Electrophilic Bromination of Micelle-Associated Alkenes as a Probe of Micelle Structure

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Abstract: The products and kinetics have been examined for the bromination in aqueous micelles of a series of unsaturated fatty acids, esters, and alcohols. A limited kinetic study of mercuration in SDS micelles is also reported. Bromination products are the following: CTAB micelles, 100% dibromide; CTAC, principally α-bromochloride, with some bromohydrin and trace dibromide; SDS, a 2:1 mixture of bromohydrin and a bromosulfate ester derived from reaction with the headgroup of the micelle. These products are formed stereospecifically anti, and there is no significant dependence on the original position or geometry of the double bond. The bromination kinetic studies, carried out in SDS, Brij-35, and CTAB micelles, reveal considerably slower rates as compared to those in water and, in contrast to homogeneous media, sensitivities to the double bond position, its geometry and the presence of other unsaturated chains, and an enhanced terminal alkene reactivity. A dependency on micelle charge type and added salts is also observed. Both products and kinetics support a mechanism where the bromonium ion intermediate is formed and trapped in a relatively polar region of the micelle, intimately associated with the headgroup and its counterions. A model, the segment protrusion model, is proposed in which the double bond enters the "reactive" region by protrusion of a chain segment from the relatively nonpolar hydrocarbon region. The rate of reaction is determined by the absolute rate in this region, which is large, offset by the probability of the double bond being found there, which is small. The fraction of double bonds in a reactive state is determined by two factors: the probability that the chain segment containing the double bond will reach an interfacial location and the free energy cost of solubilizing a chain segment in a polar environment. This model is examined in the context of other recent experimentally and theoretically based models of micelles.

The modification of chemical reactions by incorporation of the reagent molecules into aqueous micelles and other organized assemblies has received considerable investigation.[1-4] Examples have been found where rates, products, and even stereochemistry have been significantly affected. Attention has naturally also focussed on a detailed understanding of such effects. Central concerns here are the structures of the organized assemblies themselves, the nature of their interaction with guest reagent molecules, the nature of the environment ("microenvironment") experienced by the guest molecule, and the nature and location of transition states of reactions occurring within.

In this paper we present an analysis of SDS (anionic), Brij-35 (neutral), and CTAB and CTAC (cationic) micellar systems based upon the bromination of micelle-associated unsaturated amphiphiles. As a class of reactions electrophilic alkene additions have been extensively studied and, particularly for bromination, a reasonable understanding has emerged of the mechanistic behavior in homogeneous solutions.[5-7] These reactions exhibit properties which make them excellent candidates as probes of micellar influence, since their rates and products are extremely sensitive to conditions. Unsaturated fatty acids, esters and alcohols have been employed as the alkene component, in order to provide a minimal perturbation to the structure of the micelle, if this is possible.[8] These alkenes should also be tightly bound to the micelle, forcing their reaction to occur there (as will be established). A limited study has also been carried out of the kinetics of mercuration in SDS micelles of the same alkenes. Mercuration is mechanistically similar to bromination,[7] but because it is charged the mercuric ion electrophile will have a very different degree of hydrocarbon partitioning when compared to bromine. Thus a comparison of the two systems can become very interesting. The results with the fatty acid alkenes also provide a comparison with those recently reported for micellar bromination of some amphiphilic and hydrophobic stilbenes.[10]

Experimental Section

Surfactants.[10] Sodium dodecylsulfate (**SDS**) (Biorad, electrophoresis grade) was purified by repeated washing with anhydrous ether and was dried and stored in a vacuum desiccator. Cetyltrimethylammonium bromide (CTAB) (Aldrich or Fluka) was purified by the procedure of Duynstee and Grunwald;[11] mp 238 °C dec (lit.[11] mp 237 °C dec). Cetyltrimethylammonium chloride (CTAC) (Eastman) was washed with anhydrous ether and stored in a vacuum desiccator. Poly(oxyethylene) (23) lauryl ether (Brij-35[12]) (Aldrich) was used as received.

Unsaturated Amphiphiles.[10] Table I lists alkenes along with a shorthand notation.[13] Commerical alkenes were used as received and were the highest purity available (>99%). The isomeric purity of the frequently used alkenes was checked by 200-MHz ^{1}H nmr, where the limit of detection of contaminating isomers is about 5%.

Dimethyl (*E*)-13-hexacosendioate was prepared by the metathesis route of Boelhouwer and co-workers.[14] Tetramethyltin (Aldrich) (150 mg, 0.066 mmol) was added under nitrogen to the deep blue dispersion obtained from tungsten(VI) chloride (Alfa) (300 mg, 0.066 mmol) and methyl erucate (Sigma) (13 mL, 33 mmol), and the resultant mixture was heated at 80–85 °C for 3.5 h. After the mixture was cooled, 20 mL of pentane was added, followed by concentrated ammonia. This results in a white colloidal precipitate which was separated by decantation. The yellow pentane layer was dried over $MgSO_4$ and the pentane removed. Two recrystallizations from pentane gave 1.24 g of the desired product; mp 58.5–59.5 °C (lit.[14b] mp 47 °C). Anal. Calcd for $C_{26}H_{46}O_4$; C, 77.78; H, 12.75. Found: C, 77.63; H, 12.72. A critical factor in this

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(8) (a) There has been concern that even apparently innocuous extrinsic probes significantly affect native micellar structure.[8b,c] An alternative view[9] is that from the viewpoint of understanding the chemical reaction in the micelle, it is the structure of micelle–guest complex which is important, not the structure of the empty micelle. (b) Lindman, B.; Wennerstrom, H. *Top. Curr. Chem.* **1980**, *87*, 1–81. (c) Dill, K. A. In *Surfactants in Solution*; Mittal, K. L.; Lindman, B., Eds.; Plenum Press: New York, 1983; Vol. 1, pp 307–320.
(9) Mizutani, T.; Whitten, D. G. *J. Am. Chem. Soc.* **1985**, *107*, 3621.
(10) The term "surfactant" is used for molecules which are integral components of the micelle. The term "unsaturated amphiphile" refers specifically to the alkene.
(11) Duynstee, E. F. J.; Grunwald, E. *J. Am. Chem. Soc.* **1959**, *81*, 4540.
(12) Trademark of ICI Americas.
(13) Because the dialkylalkenes are all 1,2-dialkylethylenes, a cis/trans description is used rather than (*E*)/(*Z*). Note also that the shorthand notation refers to the carboxylic acid, unless otherwise specified.
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0002-7863/86/1508-3771$01.50/0

Table I. Unsaturated Amphiphiles

name	trivial name	abbreviation	supplier
(*Z*)-6-octadecenoic acid	petroselinic acid	18Δ6c	*a*, *b*
(*Z*)-6-octadecen-1-ol	petroselinic alcohol	18Δ6c(OH)	*a*
(*Z*)-9-octadecenoic acid	oleic acid	18Δ9c	*a*
(*Z*)-9-octadecen-1-ol	oleoyl alcohol	18Δ9c(OH)	*a*
methyl (*Z*)-9-octadecanoate	methyl oleate	18Δ9c(Me)	*a*
(*E*)-9-octadecenoic acid	elaidic acid	18Δ9t	*a*
(*E*)-9-octadecen-1-ol	elaidyl alcohol	18Δ9t(OH)	*a*
(*E*)-11-octadecenoic acid	*trans*-vaccenic acid	18Δ11t	*a*
(*Z*)-13-docosenoic acid	erucic acid	20Δ13c	*a*
(*Z*)-13-docosen-1-ol	erucyl alcohol	20Δ13c(OH)	*a*
methyl (*Z*)-13-docosenoate	methyl erucate	20Δ13c(Me)	*a*
(*E*)-13-docosenoic acid	brassidic acid	20Δ13t	*a*
(*Z*)-15-tetracosenoic acid	nervonic acid	24Δ15c	*a*
[(*R*)-(*E*)]-12-hydroxy-9-octadecenoic acid	ricinelaidic acid	18Δ9t(12OH)	*a*
10-undecenoic acid		11Δ10	*c*
16-heptadecenoic acid		17Δ16	*d*
(*Z*,*Z*)-9,12-octadecadienoic acid	linoleic acid		*a*
(*Z*,*Z*,*Z*)-9,12,15-octadecatrienoic acid	linolenic acid		*a*
1-monooleoyl-*rac*-glycerol	monoolein[f]		*a*
dioleoyl-*rac*-glycerol	diolein[g]		*a*
1,2,3-trioleoyl-*rac*-glycerol	triolein		*a*, *c*
dimethyl (*E*)-13-hexacosendioate		26Δ13t(diester)	*e*

[a] Sigma. [b] Serdary Research, London, Canada. [c] Aldrich. [d] Gift from M. A. Winnik. [e] This work. [f] Less than 1% 2-isomer. [g] 85%, 1,3; 15% 1,2.

synthesis was found to be control of over-reaction. A lower alkene catalyst ratio (20:1) or longer reaction time (18 h), as suggested in the literature,[14] led to an intractable dark oil after workup. The drying of both the methyl erucate and the tetramethyltin over 4A molecular sieves was essential for a successful reaction. The assignment of *E* or trans geometry to this compound is tentative, being based only on homogeneous solution reactivities (see Results—Table V).

Solution Preparation. Concentrated stock solutions of the alkenes were prepared in tetrahydrofuran or carbon tetrachloride and stored in the dark at 4 °C. An aliquot of this solution was transferred to a beaker by use of a Gilson micropipet dispenser. The solvent was blown off under a stream of nitrogen, and the alkene was left as a thin film on the beaker bottom. Surfactant solution was then added and the solution was sonicated with a probe-type ultrasonicator (Fisher/Artek, Toronto) at a setting of about 60% for 0.5–1.0 min. Incorporation of the unsaturated amphiphile was deemed complete when no visible turbidity was evident. This solution was allowed to sit for at least 30 min before use. The sonication technique is advantageous since it provided quick dispersal of the water-insoluble alkenes into the micelle, circumventing the need for addition of co-solvents. The procedure also led to high reproducibility in interbatch experiments, especially in kinetic experiments, indicating that the alkene incorporation is uniform.

Products Bromination Method. Conditions were chosen as closely as possible to match those of the kinetic experiments. Alkene concentrations were 1.0–1.5 mM; surfactant concentrations were 20 mM (CTAB), 15 mM (CTAC), and 100 mM (SDS). The alkene/surfactant solution was prepared as described above and a concentrated aqueous bromine solution was added with rapid stirring. The bromine color was discharged instantly until the point of complete alkene consumption, after which a faint yellow persisted. Sodium thiosulfate was added to consume the excess bromine. The presence of $Na_2S_2O_3$ was shown to have no effect on the product composition. Consumption of the excess Br_2, however, improved the stability of the products when they were left for several days.

Product Isolation. SDS.[15,16] Solid calcium chloride (10 g per 250 mL of solution) was added to the solution with stirring, resulting in a white precipitate. This solid contains a mixture of SDS as its calcium salt and the products of alkene bromination which upon precipitation of the micelle are no longer solubilized in the aqueous medium. Complete precipitation was monitored by the addition of a saturated $CaCl_2$ solution to the supernatant. The precipitate was isolated by filtration and air dried. After 30 min of drying, the solid was washed with three 75-mL volumes of hexane to redissolve the bromination products, and the washings were dried over anhydrous $MgSO_4$ or 4A molecular sieves. Filtration and rotary evaporation of the solvent yielded an oily sample (colorless or pale yellow) which was submitted to ^1H NMR analysis.

CTAB–Ion exchange.[15] This method involved the use of a strongly acidic (sulfonate) ion exchange resin (Dowex-50, Sigma) packed in a 25 × 2 cm column. This serves to selectively remove the tetralkylammonium surfactant molecules. The column was initially prepared by elution with 1 M HCl (500 mL) after which the entire reaction mixture (250–500 mL) was added to the column. Elution was repeated six to ten times until there was no indication of surfactant in the eluent. This was monitored by simply observing the ability of the eluent to foam when vigorously shaken. The column was then eluted with 200 mL of methanol followed by 200 mL of ether. The combined organic solvent eluent was reduced in volume by rotary evaporation, dried over $MgSO_4$, filtered, and brought to dryness by further rotary evaporation. The resulting pale yellow oil was submitted to NMR analysis. A variation of this procedure involved stirring the reaction mixture with 25 g of Dowex-50 overnight and following the preceding workup procedure.

CTAB/CTAC Precipitation. This procedure was analogous to that used for SDS. Solid potassium iodide was added to the surfactant/products mixture with stirring. The resulting white precipitate (products and presumably CTAI) was isolated by filtration, air dried, and washed with three 75-mL volumes of hexane. After being dried over $MgSO_4$ or 4A molecular sieves and filtration, the hexane solution was evaporated to dryness, leaving a pale yellow oil which was submitted to NMR analysis. Because of its overall simplicity this procedure was used for the majority of product studies in these micelles.

Product Standards. Bromohydrins.[17] The alkene (0.01 mol) was added to a stirred solution of dimethyl sulfoxide (Me_2SO) under nitrogen. To this solution was added 0.02 mol of distilled water, followed by 0.02 mol of *N*-bromosuccinimide. The solution turned dark orange and evolved heat immediately. After 15 min of stirring, 20 mL of water was added to quench the reaction. The aqueous Me_2SO mixture was extracted with *n*-hexane, the hexane fraction was dried over $MgSO_4$, and the hexane was removed by rotary evaporation. The residual colorless oil was used directly.

Dibromides. Bromine was added dropwise to a rapidly stirred carbon tetrachloride solution (40 mL) containing alkene (0.01 mol). The solution was protected from light by aluminum foil. The bromine was added until a pale coloration persisted, after which stirring was continued for 30 min. Removal of the excess bromine and carbon tetrachloride by rotary evaporation provided a pale yellow oil which was analyzed by ^1H NMR. Both dibromo and bromochloro products (see below) appeared to be unstable, neat samples turning darkly colored on standing. This instability has been noted previously.[18]

α-Bromochlorides.[19] Anhydrous lithium bromide (0.22 g, 0.0025 mol) was added with stirring to carbon tetrachloride (10 mL) followed by antimony pentachloride (0.75 g, 0.0025 mol). The solution immediately developed a dark orange coloration and the lithium bromide appeared to be completely consumed. After 5 min of stirring, alkene (0.01 mol) was added. Water (10 mL) was added after an additional 10 min, a white precipitate was filtered, the CCl_4 fraction was separated and dried ($MgSO_4$), and the solvent was removed by rotary evaporation.

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NMR Analysis. The products of both standard and surfactant-mediated reactions were analyzed by ^1H NMR: 60 MHz, Varian T60; 200 MHz, Varian XL-200; 360 MHz, Nicolet. Samples were dissolved in $CDCl_3$ containing Me_4Si. Chemical shifts are reported relative to Me_4Si in the units of ppm. Relative yields were determined by integration.

Bromination Kinetics. All kinetic runs were performed on a Durrum-Gibson stopped-flow spectrophotometer thermostated at 25.0 ● 0.1 °C. One syringe of this apparatus contained the micellar alkene solution plus acetic acid (0.01 M) while the other syringe contained bromine, a bromide salt (usually LiBr), and 0.01 M HOAc. The acetic acid was present to maintain the pH below 3, and thus suppress formation of HOBr.[20] Accounting for micelle-induced pK_a changes,[21] at this pH the fatty acid alkenes are probably fully protonated in the SDS and Brij micelles but partially deprotonated in the CTAB micelles. Bromine concentrations after mixing were of the order of 10^{-5} M, and pseudo-first-order conditions were maintained by use of at least a tenfold excess of alkene. (Conditions are discussed in detail in the Results section.) The progress of the bromination reaction was followed by monitoring the decrease in absorbance at 270 nm due to the tribromide ion. The stopped-flow apparatus was linked via a digitizing device (Chemistry Department Analytical Services) to a Tektronix 4051 microcomputer. For each individual kinetic run 118 absorbance readings were obtained over a period of time corresponding to 75–90% of the reaction. Pseudo-first-order rate constants, k_{obsd}, were calculated by the infinity method,[22] as the slopes of plots of ln $(A - A_\infty)$ vs. time, where A_∞ was the final absorbance (usually near zero). In general, the rate constants were determined as the average of five to ten kinetic runs. Repeat kinetic runs on the same solutions exhibited excellent reproducibility with standard deviations in k_{obsd} being better than 3%. For different preparations the reproducibility was a little poorer, but it was always better than 15%. Precautions to exclude light were found to be unnecessary and were discontinued.

Rate constants were also obtained for representative unsaturated compounds in anhydrous acetic acid (prepared by refluxing glacial acetic acid with 10% acetic anhydride, followed by fractional distillation). An excess of alkene dissolved in HOAc/0.05 M KBr was mixed with bromine in the same solvent mixture on the stopped-flow spectrophotometer, and the disappearance of tribromide at 270 nm was monitored. Calculations were carried out as described above.

Mercuration Kinetics. The mercuration reaction was monitored by the increase in absorbance at 230 nm,[23] again with use of stopped-flow spectrophotometry. One syringe contained 2×10^{-4} M $Hg(OAc)_2$ (BDH Chemicals, Poole, U.K.)/0.01 M $HClO_4$ and the other syringe contained micelle, alkene, and 0.01 M $HClO_4$. An excess of alkene was employed, and the absorbance vs. time data were analyzed as described for bromination to give first-order rate constants k_{obsd}. Kinetics were limited to SDS micelles because both Brij and CTAB/CTAC precipitated on mixing with Hg^{2+} (either as $HgCl_2$ or $HgBr_2$).

Results

Kinetics. Because the alkenes have negligible UV absorbance above 215 nm, and because bromine itself is only weakly absorbing, bromination studies were carried out in the presence of bromide, which sets up the following equilibrium: $Br_3^- \rightleftarrows Br_2 + Br^-$. The tribromide ion is strongly absorbing with an extinction coefficient of 3.4×10^4 at its λ_{max} of 270 nm in water.[24] The equilibrium constant $[Br_2][Br^-]/[Br_3^-]$ is 0.059 M in water,[25] so that with sufficient bromide present a considerable amount of bromine is converted into tribromide and good absorbance changes can be observed even for 10^{-5} M Br_2. Solutions could therefore be prepared with alkene (10^{-4} M) in excess of bromine, providing pseudo-first-order kinetic conditions, and with surfactant (10^{-2} M) in excess of alkene so that minimal perturbation of the micelle occurs upon alkene incorporation. A typical absorbance–time trace is shown in Figure 1. The observation that the tribromide absorbance is different in the absence and presence of surfactant suggests that partitioning into the micelle is altering the tribromide formation constant. The absorbance increase in Brij implies a preferential solvation of tribromide by the micelle. Both CTAB and SDS decrease the absorbance suggesting preferential solvation

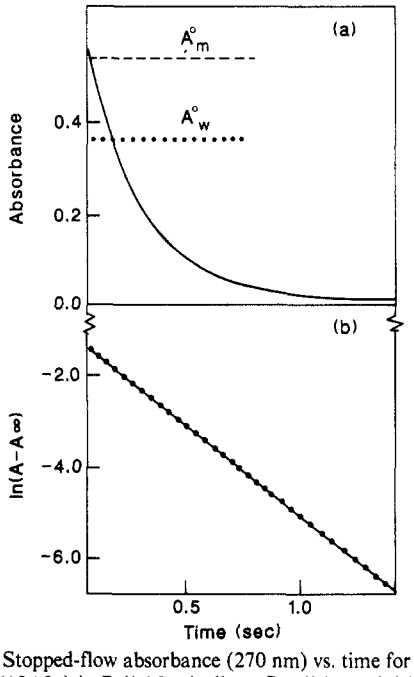

Figure 1. (a) Stopped-flow absorbance (270 nm) vs. time for bromination of oleic acid (18Δ9c) in Brij-35 micelles. Conditions: initial $[Br_2] = 1 \times 10^{-5}$ M; $[18\Delta 9c] = 1.25 \times 10^{-4}$ M; [Brij] = 0.010 M; [LiBr] = 0.10 M; [HOAc] = 0.01 M. The absorbance A^0_m is obtained in the absence of alkene; A^0_w is obtained in the absence of alkene and surfactant. (b) First-order plot for data in part a.

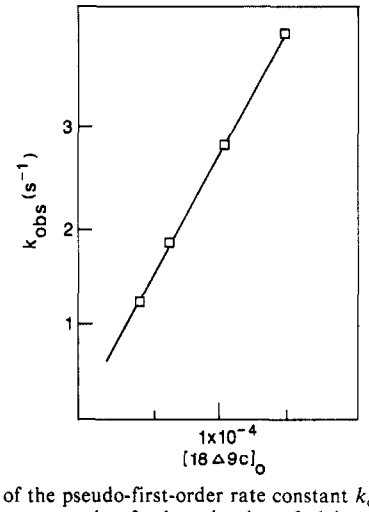

Figure 2. Plot of the pseudo-first-order rate constant k_{obsd} vs. stoichiometric alkene concentration for bromination of oleic acid in 0.010 M Brij-35, 0.10 M LiBr, and 0.01 M HOAc.

of bromine. Of particular importance is the observation that these absorbance shifts are very fast, being complete within the 3-ms dead-time of the stopped-flow apparatus. This signifies that both the partitioning processes in and out of the micelle and the tribromide equilibration are rapid,[26] in particular when compared to the reaction of interest. As illustrated in Figure 1b, excellent first-order plots for tribromide disappearance were generally obtained. Poor linearity was observed for relatively unreactive substrates in Brij micelles. This was traced to a reaction with the micelle itself, since even in the absence of substrate a slow decrease (minutes time scale) in tribromide absorbance was observed. The reaction involved here is possibly bromine oxidation of the micelle's ether headgroup.[27]

As seen in Figure 2, under conditions of constant bromide and surfactant concentration, a linear plot is obtained of the pseu-

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Table II. Dependence of Second-Order Rate Constant on Alkene Composition

alkene	$10^{-4}k_{app}$ (M^{-1} s^{-1}) SDS[a]	Brij-35[b]	CTAB[c]
18Δ6c	197	3.9	1.36
18Δ6c(OH)	200		
18Δ9c		2.7	0.67
18Δ9c(OH)	134	3.0	0.70
18Δ9c(Me)			0.69
18Δ9t	22	0.49	0.058
18Δ9t(OH)	21		
18Δ9t(12OH)	121	2.2	0.50
18Δ11t		0.13	
20Δ13c	22	0.86	0.12
20Δ13c(OH)			0.17
20Δ13t		<0.02[e]	
26Δ13t(diester)	13.7	0.07	0.053[f]
24Δ15c	*d*	0.19	
11Δ10	12.5	3.0	0.097
17Δ16		0.32	
linoleic acid		1.02[g]	
linolenic acid		2.5[g]	
monoolein	21	3.4	0.81
diolein	1.8	0.58[g]	0.39[g]
triolein	*d*	<0.02[e,g]	*d*

[a] 0.05 M SDS, 0.75 M LiBr, 0.010 M HOAc, 1.25×10^{-4} M alkene. [b] 0.01 M Brij-35, 0.10 M LiBr, 0.010 M HOAc, 1.25×10^{-4} M alkene. [c] 0.01 M CTAB, 0.75 M LiBr, 0.010 M HOAc, 1.25×10^{-4} M alkene. [d] Alkene not fully soluble at this surfactant concentration. [e] Reaction of bromine with surfactant competes. [f] 20 mM CTAC. [g] Corrected for the number of double bonds.

Table III. Dependence of Second-Order Rate Constant on Bromide Counterion

cation	10^{-4} k_{app} (M^{-1} s^{-1}) 18Δ6c–Brij[a]	18Δ9t–Brij[a]	18Δ9c–SDS[b]
Li^+	4.1	0.56	134
K^+	4.1	0.59	
Rb^+	4.1	0.63	
NH_4^+	4.2	0.62	
$(n\text{-}Bu_4)N^+$	0.41	0.07	17.2

[a] 0.01 M Brij-35, 0.01 M HOAc, 0.10 bromide salt. [b] 0.05 M SDS, 0.01 M HOAc, 0.20 M Bromide salt.

do-first-order rate constants vs. stoichiometric alkene concentration (moles of species divided by the total volume of solution after mixing). The proportionality of k_{obsd} and alkene concentration is of course not unexpected. It does, however, provide further evidence that the alkene bromination is rate limiting rather than some physical partitioning process. The linearity also establishes that differing quantities of unsaturated amphiphile do not change or create new structures in the host micelle to the extent that the probe signal (reactivity) changes. This is an indication of the relatively nonperturbing nature of the alkene.

Second-order rate constants, defined as k_{app}, were calculated by dividing the pseudo-first-order rate constants k_{obsd} by the stoichiometric alkene concentration. Table II lists rate constants for a variety of alkenes in the three micelles SDS, Brij-35, and CTAB. Numbers for each micelle refer to the same concentration of surfactant and bromide. Higher concentrations of bromide were required for the SDS and CTAB micelles because of the unfavorable shift in the tribromide formation constant, as discussed previously. A higher concentration of SDS was required in order to solubilize some of the alkenes. Table III illustrates the effect of the bromide counterion on k_{app} in Brij and SDS micelles.

Table IV presents results in Brij-35 where the bromide ion concentration was varied at constant surfactant concentration and vice versa. In both cases a monotonic decrease in k_{app} was observed as concentration increased. These variations can be analyzed[28] in terms of a classical pseudophase micellar model.[29] The bromide

Table IV. Dependence of Second-Order Rate Constants in Brij-35 on Bromide Ion Concentration and Surfactant Concentration

	10^{-4} k_{app} (M^{-1} s^{-1}) 18Δ6c	18Δ9c	18Δ9t	20Δ13c
$[LiBr]_0$[a]				
0.005	32.4	22.6	4.19	7.29
0.0125	16.7	13.1	2.11	4.03
0.025	10.2	7.69	1.42	2.43
0.050	7.34	5.14	0.901	1.58
0.100	3.89	2.66	0.491	0.86
$[Brij\text{-}35]_0$[b]				
0.002	18.3	13.0		
0.004	14.2	8.41	0.849	
0.006		5.10	0.573	
0.008	8.15	4.15	0.456	
0.010	3.70	2.91	0.394	

[a] Ionic strength (μ) = 0.10 (LiBr + $LiNO_3$); 0.01 M HOAc, 0.01 M Brij-35, 1.25×10^{-4} M alkene. [b] 0.01 M HOAc, 0.10 M LiBr.

Table V. Second-Order Rate Constants for Bromination in Acetic Acid

alkene	k_{app} (M^{-1} s^{-1})
18Δ6c	2.54
18Δ9c	2.40
18Δ9t	1.24
20Δ13c(Me)	1.98
26Δ13t(diester)[b]	1.18
triolein	1.49[c]
11Δ10	0.114
17Δ16	0.109

[a] Anhydrous acetic acid, 0.05 M KBr, 1.3×10^{-3} M alkene, 5×10^{-6} M Br_2. [b] Assigned a trans geometry on the basis of the similarity of its rate constant to that of 18Δ9t. [c] k_{app} = 4.47. Number shown herre is per double bond.

ion dependency arises because of conversion of the electrophile bromine into the unreactive tribromide form as bromide concentration is increased. Plots of $1/k_{app}$ vs. $[Br^-]_0$ (not shown) are excellently linear, as predicted by the model. The micelle concentration dependency occurs because of dilution of the reagents in the micelle with increased surfactant concentration. Maxima typical of many bimolecular micellar reactions[29] are not observed in the present case because of the complete association of the alkene. What is also important about the data in Table IV is the demonstration that as bromide or surfactant concentrations are varied k_{app} differences among the different alkenes remain within experimental error constant. Thus for the more extensive data in Table II, the k_{app} variations within each micelle series represent inherent differences in micellar reactivities of the various alkenes.

The possibility that a free radical bromination[30] is being observed can be discounted on the basis that observed rate constants are the same in the presence of isoamyl nitrite, a radical inhibitor.[31] Furthermore, features characteristic of radical reactions such as lag times and nonintegral orders are not observed. In homogeneous solution, ionic bromination obeys a three-term rate law,[5,6] rate = $(k_2[Br_2] + k_3[Br_2]^2 + k_3'[Br_3^-])[A]$. The k_3 process is favored in nonpolar solvents and usually requires higher bromine concentrations,[32] but it is a possibility in the present case if high concentrations of bromine were to localize in the nonpolar core of the micelle. The presence of this process can obviously be ruled out by the excellent first-order kinetics in bromine.[33] The k_3' process is kinetically equivalent to one involving one bromine

(28) Lennox, R. B. Ph.D. Thesis, University of Toronto, 1984.
(29) Berezin, I. V.; Martinek, K.; Yatsimirskii, A. K. *Russ. Chem. Rev.* **1973**, *42*, 787.

(30) (a) This reaction can occur in a hydrocarbon environment at low bromine concentration,[30b] possible conditions experienced by the micelle-bond alkenes of this study. (b) Byrnell, C. J. A.; Coombes, R. G.; Hart, L. S.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1079.
(31) Warner, P.; La Rose, R.; Schleis, T. *Tetrahedron Lett.* **1976**, 4443.
(32) (a) Schmid, G. H.; Toyonaga, B. *J. Org. Chem.* **1984**, *49*, 761. (b) Toyonaga, B. Ph.D. Thesis, University of Toronto, 1984.
(33) (a) A Poissonian statistical analysis of the distribution of a solute in a micelle population[33b] also shows that at the conditions employed in this study, less than 1% of the micelles contain two or more bromine molecules. (c) Turro, N. J.; Gratzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 675.

Table VI. Second-Order Rate Constants for Mercuration in SDS Micelles

alkene	$10^2 k_{app}$ (M^{-1} s^{-1})
18Δ6c	83.6
18Δ9c	49.9
20Δ13c	22.9
monoolein	0.91
diolein	0.18
26Δ13t(diester)	2.16

[a] 0.05 M SDS, 0.01 M $HClO_4$, 1×10^{-4} M $Hg(OAc)_2$, 1.25×10^{-4} M alkene.

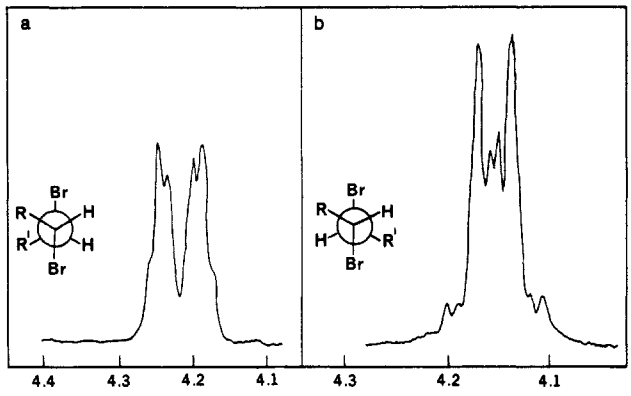


Figure 3. 200-MHz proton NMR spectra in the bromomethine region of the dibromo product of (a) 18Δ9c and (b) 18Δ9t.

molecule and a bromide ion. This can be ruled out from the dependency of the observed rate on bromide concentration.[28]

The homogeneous solution reactivities of a selected series of alkenes were examined in glacial acetic acid containing KBr. Second-order rate constants obtained by dividing the pseudo-first-order rate constants by the alkene concentration are listed in Table V.

The reactivity toward Hg^{2+} was examined for a selected series of alkenes in SDS micelles, and results are given in Table VI. Alkene was in excess over $Hg(OAc)_2$ in these experiments and the listed k_{app} values are pseudo-first-order rate constants divided by alkene concentration.

Products. Since the standard kinetic conditions involved micelle in considerable excess of alkene, it was necessary to separate the products derived from the latter away from the former. With the ionic micelles of SDS, CTAB, and CTAC this proved possible with use of precipitation or ion exchange techniques. However, with Brij micelles no separation could be accomplished. Initial attempts to analyze the products involved HPLC and TLC, but these were unsuccessful, possibly because retention times are mainly determined by the chain length and polar group, and for a given system these are constant. High field proton NMR spectroscopy, however, was able to resolve the components, in terms of the resonances associated with the two methine protons on what was originally the carbon–carbon double bond. For comparison purposes authentic samples of possible products were prepared under standard conditions. The ^1H NMR characteristics of these are described first, followed by an analysis of the micellar results.

Dibromides were prepared by carbon tetrachloride bromination. Representative spectra in the region of interest are shown in Figure 3. In general, and this is true for the other two products as well, the spectra and chemical shifts associated with the CH–CH grouping are completely independent of the initial double bond position (for example, 18Δ6c, 18Δ9c, and 20Δ13c). Electrophilic bromination, paticularly of 1,2-dialkyl-substituted double bonds, usually occurs stereospecifically anti,[5,6] a cis alkene producing exclusively threo product and a trans alkene the erythro diastereomer.[34] The addition is clearly stereospecific here, the dibromides from the two alkenes in Figure 1 exhibiting quite different spectra. In the methine region these in fact match spectra obtained with more simple alkenes,[35] thus establishing that addition in the present case is also anti. One further point of interest is that the methine protons in these bromides are chemically nonequivalent, since the alkyl groups attached to each are different. However, even at 360 MHz these two protons appear magnetically equivalent. The headgroup, even in products from 18Δ6c, is sufficiently far removed that it has no effect.

(34) Although the terms threo and erythro are meant for the dibromo products of symmetrical 1,2-disubstituted alkenes, we will employ them here to describe all the products.

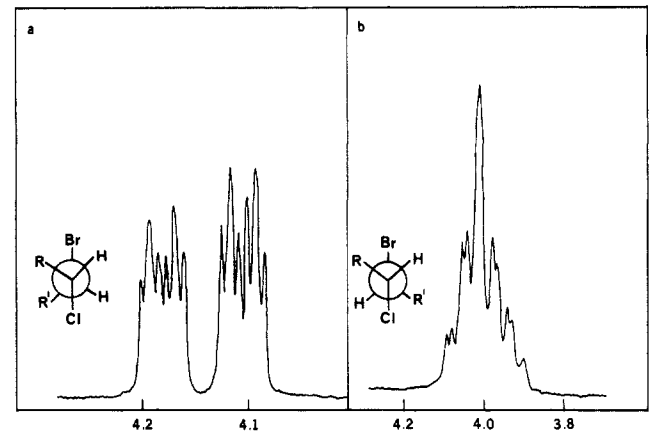


Figure 4. 200-MHz proton NMR spectra in the methine region for the bromochlorination of (a) 18Δ9c and (b) 18Δ9t.

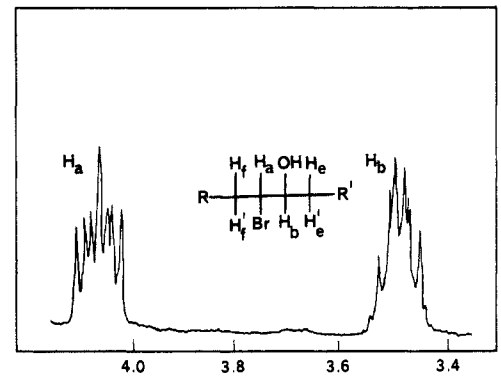


Figure 5. 200-MHz proton NMR spectrum in the methine region for the bromohydrin derived from 20Δ13c.

Bromochlorides (Figure 4) were produced from the reaction of the alkene in carbon tetrachloride with BrCl, the latter being generated in situ from bromide ion and antimony pentachloride.[19] **Bromohydrins** (Figure 5) were produced from the reaction of the alkene and *N*-bromosuccinimide in Me_2SO containing a small amount of water.[17] In this case the products from cis and trans alkenes had similar spectra, and only one spectrum is shown. It can be noted that with the bromochlorides and bromohydrins there are two regioisomers possible. The NMR spectra show no evidence for the presence of two products. However, the headgroup is far removed and thus the NMR spectra for the two regioisomers are likely to be extremely similar. Thus no statement can be made regarding the regiochemistry. Both regioisomers are likely present but simply cannot be resolved.

Table VII summarizes the results of the micellar brominations. As illustrated in Figure 6 (compare to Figure 3a), the only product observed in the reaction of CTAB-associated alkenes was the dibromide, formed stereospecifically anti. The water-incorporated product which would have given characteristic signals near 3.5 ppm is not present. One CTAB bromination was also carried out in the presence of lithium chloride. In this case a significant quantity of the bromochloro product could be detected along with dibromide. This experiment led us to explore CTAC micelles where no external bromide was present. A representative spectrum is shown in Figure 7, along with structural assignments based on

(35) Anet, F. A. L. *J. Am. Chem. Soc.* **1962**, *84*, 747.

Table VII. Products of Micelle-Mediated Brominations

alkene–micelle	% dibromide	bromochloride or bromosulfate	bromohydrin
18Δ6c–CTAB[a]	100	0	0
18Δ9t–CTAB[a]	100	0	0
20Δ13c–CTAB[a]	100	0	0
20Δ13c–CTAB[b]	34	66[g]	0
18Δ6c–CTAC[c]	≈5	75[g]	20
18Δ9c–CTAC[c]	≈5	60[g]	35
18Δ9t–CTAC[c]	≈5	>90[g]	<5
20Δ13c–CTAC[c]	≈5	85[g]	10
18Δ6c–SDS[d]	0	40[h]	60
18Δ9c–SDS[e]	0	35[h]	65
18Δ9c–SDS[f]	0	45[h]	55
18Δ9c(Me)–SDS[f]	0	35[h]	65
18Δ9t–SDS[e]	0	25[h]	75
18Δ9t–SDS[f]	0	25[h]	75
20Δ13c–SDS[f]	0	25[h]	75

[a] 1 mM alkene, 0.02 M CTAB, 0.01 M HBr, 0.01 M LiBr. [b] 1 mM alkene, 0.02 M CTAB, 0.01 M HCl, 0.10 M NaCl. [c] 1 mM alkene, 0.015 M CTAC, 0.01 M HCl, 0.01 M NaCl. [d] 1 mM alkene, 0.10 M SDS, 0.01 M HBr. [e] 1 mM alkene, 0.10 M SDS, 0.01 M HBr, 0.20 M NaBr. [f] 1 mM alkene, 0.10 M SDS, 0.01 M HCl, 0.20 M NaCl. [g] Bromochloride. [h] Bromosulfate, measured as bromosulfate or dodecanol.

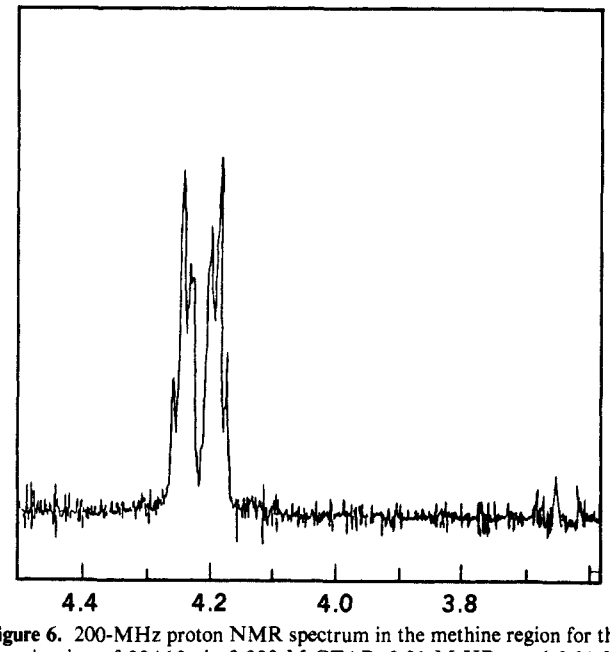
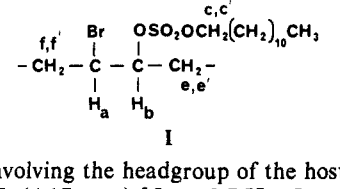


Figure 6. 200-MHz proton NMR spectrum in the methine region for the bromination of 20Δ13c in 0.020 M CTAB, 0.01 M HBr, and 0.01 M LiBr.

the standard spectra. Several sets of signals, some of which overlap somewhat, are observed. Significant quantities of the bromohydrin are now present, as seen in particular from the signals near 3.5 ppm. The major product is the bromochloride, but a trace of dibromide is possibly also still present.

A representative spectrum of the SDS products is shown in Figure 8. The bromohydrin is clearly present, with no dibromides or bromochlorides. There is in addition a species which does not correspond to any standard. This is characterized by a one-proton multiplet at 4.2 ppm, a second one-proton multiplet significantly downfield at 4.7 ppm, and a two-proton triplet at 4.3 ppm. These resonances are assigned to the dodecyl sulfate adduct I, formed



I

by a reaction involving the headgroup of the host micelle. Assignments are H_a (4.17 ppm) [J_{ab} = 9.7 Hz, J_{af} = 3.6 Hz = $J_{af'}$]

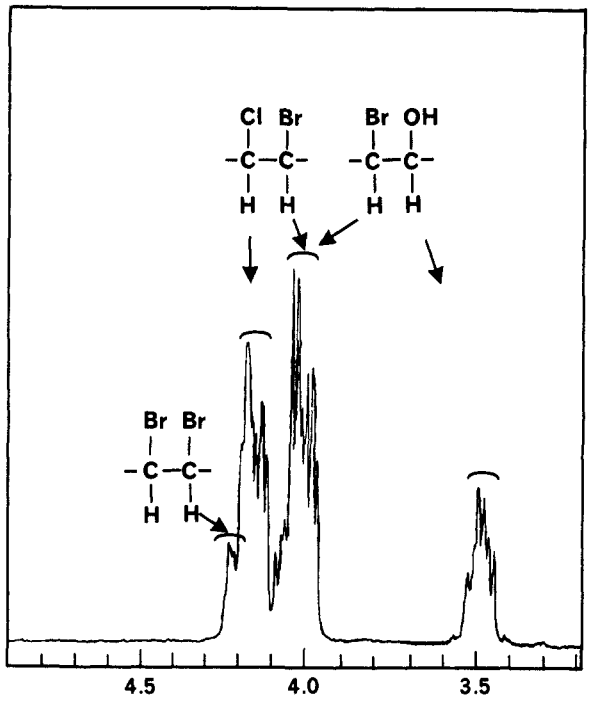


Figure 7. 200-MHz proton NMR spectrum in the methine region for the bromination of 18Δ9c in 0.015 M CTAC, 0.01 M HCl, and 0.01 M NaCl.

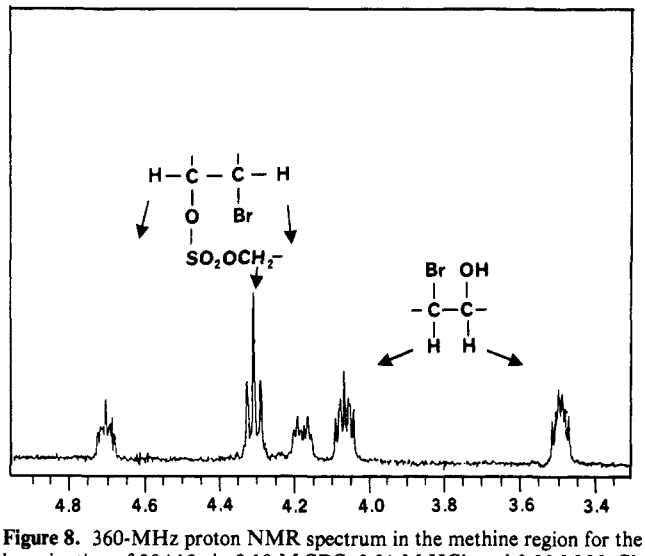


Figure 8. 360-MHz proton NMR spectrum in the methine region for the bromination of 20Δ13c in 0.10 M SDS, 0.01 M HCl, and 0.20 M NaCl.

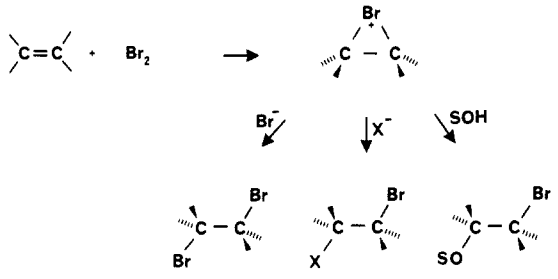
and H_b (4.70 ppm) [J_{ba} = 9.7 Hz, J_{be} = 6.3 Hz, and $J_{be'}$ = 4.7 Hz]. The latter proton is considerably downfield from signals seen in the standards because of the adjacent ester. The triplet at 4.30 ppm is assigned to the protons H_c and $H_{c'}$. In addition to these spectral characteristics this product is supported by several other pieces of evidence. (i) Some product mixtures show a triplet at 3.68 ppm not apparently associated with any other signals in this region. This triplet corresponds to the CH_2O protons of 1-dodecanol, which can form through the hydrolysis of the diester I. The other product of this hydrolysis is a sulfate monoester anion ($ROSO_3^-$) where R is derived from the original alkene. This would be precipitated as the calcium salt during the isolation. (ii) An experiment was carried out where the isolated product mixture containing this adduct was dissolved in Me_2SO-d_6 and treated with potassium iodide. On addition of KI, the triplet at 4.3 ppm disappears and a new triplet at 3.35 ppm appears. On the basis of comparison with an authentic sample of 1-iodohexane the latter can be assigned to the CH_2I protons of 1-iododecane, the product of an S_N2 reaction of the dodecyl sulfate with iodide. This reaction also produces other changes in the spectra, in particular the

multiplet at 4.7 ppm assigned to H_b of the diester disappearing with a new multiplet appearing at 4.4 ppm. This is consistent with the change $CHOSO_2OR$ to $CHOSO_3^-$. (iii) Although this is not apparent in Figure 8, on expansion, the triplet at 4.3 ppm turns out to be two triplets separated by 0.002 ppm. The $-CH_2OSO_2OR$ protons of the diester are chemically nonequivalent because of the chiral centers in R, and although these are quite remote there is apparently enough of an effect to cause this very small separation. The isolation of an adduct derived from the dodecyl sulfate headgroup has apparently not been previously reported in micellar chemistry. Sukinek and Bergman have proposed that an unstable dialkyl sulfate forms in the SDS-mediated solvolysis of alkyl (*p*-trimethylammoniumbenzene)sulfonates although no isolated product was reported.[36]

NMR integration was employed to determine the relative yields in Table VII, and thus these have a precision of about ±10%. In cases where no product was detected the limit of detectability was 5%. There could be some concern that the separation procedures may selectively alter or remove products. This possibility was evaluated by redissolving analyzed product mixtures in aqueous micellar solution followed by standard workup. Comparison of the original NMR spectrum with that of the recycled product revealed no differences.

Discussion

Location of the Product-Determining Step. Ionic bromination of 1,2-dialkylethenes proceeds with rate-limiting formation of a cyclic bromonium ion, which is trapped in a stereospecific manner by bromide, other nucleophiles, and solvent.[5,6] Dibromides ob-



viously result if there are no other nucleophiles, including solvent. Aqueous brominations on the other hand generally give bromohydrins, with quite high concentrations of bromide being required before dibromides form in significant quantities.[37] The reactions in question here are "aqueous" brominations, but clearly the association with the micelle is having a significant effect.

In the SDS micelle, products are the bromohydrin and a sulfate ester derived by trapping with the headgroup of the micelle. The absence of dibromide implies that the product-determining step does not occur within a nonpolar region of the micelle. In such a case the bromide ion released in the rate-limiting step would be the major nucleophilic species present. The absence of the dibromide product also suggests that the bromohydrin which is observed does not arise from trapping with bulk water molecules. This statement is made since a reaction was carried out in the presence of 0.2 M bromide, and in this case a bulk phase reaction would have given some dibromide.[37] The indication therefore is a reaction site in a region of the micelle containing water and the micelle's anionic headgroups. Halide ions are expelled from this region because of electrostatic repulsion by the headgroup. At the same time reaction with the headgroup is promoted simply through proximity. The ratio of headgroup-incorporated to water-incorporated products is relatively insensitive to alkene structure, differences in double bond position, double bond geometry, and polar end group (COOH vs. COOMe). This observation implies that the trapping reaction environment is essentially the same for each substrate, even, for example, as the distance between the polar end of the alkene and the double bond is varied. Also of significance is the actual formation of the product derived from the headgroup. The sulfate anion is an extremely poor nucleophile, and for it to have effectively competed its concentration in the trapping region relative to that of water must be high.

Products in CTAB/CTAC micelles are quite different from those in SDS, but they in fact point to a similar reaction location. The absence of bromohydrin in CTAB reactions implies that no bulk-phase reaction occurs. The low yield of dibromides in CTAC rules out bromination in the nonpolar core of the micelle since it implies that the trapping halide is externally added and does not come from the electrophile itself. (Up to 1 mM bromide is in fact present in the CTAC experiments, being formed as the bromination proceeds, and this is probably the origin of the trace dibromide.) The products are consistent with a reaction occurring in a polar micellar region containing some water and associated with the surfactant headgroups, or more particularly, their counterions which in this case are the "external" nucleophiles. In the CTAB/Cl^- experiment both bromide and chloride were present, and although there was a 13-fold stoichiometric excess of the latter, only two-thirds of the products derived from it. However, bromide ion binds more strongly to cetyltrimethylammonium micelles[38] and is probably more nucleophilic[39] and is thus more competitive. In fact bromide is present in sufficient concentration and is sufficiently nucleophilic that in CTAB micelles its reaction dominates that of water. A similar result has been previously reported in the CTAB-mediated decomposition of diazonium ions.[40] Chloride ion, however, is not so competitive and thus some bromohydrin forms in CTAC micelles. Extrapolation of aqueous solution data giving the dibromide/bromohydrin dependence on bromide ion[37] shows that a bromide ion concentration greater than 15 M is required in the trapping region to account for the absence of dibromide in CTAB. This figure must be viewed with caution since the trapping region is not an aqueous solution and relative nucleophilicities of bromide and water may be very different here.[41] This calculation does, however, emphasize that in the trapping region bromide ion concentrations are large.

In summary, products obtained in both micellar types support a model where the product-determining step occurs in a polar micellar region containing relatively high concentrations of headgroup and its counterions.

Location of the Rate-Limiting Step. The lifetime of the bromonium ion is probably very short,[42] and it seems unlikely that it would be around long enough to diffuse very far. This would be particularly true if it formed in a nonpolar region of the micelle, since in this case it would form as an ion pair with bromide, and this should collapse to dibromide products very quickly. It can also be noted that although diffusion could be aided in SDS by attraction toward the anionic headgroup, the cation would be repelled from the headgroup region in CTAB and CTAC micelles. In other words it is unlikely that the bromonium ion intermediate

(36) Sukenik, C. H.; Bergman, R. *J. Am. Chem. Soc.* **1976**, *98*, 6613.
(37) Atkinson, J. R.; Bell, R. P. *J. Chem. Soc.* **1963**, 3260.
(38) Lindman, B.; Puyal, M. C.; Kamenka, N.; Rymeden, R.; Stilbs, P. *J. Phys. Chem.* **1984**, *88*, 5048.
(39) Relative nucleophilicities will be affected by the micellar environment. There is also a question of the importance of nucleophilic strength when dealing with reactive intermediates like the brominium ion, since activation barriers for combination will be low.
(40) Moss, R. A.; Dix, F. M.; Romsted, L. *J. Am. Chem. Soc.* **1982**, *104*, 5048.
(41) (a) In aqueous brominations, for example, cations such as Bu_4N^+ lead to a greater amount of anion-incorporated product.[41b] The region in question is of course rich in this type of cation. (b) Balou, D.; Dubois, J. E. *J. Chem. Res., Miniprint* **1980**, 4459.
(42) (a) Short lifetimes are suggested by the bromide/water competition data for aqueous brominations[27] which show that water and bromide ion are about equally reactive toward this intermediate. Thus the bromonium ion is so reactive that it shows very little discrimination in its reaction with nucleophiles. An indirect piece of evidence comes from suggestions that with some styrene derivatives the intermediate is an α-bromocarbonium ion, the explanation being that in these cases the latter cation is more stable than the bridged cation.[42b] The carbonium ions in question here, however, are phenethyl cations, whose lifetimes in water have been estimated to be very short.[42c] The implication then is that the less stable bromonium ion would have an even shorter lifetime. (b) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1477, 1483. (c) Richard, J. P.; Rothenberg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361.

is formed in a different location and diffuses to the trapping region. The rate-limiting step must occur within the same polar micellar region as the product-determining step.

Some support for this interpretation can be obtained in the kinetic data. Significant reactivity differences are observed as the nature of the micelle is varied with the order SDS (anionic) > Brij-35 (neutral) > CTAB (cationic). In simple terms, this order appears reasonable, the enhanced rate in SDS being explained by the sulfate headgroup stabilizing the incipient bromonium ion, with a destabilizing effect in CTAB reducing the rate. This explanation, however, cannot be correct. Medium effects on bromination are generally interpreted as being determined by the solvation of the bromide ion leaving group, with stabilization of the developing cation being only of relatively minor importanee.[43-45] On this basis stabilization by the cationic headgroup and destabilization by the anionic headgroup is predicted, with an order of reactivity opposite to that observed. However, a mechanism where the bromination actually occurs in a region of the micelle where the transition state is exposed to the counterions of the headgroup does account for the order. In this way SDS micelles could stabilize the transition state through a favorable interaction of the bromide and the Na^+ counterion, while CTAB would destabilize since the bromide ion would have to be released into a region already rich in bromide.

A second effect would also come into play in this region. Salt effects on aqueous bromination reveal a rate acceleration for structure-breaking cations such as Na^+, with rate deceleration for structure-breaking anions such as R_4N^+.[41b] Thus the reactivity difference between SDS and CTAB could simple be associated with the cation type, with Brij, the neutral micelle, in the middle. Evidence that the cation type is important is seen from the results in Table III. By replacing the Na^+ ions in SDS micelles with tetrabutylammonium ions,[46] an 8-fold decrease in rate is observed, and the SDS micelle starts looking more like CTAB. A similar effect is observed with Brij, Bu_4N^+ again resulting in a significant (8–10-fold) rate decrease.

Additional evidence is provided by the limited mercuration data. The reaction here involves a charged electrophile which is unlikely to penetrate the hydrocarbon regions of the micelle. A binding site associated with the SDS headgroup is most probable, and that is also the likely location for the reaction with alkenes. As seen by comparing data in Tables II and VI, the mercuration shows the same alkene structural effects[47] as the bromination reaction, consistent with the idea that the latter also occurs in the polar headgroup region.

Micellar Alkene Structural Effects. This latter point is illustrated graphically in Figure 9. Despite differences in absolute reactivities, the various effects associated with changing alkene structure are observed to more or less the same extent in all four systems examined—the brominations in the three micelles and the mercuration in SDS. A further comparison, this time with homogeneous solution data, reveals that the effects in the micellar environment are quite different. In the following, bromination data are specifically considered and the effects are broken down into various subsections.

(i) Positional Selectivity. In homogeneous solution double bonds with the same number of alkyl groups and the same geometry are approximately equally reactive regardless of the chain length or the position of the double bond in the chain (see Table V and ref 48). Micellar bromination exhibjts a monotonic decrease in rate as the double bond becomes further removed from the polar headgroup of the alkene. This effect is seen with each type of alkene studied—cis disubstituted, trans disubstituted, and terminal.

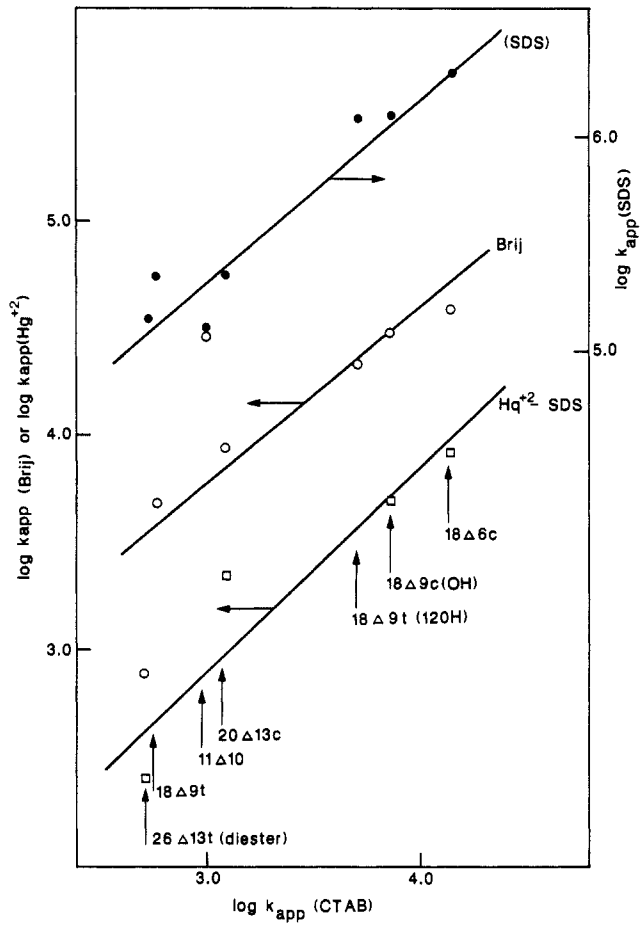


Figure 9. Linear free energy correlations of micellar bromination and mercuration reactivity. k_{app} data from Tables II and VI. Lines drawn are based on linear regression through all the points and have slopes of 0.86 (SDS), 0.82 (Brij), and 0.98 (Hg^{2+}).

(ii) Geometric Selectivity. Because of initial state enthalpy differences,[49] cis alkenes are more reactive than their trans isomers, but the differences in homogeneous brominations are small, reactivity ratios being in the range 1.05 to 2 (see Table V and ref 50). In micelles the geometric difference is considerably enhanced, k_{cis}/k_{trans} for the same chain position varying from 5 to 12.

(iii) Enhanced Terminal Alkene Reactivity. Internal double bonds are considerably more reactive than terminal double bonds in homogeneous brominations (Table V). In the micellar bromination this is clearly not true. In a comparison involving double bonds located at similar positions with respect to the headgroup, the terminal alkene 10-undecenoic acid (11Δ10) is of similar reactivity to the cis-internal alkene oleic acid (18Δ9c). Enhanced terminal alkene reactivity in micelles has previously been observed, both in permanganate oxidations[51] and in stilbene brominations.[9]

(iv) Multiple Chain Effect. The attachment of two or more unsaturated chains to a common backbone results in large micellar rate decreases, as seen for the data for mono-, di-, and triolein. As shown in the next section, it is the di- and trioleins which are unusually slow, monolein having rates typical of its alkene type. In homogeneous solution there is very little effect of the additional chains (compare 18Δ9c and triolein in Table V).

(43) Garnier, F.; Dubois, J. E. *Bull. Chim. Soc. Fr.* **1968**, 3797.
(44) Ruasse, M. F.; Zhang, B. L. *J. Org. Chem.* **1984**, *49*, 3207.
(45) (a) In the same way that solvation of the incipient halide dominates solvent effects on S_N1 alkyl halide solvolysis.[45b-e] (b) Parker, A. J.; Mayer, U.; Schmid, R.; Gutmann, V. *J. Org. Chem.* **1978**, *43*, 1843. (c) Luton, P. R.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1507. (d) Abraham, M. H.; Taft, R. W.; Kamlet, M. J. *J. Org. Chem.* **1981**, *46*, 3053.
(46) Some Na^+ was obviously still present in this experiment from the SDS salt. Solubility problems prevent the addition of greater than 0.2 M Bu_4NBr to SDS.
(47) (a) Significant positional selectivity has been observed previously in products from dienes plus Hg^{2+}–SDS.[47b] (b) Sutter, J. K.; Sukenik, C. N. *J. Org. Chem.* **1982**, *41*, 4174.
(48) (a) *cis-n*-Undecenes in methanol have relative reactivities[48b] of n = 2, 1.00; n = 3, 1.57; n = 4, 1.03; n = 5, 1.14. (b) Asinger, F.; Fell, B.; Hadik, G.; Steffan, G. *Chem. Ber.* **1964**, *97*, 1568.
(49) Yates, K.; MacDonald, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 6297.
(50) (a) A series of undecenes in methanol has k(cis)/k(trans) of 1.6–1.7,[48b] while for a series of butenes, pentenes, and hexenes the ratio is 1.2–1.4 in acetic acid and 1.06–1.2 in trichloroethylene.[50b] (b) Modro, A.; Schmid, G.; Yates, K. *J. Org. Chem.* **1977**, *42*, 3673.
(51) Menger, F. M.; Doll, D. W. *J. Am. Chem. Soc.* **1984**, *106*, 1109.

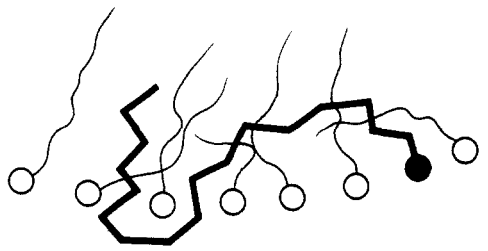


Figure 10. Schematic representation of a segment protrusion event placing a double bond in a reactive position.

(v) Absence of Headgroup Effect. No significant effect is observed on micellar bromination as the nature of the alkene polar headgroup is varied.[52] There are several entries in Table II illustrating this; the most complete involve the data in CTAB for monolein, $CO_2CH_2CHOHCH_2OH$ headgroup: 18Δ9c (OH), CH_2OH, 18Δ9c(Me), CO_2Me, and 18Δ9c, CO_2H/CO_2^-. The absence of an effect implies that the headgroup is not directly involved in the reaction and only serves to orient the substrate within the micelle. Also implied here is the relatively nonperturbing nature of the alkene, in that even with very different alkene headgroups the micelle provides the same "microenvironment".

(vi) Additional Polar Group Effect. The alkene (18Δ9t(12OH)) has the same chain length, double bond position, and geometry as 18Δ9t, but the former is 6–8 times more reactive. Thus, attachment of a second polar group to the chain results in a rate acceleration.

(vii) Apparent Polarity. Homogeneous brominations exhibit a very pronounced solvent polarity dependency,[43,44] and the reaction of disubstituted alkenes in water is in fact close to diffusion controlled. The rate constants in the micelles correspond to an apparent polarity ranging from that of methanol (relatively polar) to something in between that of *tert*-butyl alcohol and carbon tetrachloride (relatively nonpolar). The micelle thus has caused quite significant rate retardations on what is otherwise an aqueous bromination (although the micelle is required to solubilize the alkene in the first place).

Segment Protrusion Model. In order to explain these effects we note the previous conclusion that the reactions are actually occurring in a region closely associated with the headgroup and its counterions. This being the case, in order for the alkene to achieve a reactive state, a chain segment containing the double bond must find its way into this region (Figure 10). This suggests a model where the reactivity depends upon two factors, the actual rate in the reactive region and the fraction of time that the double bond is located there, or, in other words, the probability of a chain protrusion event. The latter can be further separated, into a factor dependent upon the configurational properties of the chain and a factor dependent upon the extent of hydrocarbon–water contact which occurs during the protrusion event.

The configurational factor is related to the probability that a particular chain segment will reside in a location adjacent to the reactive region. An analogous problem has been addressed in theoretical polymer studies.[53] Self-avoiding walk calculations have considered the probability of a chain segment interacting with an impentrable surface when there is one point of attachment and have found that the closer the segment of interest to the point of attachment the greater the probability. The relevance to the micellar system is readily apparent, since the alkenes are fixed by their polar headgroups at the water–hydrocarbon interface. **Positional selectivity** is then explained by a decrease in the probability of the double bond in finding the interface as it moves further away from the headgroup. The argument is that for alkenes of the same degree of substitution and geometry, the rate in the reaction region is independent of double bond position, as in homogeneous solution. Reactivity differences arise from an

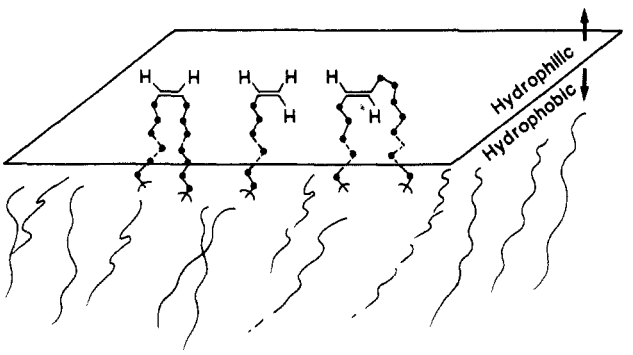


Figure 11. Comparison of protrusion events for cis, trans, and terminal alkenes. Note that in each case one of the chains extending into the hydrophobic region must loop back to the interface where it is fixed by the headgroup.

"extra-kinetic" effect—the probability of the double bond finding the reactive environment. This model also explains the **additional polar group effect**. The additional group here can be envisaged as a second headgroup, reducing the effective distance between the double bond and a polar group. The rate constant for the 18Δ9t(12OH) compound in fact suggests that it behaves more like a Δ3 or Δ4 than a Δ9 compound. A second polar group has indeed been found to act as a second headgroup in lipid monolayers,[54] although the effect is not as strongly manifested in micelles.[55] Interestingly 26Δ13t(diester) which has two headgroups is of similar reactivity (perhaps slightly faster) to monopolar analogues. The double bond in this compound, however, is still situated at the 13th position with respect to either headgroup, and thus has little increased probability of finding the surface as compared to a similar double bond with one headgroup.

The chain configurational properties are important because a protrusion event cannot be initiated unless chain–interface contact has been achieved. This probability factor is dependent upon the segment position, but it should be relatively independent of the geometry and nature (internal/terminal) of the double bond. These latter factors, however, can influence the probability of protrusion of a double bond already situated at the interface. The free energy of hydrocarbon solubilization is large and positive, so that as the amount of hydrocarbon which must be transferred to the polar region increases the frequency of protrusion must decrease. Figure 11 illustrates that a significant difference exists for protrusion of an internal double bond and a terminal double bond, in that the former requires two anchors into the hydrocarbon medium whereas the latter only requires one. In other words, protrusion of an internal double bond exposes considerably more hydrocarbon to a polar aqueous environment than does protrusion of a terminal bond. Thus for the same chain position the terminal protrusion event is more favorable. This effect opposes the lower inherent reactivity of the terminal bond and thus explains **enhanced terminal alkene reactivity**. Figure 11 also indicates a difference between cis and trans protrusion events (**geometric selectivity**), in that the trans double bond must solubilize more hydrocarbon. In this case the small inherent reactivity difference favoring the cis isomer is considerably enhanced because of relative protrusion probabilities.

The multiple chain effect requires that as the additional alkene chains are attached to the same headgroup, the overall probability of a double bond achieving the reactive aqueous state decreases. The multiple chain alkenes diolein and triolein are perhaps more similar to amphiphiles which form bilayer membranes. The incorporation of two unsaturated chains in such aggregates results in significant increases in chain order.[56] The occurrence of this effect upon incorporation of these alkenes into micelles would result in the observed effect, the increased order tending to keep the

(52) There would also be little effect on homogeneous bromination since this group is far removed from the reaction site.

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double bond more in the hydrocarbon region.

The segment protrusion model thus provides for three chemically distinct regions in micellar solutions—a bulk aqueous region, a hydrophobic hydrocarbon micellar region, and a polar aqueous micellar region containing in the case of ionic micelles a large concentration of ions (the ionic headgroups and their counterions). The electrophilic additions prefer aqueous environments, but the alkenes prefer the hydrocarbon region. A compromise is reached therefore where the reaction occurs in the intermediate region. Because of its polar nature, rate constants in this region can be very fast. However, the observed rates are slower because of the small probability of the double bond finding a reactive condition. The evidence does not support a bromination reaction occurring within a hydrocarbon core. The concentration of alkene is high in this region, and, according to homogeneous bromine hydrocarbon:water partitioning ratios,[57] high concentrations of bromine can also be present. A simple explanation for the lack of reaction is that the polarity is low and the resultant slow bromination cannot compete with that occurring in the polar region.

It can also be noted that according to this model, the **apparent polarity** as determined by relative rates is an artifact. In this connection it is interesting that the recent kinetic study of the bromination of stilbenes in SDS reveals micellar rates only slightly slower than those in pure water, in contrast with the case for the alkenes of this study. One simple explanation is that the stilbenes actually reside at the interface[58] and are already in the vicinity of the reaction site. Thus there is not nearly so large a rate decrease associated with the low probability of finding the double bond in a reactive state.

Other Models. There has been some discussion recently about the structure of micelles,[59,60] and it is worth considering the present results in terms of this. One model, the **interphase model**,[60] is a statistical representation of the micelle based upon a micellar core filled with randomly distributed chain segments.[61-65] This treatment also imposes the condition that the polar end of the surfactant chain is located at the polar–hydrocarbon interface, that the interface is reasonably well defined, and that there is no water penetration into the core of the aggregate. The results of this study and explanation in terms of segment protrusion are not inconsistent with such a description. The interphase treatment in particular calculates a parameter describing the probability of a chain segment residing in the outermost layer. This parameter exhibits a monotonic decrease as the segment position moves further from the headgroup. This same decrease was used in the segment protrusion model to explain the positional selectivity. Interphase theory has recently been shown to provide good agreement with small-angle neutron scattering (SANS) experiments.[66] These experiments have also concluded that no water penetration into the hydrocarbon core occurs.[66-68]

A second model, the **water penetration model**,[59] pictures the micelle with an ill-defined interface and with extensive water–hydrocarbon chain contact.[9,51,69-74] Although exact details vary, a current description[59] involves a small central hydrocarbon core of <50% of the micellar volume surrounded by a much larger region composed of hydrocarbon, water, headgroups, and counterions, and, perhaps the most controversial aspect, the existence within the micelle of "transient water-filled cavities". Positional selectivity as observed in this study is consistent with such a model, in terms of a water concentration profile which leads to a gradual decrease in water–hydrocarbon contact as the double bond position from the headgroup increases. However, other observations are perhaps not so consistent.

(i) In the water penetration model, the degree of water contact with chain segments should be a function of chain segment number only. Cis and trans isomers should experience the same medium and thus show a normal reactivity difference. In a similar way mono-, di-, and triolein should react at essentially the same rate.

(ii) Rates of micellar bromination seem too slow for a model with extensive water–alkene contact. The most reactive alkene 18Δ6c, for example, undergoes bromination 10^4–10^6 times slower than expected for an aqueous reaction, and differences for other alkenes are even greater. Some rate decrease is obviously expected for the water penetration model since the double bond is not entirely exposed to water, but the actual rate decrease appears too large to be consistent.

(iii) Large-terminal-alkene reactivities seem inconsistent with a simple water penetration model since as discussed in (i) the degree of water contact should be relatively independent of double bond position. This effect has been explained in terms of a "looping" process in which the terminal double bond has extensive water contact.[75] However, bromination reactivities are inconsistent with such a situation, rates for terminal alkenes being 10^3–10^5 slower than expected for an aqueous reaction. It can also be noted that SANS data have given no indication of looping in fully saturated micelles.[65]

(iv) The same reactivity trends observed in ionic micelles are observed in the non-ionic micelle and to roughly the same extent. There is some evidence that non-ionic micelles have dry hydrocarbon cores[76,77] and thus should have been different. The similar reactivity trends for both bromination and mercuration in SDS are also significant since these suggest that the two electrophiles are reacting in similar locations. On the basis of a water penetration model the bromination might have been expected to occur further into the interior, with mercuration more in the vicinity of the headgroup.

(v) Finally the bromination products in the charged micelles point to a reaction intimately associated with the headgroup region. A micelle with significant water penetration would be expected to give products more like those of an aqueous bromination. Particularly significant here is the complete absence of bromohydrin, the aqueous product, in CTAB micelles. The reaction region is undoubtedly polar and water must be present. As has been argued, however, the concentration of headgroup and counterions must be very high in this region, and a micelle with water pools seems inconsistent.

Summary. There is some current controversy over the structure of micelles[58,59] and a distinct possibility that even molecules as inoccuous as the fatty acid alkenes of this study can cause large perturbations and/or give misleading information. There can be no question that a number of micellar probes have suggested significant contact with polar or even aqueous media, and such an interpretation does explain at least some of the results for micellar bromination/mercuration. We feel, however, that a consideration of all the results, products and rates, leads to a consistent picture involving a more classical micelle, one with

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(66) Dill, K. A.; Koppel, D. E.; Cantor, R. S.; Dill, J. D.; Bendedouch, D.; Chen, S. H. *Nature (London)* **1984**, *309*, 42.
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segregated hydrocarbon and polar regions, a relatively dry hydrocarbon core, and significant water contact only at the core interface. Micellar chains are highly disordered, a point on which there is general agreement, and chain bending can place double bond segments part of the time at or near the interface where they will be exposed to water. If reaction occurs during that time it can take on some of the characteristics of an aqueous or polar process and thus give misleading information about the overall exposure of the hydrocarbon to water. A process such as segment protrusion accounts for apparent polar micellar reactivities without having to propose significant water penetration into the micelle.

Acknowledgment. The continued support of NSERC Canada is gratefully acknowledged. R.B.L. thanks the Government of Ontario and NSERC for the provision of fellowships.

Registry No. CTAB, 57-09-0; CTAC, 112-02-7; SDS, 151-21-3; Brij-35, 9002-92-0; (*Z*)-6-octadecenoic acid, 593-39-5; (*Z*)-6-octadecen-1-ol, 2774-87-0; (*Z*)-9-octadecenoic acid, 112-80-1; (*Z*)-9-octadecen-1-ol, 143-28-2; methyl (*Z*)-9-octadecenoate, 112-62-9; (*E*)-9-octadecenoic acid, 112-79-8; (*E*)-9-octadecen-1-ol, 506-42-3; (*E*)-11-octadecenoic acid, 693-72-1; (*Z*)-13-docosenoic acid, 112-86-7; (*Z*)-13-docosen-1-ol, 629-98-1; methyl (*Z*)-13-docosenoate, 1120-34-9; (*E*)-13-docosenoic acid, 506-33-2; (*Z*)-15-tetracosenoic acid, 506-37-6; [(*R*)-(*E*)]-12-hydroxy-9-octadecenoic acid, 540-12-5; (*Z*,*Z*)-9,12-octadecadienoic acid, 60-33-3; (*Z*,*Z*,*Z*)-9,12,15-octadecatrienoic acid, 463-40-1; 1-monooleoyl-*rac*-glycerol, 30836-40-9; dioleoylglycerol, 25637-84-7; 1,2,3-trioleoylglycerol, 122-32-7; dimethyl (*E*)-13-hexacosendioate, 102072-63-9.

A N–N Three-Electron σ Bond. Structure of the Radical Cation of *N*,*N*′-Trimethylene-*syn*-1,6:8,13-diimino[14]annulene as Studied by ESR Spectroscopy and X-ray Crystallographic Analysis

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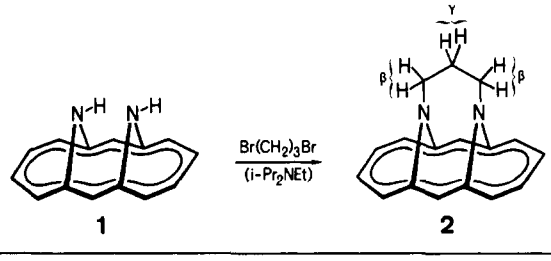
Abstract: *N*,*N*′-Trimethylene-*syn*-1,6:8,13-diimino[14]annulene (**2**), synthesized from the parent diimino[14]annulene (**1**), is easily oxidized in solution to its radical cation $\mathbf{2}^{\bullet+}$ ($E_{1/2}$ = +0.24 V vs. SCE). The high thermodynamic and kinetic stability as well as the large ^{14}N hyperfine coupling constant (1.685 mT) strongly suggest that $\mathbf{2}^{\bullet+}$ is a N-centered radical cation with a N–N three-electron σ bond formed upon oxidation of **2**. This structure is fully confirmed by an X-ray analysis carried out on the red-brown crystals of $\mathbf{2}^{\bullet+}ClO_4^-$. A substantial decrease in the N–N interatomic distance from 2.705 Å in **2** to 2.160 Å in $\mathbf{2}^{\bullet+}$ is associated with a flattening of the 14-membered perimeter.

Reaction of *syn*-1,6:8,13-diimino[14]annulene (**1**)[2] with 1,3-dibromopropane in the presence of *N*-ethyldiisopropylamine (150 °C, 48 h) affords the *N*,*N*′-trimethylene derivative **2**[3] in moderate yield. Bearing a close structural relationship to 1,5-diazabicyclo[3.3.3]undecane,[4] a medium-ring bicyclic diamine, the compound **2** should be subject to interesting chemical transformations not only at the peripheral annulene ring but also at the N–$(CH_2)_3$–N bridging group.



1 **2**

The cyclic voltammogram of **2** exhibits a reversible oxidation wave at +0.24 V (vs. SCE), as compared to +0.78 V for an irreversible wave of **1**.[5] Accordingly, **2** is easily oxidized to a thermodynamically stable radical cation $\mathbf{2}^{\bullet+}$ by a variety of agents such as Pb^{4+}, NO^+, Ag^+, and tris(*p*-bromophenyl)amminium cation. The kinetic stability (persistence) of $\mathbf{2}^{\bullet+}$ depends sensitively on the nature of the counterion; under favorable conditions (exclusion of air, with ClO_4^- as the counterion), the half-life of $\mathbf{2}^{\bullet+}$ in solution is of the order of weeks.[6]

Figure 1 shows the ESR spectrum of $\mathbf{2}^{\bullet+}$ observed at 298 K upon reaction of **2** with the $SbCl_5^-$ salt of the amminium cation in dichloromethane (g = 2.0036 ± 0.0001). Because of the trimethylene chain undergoing conformational interconversion at a rate (k) comparable to the hyperfine time scale ($\sim 10^7$ s^{-1}), several groups of lines in the spectrum are broadened beyond detection;[7] they appear in the fast exchange limit ($k > 5 \times 10^8$ s^{-1}) attained above 400 K.[8] Although poor solubility of the salts of $\mathbf{2}^{\bullet+}$ at temperatures lower than 250 K makes ESR studies in the slow exchange limit ($k < 10^6$ s^{-1}) experimentally inaccessible, an activation barrier, E_a, of 6.8 ± 0.9 kcal/mol (28 ± 4 kJ/mol) could be derived for the interconversion process.[9] Analysis of

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(3) Characterization of **2**: reddish-brown crystals (from ether), mp 154–155 °C; ^1H NMR (300 MHz, CD_2Cl_2) δ 0.19 (quint., 2 H), 1.24 (t, 4 H), 7.42 and 7.76 (AA′BB′, 8 H), 9.09 (s, 2 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 22.70, 50.31, 118.89, 128.98, 133.49, 140.95; MS (70 eV) *m*/*z* 248 (M^+, 100), 220 (53), 206 (27), 191 (28), 178 (26); IR (CsI) 3037, 1514 cm^{-1}; UV–vis (MeOH) λ_{max} = 295 nm (ϵ = 144 000), 372 (7600), 438 (1100) (sh), 572 (480). Andree, R. Dissertation, Universität Köln, 1985. Vogel, E.; Andree, R.; Marco, J. A.; Zeng, X., to be published.

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(5) Working electrode, platinum disk; counter electrode, glassy carbon; solvent, acetonitrile; supporting salt, Et_4NBF_4; temperature, 298 K; voltage scan, 200 mV/s.

(6) UV–vis spectrum of $\mathbf{2}^{\bullet+}ClO_4^-$ (MeOH): λ_{max} = 295 nm (ϵ = 92 000), 356 (4500), 375 (4700), 445 (500), 500 (550), 518 (530) (sh), 590 (ca. 50) (sh).

(7) For a closely analogous example see: Gerson, F., *High-Resolution ESR Spectroscopy*; Wiley: New York; Verlag-Chemie: Weinheim, 1970; Chapter A.2.3.

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