions. (3) Oxidation by permanganate, a monoanion, must take place in an aqueous or partially aqueous medium. Permanganate should not react with a double bond immersed in the close-packed hydrocarbon core of a classical micelle. (4) Fatty acid surfactants with double bonds positioned at various sites along the chain (e.g., 11-undecylenic acid and oleic acid) are commercially available so that we could readily examine olefinic reactivity as a function of "primary" location. (5) The double bond is a small, apolar functionality prevalent in naturally occurring surfactants. Perturbations should be minimal.

## Experimental Section

A typical kinetic run was carried out in the following manner. A stock solution of 0.040 M sodium dodecyl sulfate (SDS) was prepared in water containing 0.010 N NaOH and 0.20 M NaCl. Oleic acid was weighed into a 10-mL volumetric flask, and stock was added to the mark giving a $7.8 \times 10^{-3}$ M solution of olefinic surfactant. This was then serially diluted with stock SDS. Thus, working solutions contained 0.040 M SDS but varying concentrations oleic acid anion. A 1.00-cm cuvette containing 3.00 mL of one of these solutions was placed in the chamber of a Cary 14 spectrophotometer thermostated at 25.0 ± 0.1 °C for 10 min or longer. The Cary had been set at a wavelength of 545 nm and equipped with a 0.1-mm slidewire. A small aliquot (25 μL) of an aqueous solution of $KMnO_4$ was then added with rapid stirring to the cuvette such that the initial permanganate concentration approximated $2 \times 10^{-5}$ M. The decrease in absorbance[11] (resulting from olefin oxidation and concomitant permanganate conversion to $Mn(OH)_2$) was traced as a function of time until at least eight half-lives had transpired. Six to ten olefin concentrations were used with frequent repeat runs. Observed pseudo-first-order rate constants were linearly related to the olefin concentration. The slopes of the plots provided second-order rate constants. Runs with undecylenic acid were carried out 3 times over several weeks, and the rate constants all agreed.

The above procedure belies the experimental difficulties, which were severe. We observed a considerable background reaction (10–30% of the total) with SDS stock solution containing no olefin even though the SDS had been purified (twice recrystallized from ethanol and leached once with refluxing ether).[12] This background reaction (perhaps caused by traces of dodecyl alcohol in the SDS) was subtracted from the total observed rate. Interestingly, we found that we could not use commercial standardized 0.01 N NaOH owing to an impurity that reduced $KMnO_4$. All solutions were made fresh on the day of the kinetic runs with water that had been deionized, passed through activated charcoal, and then finally distilled over $KMnO_4$. The olefinic surfactants were Sigma materials of satisfactory quality judging from NMR spectra. Purified and unpurified undecylenic acid (the key substrate in this study) gave the same rate constants. Fortunately, the rate constants did not appear sensitive to degassing, small variations in NaOH concentrations, or the commercial source of the $KMnO_4$. Achieving suitable reaction conditions was, however, a problem. In some cases (e.g., *trans*-3-hexenoic acid) oxidations were so fast that we could not study as wide a concentration range as we might have liked. In other cases (e.g., oleic acid) the reactions were slow, thereby accentuating the importance of the back-

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ground interference. These difficulties resulted in an uncertainty in the rate constants of perhaps ±15%. Since the rate constants for different olefinic substrates varied over a range of $10^2$, the experimental error is not serious.

**Results**

Rate constants for permanganate oxidation of double bonds in several monomeric and micellar olefins are presented in Table I. It is seen that monomeric olefins (i.e., aqueous olefins with no added surfactant) oxidize rapidly relative to certain micellar systems. Disubstituted olefins (runs 1 and 2) react twice as fast as a monosubstituted olefin (run 3) in accordance with the known effect of alkyl substitution on olefin oxidizeability.[13] Runs 3 and 5 show that the oxidation is sensitive to solvent polarity; the presence of 50% acetonitrile in the water reduces the rate by a factor of 40.

Addition of surfactant (SDS or myristate) has either no effect on the oxidation rate (runs 6 and 7) or a large effect equal to 2 orders of magnitude (runs 8, 9, and 10) depending on the structure of the olefin. Before attempting to interpret this surprising rate behavior, we must first consider an important question: To what extent are the substrates incorporated into the micelles? Note first that the critical micelle concentration (CMC) of SDS in 0.20 M in NaCl is $6.6 \times 10^{-4}$ M (as determined by the surface tension method). We purposely added large amounts of salts to lower the CMC and thereby reduce the amount of nonmicellized surfactant in solution. (Micelle size is only modestly affected by the salt).[14] If we now make the usual assumption that the concentration of monomeric surfactants equals the CMC, then only 1.5% of the 0.040 M SDS used throughout our experiments exists in the monomeric state. If we assume further that micelles do not differentiate between SDS and the substrate surfactants used in Table I, then roughly 98.5% of the substrates must be micelle bound. Although 98.5% is obviously an approximation, it is clear that the vast majority of substrate molecules are micellized in the excess SDS; to assume otherwise would require a selectivity among surfactants unprecedented in the micelle literature.

Substrate binding can be discussed from a somewhat different point of view. Solubilizates with long hydrocarbon chains, such as the substrates in Table I, bind to micelles with extremely large association constants. For example, Almgren and Swarup[15] have recently shown that octanoic acid (0.088 M) is 100% bound to 0.135 M SDS. Since our experiments used much higher SDS to fatty acid ratios, complete binding seems a certainty. Note that the very properties that make our olefin system so appealing (innocuousness; low concentration) also make it difficult to observe binding by traditional spectrometric techniques.

Fortunately, we need not rely on intuition and precedent to substantiate micellar binding of the fatty acids; we can prove it using the newly developed Armstrong method.[16] Undecylenate was chromatographed on Brinkmann Polygram Polyamide-6 sheets with SDS in aqueous base as the mobile phase. The thin-layer chromatograms were then developed with aqueous $KMnO_4$ to give a yellow spot (on a purple background) corresponding to the olfein. By measuring $R_f$ values as a function of SDS concentration, one can determine the partition coefficient of the fatty acid anion between micelle and water ($K_{MW}$). This $K_{MW}$ for undecylenate equals $2 \times 10^4$, signifying that less than 1% of the undecylenate lies outside the micelle under kinetic conditions (0.040 M SDS). Thus, SDS micelles seem unable to discriminate between SDS and undecylenate within the sensitivity of the method.

By far the most interesting conclusion from Table I relates to the different micellar reactivity of a terminal double bond (11-undecylenic acid in run 7) and internal double bonds (*cis*-palmitoleic acid, oleic acid, and *cis*-vaccenic acid in runs 8, 9, and 10). The former oxidizes at a rate similar to that of the monomeric state (run 7 vs. run 3), whereas the latter are 2 orders of magnitude slower. The difference is seen in both SDS and myristate micelles. How can these data be reconciled with current micellar theory?

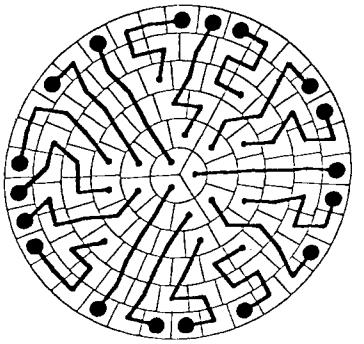

**Figure 1.** Dill–Flory lattice model representation.[7] Note that the micelle has a "crystalline" interior, an absence of looping, a completely radial distribution of chains, and a smooth spherical surface on which the ionic head groups are confined. No evidence exists for any of these attributes.

**Discussion**

Several years have passed since we first advanced a micelle model[3] at variance with the "oil droplet in an ionic coat" picture attributed to Hartley. Perhaps the gods (even the Norse gods who apparently scorn the departure from old[17]) will forgive us if we, for the sake of brevity, refer to the model as the "Menger micelle". It must be added quickly that the work of many others (deMayo,[18] Rosenholm,[19,20] Whitten,[21] Zachariasse,[22] etc.) contributed to the formulation. The important thing is not the name but the concept. Menger micelles have a central hydrophobic core; this is surrounded by a much larger region composed of hydrocarbon, water, head groups, and counterions. Disorganization is rampant, and the surface is rough. Chemists speak of "degree of water penetration", but this is not really a precise phrase in the context of a Menger micelle. Penetration is deep in the sense that the core, as we see in the next paragraph, is relatively small in volume.

Consider the works of Zana,[23] one of the most outspoken opponents of the Menger micelle: "These results also suggest a thickness of the palisade layer of about 4 Å which is penetrated by water and where the environment ... would not be too different from that of bulk water". Assume for the moment that this statement is correct. Simple volume calculations would then demand that fully 69% of an SDS micelle (*not* counting head groups) is water-like![24]

One main attribute of the Menger micelle is that it explains why the vast majority of probes, even hydrocarbon-soluble ones, reveal aqueous micellar environments. The probes bind within the Stern region onto chain segments lying outside the core in a watery milieu. Since micellar water is released in the process, the binding constitutes a typical hydrophobic association. Binding sites within the Stern region could include protruding chains, "fatty patches", and clefts in the rough periphery.[25] Whether or not the probes reside at the micelle "surface" depends strictly on the definition of "surface". Unquestionably, however, the probes are

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(24) Note that Zana uses the term "palisade layer", which has been creeping into the literature more and more. Webster defines a palisade as a "fence of stakes" implying a parallel array of posts. There exists absolutely no evidence that micelles possess either a discrete layer or a region of parallel chains. To avoid confusion (not unlike that created by the "asterisk" micelle picture), it would be best to abandon "palisade layer" and replace it with "Stern region" as suggested years ago.[3]
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situated in a voluminous domain, surrounding the core, where water pervades the spaces not occupied by surfactant.

We cannot delineate all the experimental evidence that has amassed, here and elsewhere, in support of the Menger micelle; this is best reserved for reviews.[26] Instead, we with to focus on a single question: Are our olefin oxidation data in Table I consistent with the Dill–Flory[7] and Fromherz[8] micelle models? In order to properly address this question, it is vital to understand clearly the properties of the two models beginning first with the Dill–Flory lattice representation (Figure 1).[7] Its main features include (1) a smooth spherical surface in which the head groups are packed as close to each other as are the chains, (2) a core center with a "degree of order approaching that in a crystal",[7] (3) little terminal methyl exposure to water when the chains are long but considerable exposure when the chains are short. This third property brings up an extremely important point. Figure 1 (based on the widely reproduced Figure 1b of the original Dill–Flory article) obviously manifests little or no water contact with chain termini. But this particular Dill–Flory picture represents a *cross section of an infinitely long cylinder with chains of approximately 22 carbons*! Under these circumstances, the Dill–Flory theory predicts little terminal exposure. On the other hand, with spherical micelles of 14-carbon chains (for which, regrettably, no schematic diagram was supplied), nearly 25% of the termini are exposed to water. Indeed the Dill–Flory work was among the first of the quantitative models to predict terminal group exposure. Unfortunately, others are using Figure 1 to interpret the behavior of short-chain surfactants (e.g., SDS and DTAB), which are irrelevant to the diagram. Thus, Chen and co-workers[27] related SANS data on lithium dodecyl sulfate to the inappropriate Dill–Flory diagram and concluded (in contradiction with a host of other studies) that "water penetrates the hydrocarbon core at most to the level of the first $CH_2$ group attached to the sulfate group".

The data in Table I prove that the chain termini are exposed to water a large proportion of their lifetime in micelles. Thus, the terminal double bond of 11-undecylenic acid in both SDS and myristate micelles oxidize at a rate similar to that of monomer in water (runs 4 and 7). Since our oxidizing agent is ionic and completely insoluble in hydrocarbons, a double bond would be inert were it buried in a Hartley "oil droplet". As seen from run 5, even the addition of 50% organic solvent to water reduces the monomeric rate 40-fold. Clearly, the terminal double bond of 11-undecylenate experiences an environment not too different from bulk water. These results cannot be reconciled with Figure 1, reaffirming our remarks that Figure 1 is not germane to the small micelles with which most chemists work.

The olefin oxidation data agree with our acetylenic probe work[6] mentioned in the introduction. With the olefin system, we used inoffensively labeled surfactants comicellized with conventional surfactants (SDS or myristate); in the acetylenic probe work, the *entire* micelle was composed of labeled surfactant. The latter exhibited perfectly normal colloidal behavior (e.g., CMC), which would not have been the case if the acetylenic surfactant were excessively coiled over and beyond the usual situation. Our data (along with those of Breslow[1]) thus lead *collectively* to an important conclusion: Chain bending and micelle disorder place the majority of termini outside the micelle core and within the water-rich Stern region. Stated somewhat differently, the micelle core (with much less than half the total micellar volume) contains mainly internal chain segments.

We now arrive at a serious discrepancy between the Dill–Flory micelle and our results. Dill–Flory theory assumes the total absence of chain reversals ("looping"). Partly as a result of this dubious assumption, the theory predicts that the chain termini should be *less* wet than more centrally located carbons. This conflicts with Table I, which shows a striking difference in the

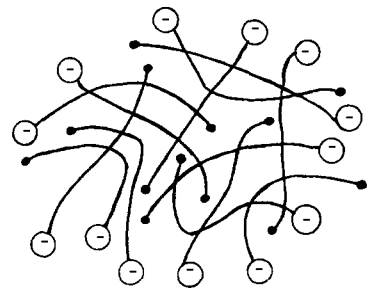


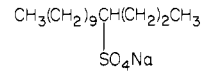
**Figure 2.** Schematic drawing of a micelle embodying many features absent in Figure 1 such as rough surface, water-filled pockets, looping, nonradial distribution of chains, and random distribution of terminal methyls. Whereas the Dill–Flory micelle possesses a core center with a "degree of order approachin that in a crystal",[7] the above model is loose and disordered and fluctuant.

micellar oxidation rates between internal double bonds (runs 8–10) and a terminal one (run 7). Although the "primary" position of the double bonds in the various surfactants are similar, the internal olefins react *2 orders of magnitude* slower. Internal micellar olefins oxidize roughly at the same rate as monomer in 50% acetonitrile–water (run 5), and it might be concluded that the time-average environment resembles such a mixture in polarity.[28] We do not want to push this comparison too far, however, because the rates of runs 8–10 are sufficiently slow that traces of monomeric surfactant could be contributing to the observed rates. All that can be stated with certainty is that internal olefin is *less* exposed to water than is the thoroughly wet terminal olefin. The simplest explanation is that the Dill–Flory model incorrectly underplays the looping and disorder in a micelle both of which would tend to place termini near the water relative to internal carbons (Figure 2). Figure 2 embodies the main characteristics of the Menger micelle: a large wet Stern region, rough surface, looping, and disorder (i.e., nonradially distributed chains).

No claim is made here that our olefins and the micellar hydrocarbon mix ideally. We have, however, attempted to minimize the impact of micellar perturbation of (1) using the small and nonpolar double bond as our probe (as opposed to the massive, multifunctional probes common with studies based on NMR, ESR, fluorescence, etc.) and (2) comparing the behavior of two types of double bonds whose nonideality should be similar. It is concluded from the *difference* in double-bond behavior within the micelles that chain termini are randomly distributed throughout the micellar volume. Since the great proportion of the micellar volume contains water (defined as the Stern region), chain termi experience considerable water contact.

Micellar radii are known to *exceed* the length of a fully extended chain plus head group.[15] This curious observation can be accommodated by a loosely packed and disordered micelle in possession of rough surfaces. Water fills the irregularities, thereby accounting for the aqueous environment experienced by the chain termini and by most of the micellized probes described in the literature.

The Fromherz micelle[8] is the antithesis of the Menger micelle; whereas the latter is disordered, the former is a low-entropy aggregate with an almost crystalline appearance. Fromherz constructed his model by placing blocks of two or three monomers (a totally arbitrarily selected number) into a cuboid structure following a series of equally arbitrary "block assembly" rules. As with the Dill–Flory micelle, chain reversals are not permitted, the model being built with linear wooden rods. Although this is not the place to discuss the virtues and faults of the Fromherz micelle in detail, there are two points worth making. First, a series of tetradecyl sulfates were studied in which the position of the sulfate group was moved one by one toward the center of the chain, e.g.:[29]

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(28) This would agree with the data in ref 5.

Micelles form readily with such branched surfactants in line with the "loose" Menger micelle. It is not clear, however, how branched surfactants would ever be able to form Fromherz micelles with their rigid parallel chains. The second point relates to the data in Table I. The Fromherz micelle can in no way accommodate our observation that chain termini are randomly distributed throughout the micelle. In summary, we must warn chemists (as was done about 50 years ago with regard to the Hartley micelle[30]) to view the Dill-Flory and Fromherz micelles for what they are: useful, perhaps ingenious, models that must not be taken literally with anionic micelles of small radii.[31]

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**Registry No.** $KMnO_4$, 7722-64-7; *trans*-$CH_3CH_2CH$=$CHCH_2COOH$, 1577-18-0; *cis*-$CH_3CH_2CH$=$CHCH_2COOH$, 1775-43-5; $CH_2$=$CHCH_2CH_2COOH$, 591-80-0; $CH_2$=$CH(CH_2)_8COOH$, 112-38-9; *cis*-$CH_3(CH_2)_5CH$=$CH(CH_2)_7COOH$, 373-49-9; *cis*-$CH_3$-$(CH_2)_7CH$=$CH(CH_2)_7COOH$, 112-80-1; *cis*-$CH_3(CH_2)_4CH$=$CH$-$(CH_2)_7COOH$, 506-17-2; SDS, 151-21-3; Myr, 13429-27-1; cyclohexene, 110-83-8; permanganate, 14333-13-2.

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(30) Hartley, G. S. "Aqueous Solutions of Paraffin-chain Salts: A Study in Micelle Formation"; Paris, Hermann and Co.: London, 1936; p 44.
(31) **Note Added in Proof**: A recent article entitled The Effect of a Terminal Double Bond on the Micellization of a Simple Ionic Surfactant concludes that a "terminal double bond does not display a significant tendency to act as a second headgroup". See: Spragne, E. D.; Dneker, D. C.; Larrabee, C. E. *J. Colloid Interface Sci.* **1983**, *92*, 416.

# Variation of Steric Effects in Metal Ion Catalyzed Proton Transfer. A Probe of Transition-State Structure

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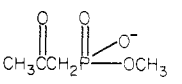
**Abstract:** The enolization of methyl 2-oxo-1-phosphonopropane (methyl acetonylphosphonate, MAcP) is catalyzed by pyridine bases in water. The catalysis is enhanced by dissolved magnesium ion or manganese ion. It is known that the metals form complexes via the phosphonate functional group of the substrate but promote catalysis by coordination to the carbonyl group. The rate of enolization is first order in substrate concentration and Brønsted base concentration. The rate is first order in metal ion concentration at low concentrations, changing to zero-order dependence (saturation) at higher levels. This saturation is used to obtain association constants: 33 $M^{-1}$ (MAcP and magnesium ion), 7.5 $M^{-1}$ (MAcP and manganese ion). The slope of the Brønsted plot for catalysis by unhindered pyridine bases in the absence of divalent metal ions is 0.69. The slope is 0.63 for reactions of the magnesium complex of MAcP and 0.82 for the manganese complex. The increase in slope with manganese catalysis appears to be inconsistent with the expectation from the reactivity-selectivity principle that acidification of the substrate will lead to an earlier transition state. Steric effects give further information about the catalytic systems. The rate constant for 2,6-lutidine falls on the Brønsted line for the manganese complex of MAcP but is a factor of 36 below the line in the uncomplexed case. The effect in the magnesium case is reduced to an intermediate value. This decreased steric effect suggests that the proton transfer transition state in the presence of the metal ions is significantly different from that in the absence of metal. It is proposed that coordination to divalent metal ions may provide a route by which a coordinated water molecule serves as a proton carrier for the very hindered base. These results show that steric effects are a valuable adjunct to Brønsted plots in multiple catalytic systems.

The conversion of a carbonyl compound to the corresponding enol is an important part of many complex organic and biological reactions. Mechanisms by which the reaction can be catalyzed by Brønsted acids and bases have been studied extensively.[1] In many biological systems, enolization is also promoted by metal ions which appear to act as catalysts by functioning as Lewis acids in conjunction with a Brønsted base.[2-5] This catalysis involves coordination of the metal ion to the carbonyl group during the step in which a proton is removed from the adjacent carbon atom by the Brønsted base or an intervening water molecule. Cox has recognized that the mechanism is analogous to that of the general acid catalyzed enolization of ketones involving a specific acid-general base mechanism.[6,7]



MAcP

We previously have studied examples of metal—catalyzed enolization reactions and have established the basic kinetic patterns of the combined metal ion-Brønsted base catalytic system.[8,9] In those studies we have used the monomethyl ester of acetonylphosphonic acid (MAcP) as a substrate for studies of the enolization reaction.[10] The phosphonate monoester functional group serves as a binding site for divalent metal ions which can serve as catalysts for reactions at the nearby carbonyl group (by a minor change in coordination).[2] This stabilizes an incipient enolate that is formed during the course of a reaction. The catalytic function of the metal ion also includes an electrostatic component in which a positively charged metal catalyst minimizes repulsions between reacting anions.[9]

It has been shown by Feather and Gold[11] and by Covitz and

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