316 (M*+ + 2, 32.30% relative to M*+), 314 (M*+), 279 (100, M*+ - Cl). Anal. Calcd for C17H18ClF3: C, 64.87; H, 5.76. Found: C, 64.68; H, 5.68.

2-Chloro-2-[4-(trifluoromethyl)phenyl]adamantane (2f): yield 73%; mp 88-88.5 °C; ¹H NMR (CDCl₃) δ 1.79 (broad s, 7 H, protons at C6, C7, C8, C10), 1.85, 1.90, 2.62, 2.69 (4s, 4 H, protons at C4 and C9), 2.00 (s, 1 H, proton at C5), 2.88 (s, 2 H, protons at C1 and C3), 7.66 (s, 4 H, C₆H₄); ¹⁹F NMR (CDCl₃) δ -13.93 (s, CF₂); ¹³C NMR²⁵ (CDCl₃) § 26.65 (C5), 27.07 (C7), 33.68 (C4, C9), 34.93 (C8, C10), 37.18 (C1, C3), 37.95 (C6), 96.16 (C2), 125.56 (C2', C6'), 125.72 (d, C3', C5', J = 2.77 Hz), 129.51 (d, C4', J = 32.00 Hz), 148.11 (C1'); IR (KBr) ν_{max} 3066, 1612, 1448, 793 (C₆H₄), 2932, 2907, 2861, 2656 (CH₂), 1322, 1164, 1125 (CF₃) cm⁻¹; MS m/z (12 eV) 316 (M⁺⁺ + 2, 33.0% relative to M⁺⁺), 314 (M⁺⁺) 279 (100, M^{*+} – Cl). Anal. Calcd for $C_{17}H_{18}ClF_3$: C, 64.87; H, 5.76. Found: C, 65.14; H, 5.67.

Kinetic Measurements. Conductimetric rate constants were measured, with the exception of studies in acetic acid, using an automatically PC-AT- or XT-monitored multichannel conductivity rate measuring system developed in this laboratory.²⁶ The

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conductivity cells were placed in the thermostat with a temperature variation of ± 0.02 °C. Solutions of $10^{-4}-10^{-5}$ M were employed in this study. In some cases, the addition of a small amount of 2,6-lutidine to the solution was found to be necessary to prevent curvature of the rate constant plot.

For acetolysis, a solution of 0.01 M was prepared and aliquots of 2 mL were titrated using the modified Volhard method.²⁷

All reactions were followed to two or more half-lives and gave excellent first-order behavior with correlation coefficients of greater than 0.99. Arrhenius plots of rate data obtained at other temperature were used to estimate rate constants at 25 °C that could not be measured directly. Each rate constant was determined at least in duplicate, and the deviation was in general smaller than 5%. The mean values of these data are listed in Table I.

Acknowledgment. We are indebted to the National Science Council for financial support of this research and to Dr. T. W. Bentley for stimulating correspondence and a preprint.

(27) Fainberg, A. H.; Winstein, S. J. Am. Chem. Soc. 1956, 78, 2770.

Micellar Effects upon Alkene Bromination. 2. The Role of Alkene Hydrophobicity[†]

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Surface polarity of cetyltrimethylammonium bromide (CTAB) aqueous micelles was checked by use of as a probe the bromination reaction of a series of 1-alkenes and a water-soluble alkene, cis-4-cyclohexene-1,2-dicarboxylic acid dimethyl ester (I). There was strong inhibition $(10^{5}-10^{6}-fold)$ of the second-order reaction rate constants relative to those in water; moreover, both kinetics and the product distributions suggested that alkenes had different locations at the micellar surface. Kinetics in the presence of added NaBr and n-decane supported this location hypothesis.

Introduction

Alkene bromination with molecular bromine has been extensively investigated in homogeneous solution,¹ and the reaction rate is very sensitive to medium polarity.² Few studies have dealt with the reaction in micelles.³ Here, we use medium sensitivity as a probe of micellar surface polarity.

The rate expression (1)

rate =
$$(k_2[Br_2] + k_2'[Br_3] + k_3[Br_2]^2)[alkene]$$
 (1)

for homogeneous alkene bromination has three terms;^{1c,d} concentrations of bromine and tribromide are related by equilibrium (2), which is also affected by medium polarity.

$$\mathbf{Br}_2 + \mathbf{Br} \xrightarrow{\mathbf{K}} \mathbf{Br}_3$$
 (2)

It is usually difficult to carry out a kinetic micellar investigation on a reaction that obeys a complex kinetic law, but by choice of conditions, eq 1 is simplified to a one-term equation and observed rate constants can be used to calculate second-order rate constants at the micellar surface.

In this paper, we report data on bromination of a series of 1-alkenes and of the water-soluble cis-4-cyclohexene-1,2-dicarboxylic acid dimethyl ester (I) in the presence of



cetyltrimethylammonium bromide (CTAB). Since micelles affect rates of bimolecular nonsolvolytic reactions by acting as a pseudophase,⁵ rate effects need to be analyzed

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^{(1) (}a) Buckles, R. E.; Juk, J. P. J. Am. Chem. Soc. 1953, 75, 5049. (b) Rolston, S. H.; Yates, K. J. Am. Chem. Soc. 1969, 91, 1469. (c) Schmid, G. H.; Garratt, D. G. The Chemistry of Doubly Bonded Functional Groups; J. Wiley and Sons: New York, 1982. (d) De la Mare, P. B. D.; Bolton, R. Electrophilic Additions to Unsaturated Systems, 2nd ed.; Elsevier: New York, 1982. (e) Fukuzumi, S.; Kochi, J. K. J. Am. Chem.

^{Elsevier: New York, 1982. (e) Fukuzumi, S.; Kochi, J. K. J. Am. Chem.} Soc. 1982, 104, 7599.
(2) Garnier, F.; Dubois, J. E. Bull. Soc. Chim. Fr. 1968, 3797.
(3) (a) Bianchi, M. T.; Cerichelli, G.; Mancini, G.; Marinelli, F. Tet-rahedron Lett. 1984, 25, 5205. (b) Mizutani, T.; Whitten, D. G. J. Am. Chem. Soc. 1985, 107, 3621. (c) Lennox, R. B.; McClelland, R. A. J. Am. Chem. 1986, 108, 3771. (d) Ramesh, V.; Labes, M. M. J. Am. Chem. Soc. 1986, 108, 4643. (e) Cerichelli, G.; Grande, C.; Luchetti, L.; Mancini, G.; Bunton, C. A. J. Org. Chem. 1987, 52, 5167. Bunton, C. A. J. Org. Chem. 1987, 52, 5167. (4) (a) De la Mare, P. B. D. Electrophilic Halogenation; Cambridge

University: Cambridge, England, 1976; p 26. (b) Ruasse, M. F.; Aubard, J.; Galland, B.; Adenier, A. J. Phys. Chem. 1986, 90, 4382.

Table I. Effect of NaBr on Rates of Bromination of cis-4-Cyclohexene-1,2-dicarboxylic Acid Dimethyl Ester (2.30 × 10⁻⁴ M Alkene, 1.50 × 10⁻⁵ M Br₂, 5.00 × 10⁻³ M HCl; $T = 25.0 \pm 0.1$ °C)

X - 20.V	± v.1 0/	
[NaBr], M	$K_{2_{\rm obs}}$, s ⁻¹ M ⁻¹	
 1.26×10^{-2}	9.48×10^{5}	
2.52×10^{-2}	8.57×10^{5}	
3.78×10^{-2}	6.48×10^{5}	
5.10×10^{-2}	6.26×10^{5}	
1.00×10^{-1}	6.13×10^{5}	

quantitatively by taking into account distributions of both reactants between water and micelles.⁶ The treatment is simplified with such substrates as the alkenes we used that have extremely low solubilities in water, so they are fully bound to micelles. In addition, we show that Br_2 is converted quantitatively into Br3⁻ in the presence of micellized CTAB.

Results

First-order rate constants were measured by following decreasing absorbance of tribromide ion with excess of alkene. The excellent linearity of the first-order plots (cc >0.9998) rules out any significant contribution from the third-order term (equilibrium 1), which is relevant only for reaction in apolar solvents at high concentrations of molecular bromine. The presence of bromide ions and the low polarity of the micellar surface shift equilibrium 2 to give quantitative formation of tribromide ion,^{3a,7,8} which then is the only brominating agent. We generally added 5×10^{-3} M HCl to suppress formation of HOBr, although in CTAB equilibrium so strongly favors Br_3^- that rates did not change on addition of HCl. First-order rate constants vary linearly with alkene concentrations (cc > 0.9997) for the reactions in the presence of CTAB and for reaction of I in water (the other alkenes are too insoluble to be used in water).

In dilute bromine, the kinetic data for reaction of I in water fit equation 3.

rate =
$$(k_2[Br_2] + k_2'[Br_3])[alkene]$$
 (3)

The overall second-order rate constant, k_{2obs} , follows eq 4,9 which allows calculation of k_2 and k_2' if \tilde{K} (equilibrium 2) is known.

$$k_{2_{obs}}(1 + K[Br^{-}]) = k_2 + k_2' K[Br^{-}]$$
(4)

Table I lists results for bromination of I in water with added NaBr. A plot of $k_{2_{obs}}(1 + K[Br])$ vs [NaBr] gives second-order rate constants $k_2' = 3.28 \times 10^5 \text{ s}^{-1} \text{ M}^{-1}$ and $k_2 = 1.06 \times 10^6 \text{ s}^{-1} \text{ M}^{-1}$ for reactions of Br₃⁻ and Br₂, re-

1979, 52, 3171. (b) Cuccovia, I. M.; Chaimovich, H. Anal. Chem. 1982, 54, 789.



Figure 1. Rate-surfactant profiles. Key: Δ , 1-hexene; O, 1heptene; D, 1-octene; X, 1-decene; •, 1-dodecene; *, I.

spectively, by using K = 16.9

The rate constants of 1-alkenes could not be directly determined in water because of their low solubility; they were estimated referring to propene rate constants in water⁹ ($k_2 = 4.5 \times 10^6$, $k_2' = 3.2 \times 10^6$, s^{-1} M⁻¹). This is reasonable since propene and 1-pentene show very similar reactivities in bromination in MeOH,10 AcOH,10 and $MeOH/H_2O$ (7/3).¹¹ We also carried out competitive experiments with 1-hexene, 1-octene, 1-decene, and 1-dodecene, using molecular bromine and tribromide ion as brominating agents in various solvents, and found that 1-alkene reactivity was independent of chain length; in fact, we obtained an equimolar amount of bromination products from the four olefins in all conditions. Moreover, bromination of 1-hexene, 1-heptene, 1-octene, 1-decene, and 1-dodecene in MeOH (Scheme I) allowed us to rule out any dependence of bromonium ion reactivity on the chain length, since the percentages of methyl ethers and dibromoderivatives were the same for the five alkenes, with and without added NaBr.

Rate-surfactant profiles for bimolecular reactions in the presence of micellized surfactants usually show a characteristic shape with rate maxima¹² corresponding to a maximum in the product of concentrations in the micellar pseudophase. Additional surfactant dilutes reactants by increasing the total volume of the micellar pseudophase and consequently decreases reaction rate. Despite this decrease, observed rates are generally higher than those in water because concentration of reactants offsets the often lower micellar second-order rate constants. Ratesurfactant profiles (Figure 1) show an unusually sharp decrease of reaction rates with increasing CTAB concentration as compared with those usually seen¹³ so that second-order rate constants must be much higher in water than in micelles.

⁽⁵⁾ Fendler, J. H. Membrane Mimetic Chemistry; Wiley-Interscience, New York, 1982.

^{(6) (}a) Martinek, K.; Yatsimirski, A. K.; Levashov, A. V.; Berezin, I. V. In Micellization, Solubilization and Microemulsions; Mittal, K. L., Ed.; Plenum: New York, 1977; Vol. 2, p 489. (b) Romsted, L. S. Mi-cellization, Solubilization and Microemulsions; Mittal, K. L., Ed.; Plecetization, Solubilization and Microemulsions; Mittal, K. L., Ed.; Plenum: New York, 1977; Vol. 2, p 509. (c) Bunton, C. A. Catal. Rev.-Sci. Eng. 1979, 20, 1. (d) Sudholter, E. J. R.; Van der Langkruis, G. B.; Engberts, J. B. F. N. Recl.; J. R. Neth. Chem. Soc. 1980, 99, 73. (e) Romsted, L. S. Surfactants in Solution; Mittal, K. L., Lindman, B., Eds.; Plenum: New York, 1984; Vol. 2, p 1015. (7) (a) Hayakawa, K.; Kanda, M.; Sataki, I. Bull. Chem. Soc. Jpn. 1979, 59, 2171. (b) Cupconic L. M.; Chemani, C. M. and Chem. 2007.

⁽⁸⁾ Dodecyltrimethylammonium chloride (DTAC) micelles produce a 50-fold increase in equilibrium formation of $I_3^{-,74}$ This equilibrium and that for formation of I_2Br^- are also strongly affected by CTAB.^{7b} We observed that an aqueous solution of dodecyltrimethylammonium bromide (DTAB) and Br₂ loses bromide as red fumes at 40 °C, even though equilibrium (2) is strongly shifted to Br_3^- by this surfactant, but an aqueous solution of Br_2 and CTAB does not lose Br_2 at 90 °C.^{3a} It is reasonable to assume that K for formation of Br_3^- in CTAB has a value of 104-105 M-1.

⁽⁹⁾ Atkinson, J. R.; Bell, R. P. J. Chem. Soc. 1963, 3260.

Ruasse, M. F.; Zhang, B. L. J. Org. Chem. 1984, 49, 3207.
 Modro, A.; Schmid, H. G.; Yates, K. J. Org. Chem. 1977, 42, 3673.

⁽¹²⁾ Bunton, C. A.; Cerichelli, G.; Ihara, Y.; Sepulveda, L. J. Am. Chem. Soc. 1979, 101, 2429.

⁽¹³⁾ Bunton, C. A.; Savelli, G. Adv. Phys. Org. Chem. 1985, 22, 213.

Table II. Second-Order Rate Constants for Alkene Bromination in Water (2.30 × 10⁻⁴ M Alkene, 1.50 × 10⁻⁵ M Br₂, 5.00 × 10⁻³ M HCl; T = 25.0 ± 0.10 °C) and CTAB (1.00 × 10⁻⁴ M Alkene, 1.30 × 10⁻⁵ M Br₂, 5.00 × 10⁻³ M HCl; T = 25.0 ± 0.10 °C)

	[NaBr], M	1-hexene	1-heptene	1-octene	1-decene	1-dodecene	I	
 H ₂ O ^a k ₂ s ⁻¹ M ⁻¹		3.20×10^{6}	3.28×10^{5}					
$\begin{array}{c} \text{CTAB} \\ k_2^{\text{m}} \text{ s}^{-1} \text{ M}^{-1} \end{array}$	10 ⁻⁴ 10 ⁻³	12.2	7.65	6.91	3.41	6.02	1.28 1.30 1.30	
	10 ⁻² 10 ⁻¹	10.6 1.90	6.61 2.00	6.00 1.90	1.52 1.33	3.81 1.82	0.94 0.62	

^a1-Alkene constant values were estimated from propene.⁹



Figure 2. Plot for the calculation of 1-dodecene micellar rate constant.

We calculated micellar second-order rate constants by using the pseudophase model,⁶ considering distributions of reactants between water and micelles and constants for equilibrium 2 in water and in the micellar pseudophase. In principle, we have four possible reactions: two in water by molecular bromine and by tribromide ion and the corresponding reactions in the micellar pseudophase. In our conditions, this situation is simplified because the alkenes are totally bound to the micelles and CTAB favors conversion of Br₂ into Br₃⁻ so strongly that equilibrium 2 is widely in favor of Br₃⁻ and CTABr₃ can be isolated as a stable solid.^{3a,7,8} Consequently, the reaction takes place only in the micellar pseudophase and Br₃⁻ is the only brominating agent.

Equation 5 fits rate-surfactant profiles for many micellar-assisted bimolecular reactions^{6,14} and is used here.

$$k_{2_{\rm ann}} = k_{\rm m} K_{\rm s} f / (1 + K_{\rm s} [{\rm Dn}])$$
 (5)

In this equation, $k_{2_{app}}$ is the overall second order rate constant, k_m is the second order rate constant in the micellar pseudophase with alkene concentration written as a mole ratio with respect to micellized CTAB, K_s is the binding constant of Br_3 , $f = [alkene_{micelle}]/[alkene_{total}]$, and Dn is the micellized surfactant. There is evidence^{3a,7,8} that Br_2 is converted completely into Br_3 , which in excess of CTAB is fully micellar bound, so that

$$k_{2_{\rm mn}} = k_{\rm m} / [{\rm Dn}] \tag{6}$$

Plots of $1/k_{2np}$ against [D_n] are linear as shown for reaction of 1-dodecene (Figure 2).

In order to obtain the micellar second-order rate constant k_2^{m} (s⁻¹ M⁻¹), which can be compared with k_2' (s⁻¹ M⁻¹) in water (eq 3), we must consider the molar volume

Table III. Observed Rate Constants for the Bromination of 1-Hexene in the Presence of *n*-Decane $(1.00 \times 10^{-4} \text{ M})$ 1-Hexene, $1.30 \times 10^{-5} \text{ M Br}_2$, $5.00 \times 10^{-3} \text{ M HCl}$; $T = 25.0 \pm 0.1 \text{ °C}$

$1 - 23.0 \pm 0.1$ C)				
[CTAB], M	[decane], M	[NaBr], M	$k_{\rm app}, {\rm s}^{-1}$	
0.018			0.53	_
0.018	2.00×10^{-4}		0.62	
0.020		0.01	0.38	
0.020	2.00×10^{-4}	0.01	0.44	
0.020		0.10	0.07	
0.020	2.00×10^{-4}	0.10	0.14	
0.023			0.46	
0.022	2.00×10^{-4}		0.58	

Table IV. Product Distribution for Bromination in Dilute Solution (2.50 × 10⁻² M CTAB, 2.00 × 10⁻⁴ M Alkene, 1.00 × 10^{-4} M Br₂, 5.00 × 10⁻³ M HCl; $T = 25.0 \pm 0.1$ °C)

alkene	% bromohydrins	% dibromide	
1-hexene	90	10	
1-heptene	63	37	
1-octene	50	50	
1-decene	38	62	
1-dodecene	45	55	
I	70	30	

of the shell at the micellar surface in which reaction takes place. This volume has been estimated in a range of 0.14-0.37 L⁶ and we use the lower limit so that

$$k_2^{\rm m} = 0.14k_{\rm m}$$
 (7)

There is extensive evidence¹³ showing that second-order rate constants for many bimolecular reactions are similar in water and micelles within ~ 1 order of magnitude. There are larger differences for spontaneous reactions,^{13,15} but even here rate constants in micelles are not very different from those in water, although in a few cases they are lower, or higher, by up to 3 orders of magnitude. Values of k_2^m for bromination of 1-alkenes and I in the presence of CTAB are reported in Table II. There is a huge inhibition with respect to reaction in water by 5-6 orders of magnitude as expected on the basis of ratesurfactant profiles (Figure 1). This behavior is highly unusual because second-order rate constants in micelles are typically similar to those in water.¹³ Moreover, on a closer inspection, the alkene structure appears to affect micellar second-order rate constants k_2^{m} , unlike the behavior in homogeneous solution.^{10,11} The micellar rate constants decrease with increasing chain length of the alkene except for an inversion between 1-decene and 1dodecene (Table II). This inversion could suggest that

^{(14) (}a) Quina, F. H.; Chaimovich, H. J. Phys. Chem. 1979, 83, 1844.
(b) Abuin, E. B.; Lissi, E.; Araujo, P. S.; Aleixo, R. M. V.; Chaimovich, H.; Bianchi, N.; Miola, L.; Quina, F. H. J. Colloid Interface Sci. 1983, 96, 293. (c) Romsted, L. S. J. Phys. Chem. 1985, 89, 5107.

^{(15) (}a) Bunton, C. A.; Minch, M. J.; Hildalgo, J.; Sepulveda, L. J. Am. Chem. Soc. 1973, 95, 3262. (b) Menger, F. M.; Yoshinaga, H.; Venkatasubban, K. S.; Das, A. R. J. Org. Chem. 1981, 46, 415. (c) Ramachandran, C.; Pyter, R. A.; Mukerjee, P. J. Phys. Chem. 1982, 86, 3198. (d) Al-Lohedan, H.; Bunton, C. A.; Mhala, M. M. J. Am. Chem. Soc. 1982, 104, 6654. (e) Bunton, C. A.; Ljunggren, S. J. Chem. Soc., Perkin Trans. 2, 1984, 355. (f) Van der Langkruis, G. B.; Engberts, J. B. F. N. J. Org. Chem. 1984, 49, 4152.

Table V. Product Distribution for Bromination in Preparative Conditions $(5.00 \times 10^{-2} \text{ M CTAB}, 1.00 \times 10^{-2} \text{ M})$ Alkene, $1.00 \times 10^{-2} \text{ M Br}_2, 5.00 \times 10^{-3} \text{ M HCl};$ $T = 25.0 \pm 0.1 \circ C$

	$T = 25.0 \pm 0.1$ °C)	
alkene	% bromohydrins	% dibromide
1-hexene	85	15
1-heptene	50	50
1-octene	12	88
1-decene	6	94
1-dodecene	8	92
I	50	50
	Scheme II	
Br ₃ + alkene	B	r + 2Br

1-decene induces a change in the aggregate surface that causes the lower reactivity. In order to test this hypothesis, we examined bromination of 1-hexene in the presence of equimolar n-decane. Results of this investigation are reported in Table III and show that bromination of 1-hexene in the presence of *n*-decane is faster than bromination of 1-hexene by itself.

Changing the structure of the alkene also affects product distributions. The yield of bromohydrin decreases on increasing the chain length of the alkene (Tables IV and V give data under kinetic and preparative conditions, respectively), and again there is an inversion between 1decene and 1-dodecene.

Addition of NaBr further inhibits the reaction rates (Table II), and again the extension of inhibition depends on alkene structure.

Discussion

The most evident result of our investigation is the huge rate inhibition of the bromination reaction (by 5-6 orders of magnitude, Table II) in CTAB micelles. We have a similar inhibition for the 1-alkenes and for cis-4-cyclohexene-1,2-dicarboxylic acid dimethyl ester (I) that we used in order to have a direct measure in water, despite the fact that in one case we had a cis double bond that was the less polar part of a flat molecule so that the double bond came out to be the hydrophobic portion of the molecule and in the other case we had a terminal double bond that was the polar (or the less apolar) part of a linear molecule, so that we did not think that the reactivity of the two kinds of double bond in the presence of CTAB could be directly compared.

We ascribe the inhibition, at least partially, to the medium polarity. The polarity of a micellar surface is lower than that of water;¹⁵ consequently, a micellar pseudophase disfavors, relative to water, a reaction (Scheme II) that involves charge separation.¹⁶

Inhibition by micellar surface was also observed in spontaneous solvolyses in the presence of both cationic and anionic surfactants.^{13,15} What is unusual in our results is the magnitude of the rate effect, since the inhibition observed in spontaneous reactions is usually within 1-3 orders^{13,15} of magnitude and is very much less for bimolecular reactions. Bromination of 1-pentene in aqueous alcohol is of 2-3 orders of magnitude slower than bromination in water.² Consequently, a polarity of the micellar surface similar to that of aqueous ethanol^{15f} can only partially

explain the observed inhibition. We think that most of the inhibition must therefore be ascribed to initial-state stabilization in CTAB relative to water. The tribromide ion is strongly stabilized by CTAB micelles;^{3a,7,8} the loss of this stabilization in transition state formation will markedly slow reaction in the micellar pseudophase.

Table II illustrates differences in micellar second-order rate constants of 1-alkenes, which depend on chain lengths although they do not affect reactivities in homogeneous solutions. It seems reasonable to ascribe these reactivity differences to different polarities of the micro environment at the micellar surface, where polarity is high close to the water interface and decreases toward the core where the water content is low. Consequently, the different reactivities correspond to different locations of the double bond of the alkenes in the micelles. We assume that the longer the alkene chain the deeper the location of the double bond in the micelle: a deeper location means a less polar medium and a slower reaction. There is an exception to this generalization since 1-dodecene is more reactive than 1-decene, and according to our hypothesis that correlates reactivity to the polarity of the medium and thus to location of the alkenes, we must postulate the deepest location for 1-decene. This hypothesis is strongly supported by product distributions as well as by kinetic experiments in 10⁻² and 10⁻¹ M added NaBr (Table II) and in 2×10^{-4} added *n*-decane. The trend of product distribution (Table IV), with the inversion for 1-decene, parallels the kinetic trends. The decrease in bromohydrin product corresponds to a decrease in reactivity. Decreased polarity and decreased water content should decrease formation of the bromohydrin. 1-Decene gives the least bromohydrin, corresponding to its postulated location in a region of relatively low polarity.

Our kinetic and product evidence suggest that average locations of the reactive centers of the alkenes at the micellar surface depend on the chain length of the alkene, and paradoxically that for 1-decene the double bond is in a less polar environment than for other alkenes of longer and shorter chain lengths. Micellar structure is very sensitive to packing of the alkyl tails that may be disrupted by insertion of a solute into the micellar core.¹⁷ A short chain length alkene will not be drawn very deeply into the micellar core and may fit into openings or defects at the surface, but deep insertion of a very long chain alkene will disrupt surfactant packing in the core. Therefore, there should be some optimum chain length that gives the deepest location of the double bond, and we suggest that this is the situation for 1-decene in CTAB.

An alternative explanation is that there are deep clefts in the micelle that can readily accommodate solutes with particular chain lengths.¹⁸

Effects of added NaBr (Table II) fit either hypothesis. Bromide ions strongly interact with the surface of the micelle.¹⁹ and we believe that relatively low concentrations will first saturate the internal locations of the active surface. We observe (Table II) that reactivity does not vary significantly for low concentrations of bromide ion (1.00 \times 10⁻³, 1.00 \times 10⁻⁴ M) because the amount of added bromide ion is small compared to that already present and

^{(17) (}a) Gruen, D. W. R. J. Phys. Chem. 1985, 89, 146. (b) Gruen, D. W. R. J. Phys. Chem. 1985, 89, 153.

<sup>W. R. J. Phys. Chem. 1985, 89, 153.
(18) Menger, F. M. Acc. Chem. Res. 1979, 12, 111.
(19) (a) Herniksson, U.; Odberg, L.; Eriksson, J. C.; Westman, L. J.</sup> Phys. Chem. 1977, 81, 76.
(b) Lindblom, G.; Lindman, B.; Mandell, L. J. Colloid Interface Sci. 1977, 60, 232.
(c) Ulmius, J.; Lindman, B.; Lindblom, G.; Drakenberg, T. J. Colloid Interface Sci. 1978, 65, 88.
(d) Bacaloglu, R.; Bunton, C. A.; Cerichelli, G.; Ortega, F. J. Phys. Chem. 1989, 93, 1490.

⁽¹⁶⁾ Lowry, T. H.; Richardson, K. S. Mechanism and Theory in Organic Chemistry, 3rd ed.; Harper & Row: New York; 1987; Chapter 4, p 361.

does not affect the micellar surface. The first appreciable variation of reactivity occurs at 1.00×10^{-2} M bromide ion. This concentration has a remarkable effect on 1-decene and 1-dodecene reactivities and a small effect on the reactivity of all other alkenes; however, at this concentration the rate constant of 1-decene reaches its lowest value, and the rate constants of 1-dodecene and of the other alkenes reach their minima at 0.10 M NaBr. At this concentration of bromide, the rate constants of all the alkenes have all been leveled. In conclusion, at a concentration of $1.00 \times$ 10^{-2} M of bromide the alkenes still experience a different polarity and at a concentration 0.10 M they all feel the same polarity. These results favor our hypothesis that 1-decene is located in the micelle deeper than the other alkenes and consequently that its double bond is in the inner region of the active surface. This location will be saturated by a relatively lower concentration of bromide, while the outer regions will be saturated only by higher concentrations of salt. At the same time, 0.10 M NaBr causes CTAB micelles to grow^{19a-c} and become rodlike. probably due to a decrease in a head-group repulsions; this "closing-up" of the head groups due to their neutralization should decrease polarity of the surface and therefore k_0^m . The effect should be smaller if the double bond of 1-decene is deeper in the surface, as we suggest, because its environment should be less affected by added Br-, whose effect will be largest at the micelle-water interface. The two effects (saturation and growth) overlap, and we cannot tell which one prevails because they both decrease reactivity.

Addition of 10^{-4} M *n*-decane increases rates of bromination of 1-hexene in CTAB (Table III), although the alkane should, if anything, decrease micellar polarity and therefore decrease reactivity. The rate increase in understandable if *n*-decane saturates the deeper clefts on the micellar surface so that the 1-hexane double bond is pushed in a more polar region.

Experimental Section

 13 C NMR spectra were recorded on a Varian XL 300 spectrometer operating at 75.429 MHz in CDCl₃ as solvent, and chemical shifts are reported in ppm downfield from TMS. Typical acquisition conditions were as follows: 30° flip angle, 1s acquisition, no delay, 16000-Hz sweep width. Inverse gated decoupled spectra were obtained by using a 90° flip angle, 2-s acquisition, 18-s relaxation delay, 16000-Hz sweep width; the decoupler was turned off during the relaxation delay.

Gas chromatography/mass spectrometry analyses were obtained on a HP 5970B system coupled with a HP 5890 GC instrument by using a $12 \text{ m} \times 0.2 \text{ mm}$ silica capillary column coated with methyl silicone gum.

Reagents. CTAB (Fluka) was purified by the procedure of Duynstee and Grunwald.²⁰ Commercial 1-alkenes (Fluka) of the highest purity were used without further purification.

cis-4-Cyclohexene-1,2-dicarboxylic Acid Dimethyl Ester. A 6.13-g (40-mmol) portion of cis-4-cyclohexene-1,2-dicarboxylic acid anhydride (Fluka) and 0.40 g (40 mmol) of concentrated H₂SO₄ were added to 40 mL of methanol. After 18 h under reflux, the solvent was removed by rotary evaporation. The residue was dissolved in 100 mL of Et₂O and washed with 0.10 M Na₂CO₃, brine, and then dried over Na₂SO₄. Removal of ether by rotary evaporation yielded 6.98 g of a pale yellow oil that was identified by elemental analysis as the cis-4-cyclohexene-1,2-dicarboxylic acid dimethyl ester. Anal. Calcd for C₁₀H₁₄O₄: C, 60.59; H, 7.12. Found: C, 60.57; H, 7.99. ¹³C NMR: CH₃ δ = 51.21, CH₂ δ = 25.22, carboxylic carbons δ = 173.13, olefinic carbons δ = 124.60, CH δ = 39.13.

Product Standards. Bromohydrins. Bromohydrins were prepared according to Dalton and Jones.²¹ The alkene (10 mmol)

fraction was dried over MgSO4. Removal of ether by rotary evaporation yielded a colorless oil that was a mixture of two compounds in a ratio of 3/2 on the basis of GLC analysis. The two products were identified by elemental analysis and ¹³C NMR as the two isomeric bromohydrins, the major component being the 1-bromo-2-hydroxyalkane. Anal. Calcd for $C_6H_{13}BrO$: C, 39.80; H, 7.24; Br, 44.13. Found: C, 39.71; H, 7.22; Br, 44.10. ¹³C NMR: $CH_2OH \delta = 67.17$, $CHBr \delta = 59.84$, $CH_3 \delta = 13.86$, CH_2Br $\delta = 40.50$, CHOH $\delta = 70.98$, CH₃ $\delta = 13.93$. Anal. Calcd for $C_7H_{15}BrO: C, 43.09; H, 7.75; Br, 40.96.$ Found: C, 42.97; H, 7.71; Br, 40.95. ¹³C NMR: CH₂OH δ = 66.78, CHBr δ = 59.11, CH₃ $\delta = 13.78$; CH₂Br $\delta = 39.95$, CHOH $\delta = 70.60$, CH₃ $\delta = 13.80$. Anal. Calcd for C₈H₁₇BrO: C, 45.95; H, 8.19; Br, 38.21. Found: C, 45.85; H, 8.14; Br, 38.17. ¹³C NMR: CH₂OH δ = 67.29, CHBr δ = 60.16, $CH_3 \delta = 14.05$; $CH_2Br \delta = 40.68$, $CHOH \delta = 71.09$, $CH_3 \delta = 14.07$. Anal. Calcd for $C_{10}H_{21}BrO$: C, 50.64; H, 8.92; Br, 33.69. Found: C, 50.52; H, 8.86; Br, 33.67. ¹³C NMR: CH₂OH δ = 67.08, CHBr $\delta = 59.64$, CH₃ $\delta = 14.02$; CH₂Br $\delta = 40.33$, CHOH $\delta = 70.92$, CH₃ $\delta = 14.02$. Anal. Calcd for C₁₂H₂₅BrO: C, 54.34; H, 9.50; Br, 30.13. Found: C, 54.30; H, 9.48, Br, 29.96. ¹³C NMR: CH₂OH δ = 67.29, CHBr $\delta = 60.17$, CH₃ $\delta = 14.12$; CH₂Br $\delta = 40.67$, CHOH $\delta = 71.10$, CH₃ δ = 14.12. Anal. Calcd for C₁₀H₁₅BrO₅: C, 40.70; H, 5.12; Br, 27.07. Found: C, 40.68; H, 5.05; Br, 26.99. ¹³C NMR: CH₃ δ = 52.68, 52.11, CH₂ δ = 33.92, 33.45, carboxylic carbons δ = 171.78, 172.76, CH δ = 43.51, 40.95, CHBr δ = 58.09, CHOH δ = 71.61. The mass spectra (EI, 70 eV) of this class of compounds do not show the molecular ion.

was dissolved in DMSO (50 mL) containing water (25 mmol).

N-Bromosuccinimide (20 mmol) was added under N2. The so-

lution turned yellow and evolved heat; after 15 min of stirring,

the reaction was quenched by adding 20 mL of water. The

aqueous DMSO mixture was extracted with Et₂O and the ether

Dibromides. Bromine was added dropwise to a rapidly stirred 50-mL solution of 0.01 M alkene in CHCl₃ up to persistence of color. Removal of chloroform by rotary evaporation yielded a pale yellow oil. The product was pure by GLC analysis. The dibromides were characterized by elemental analysis and ¹³C NMR since the mass spectra (EI, 70 eV) of this class of compounds do not show the molecular ion. Anal. Calcd for $C_6H_{12}Br_2$: C, 29.54; H, 4.96; Br, 65.50. Found: C, 29.60; H, 4.87; Br, 65.47. ¹³C NMR: $CH_3 \delta = 13.86$, $CH_2Br \delta = 36.28$, $CHBr \delta = 52.98$. Anal. Calcd for $C_7H_{14}Br_2$: C, 32.59; H, 5.47; Br, 61.94. Found: C, 32.57, H, 5.41; Br, 61.96. ¹³C NMR: CH₃ δ = 13.99, CH₂Br δ = 36.35, CHBr δ = 53.14. Anal. Calcd for C₈H₁₆Br₂: C, 35.32; H, 5.93; Br, 58.75. Found: C, 35.25; H, 5.82; Br, 58.93. ¹³C NMR: CH₃ δ = 14.05, $CH_2Br \ \delta = 36.34$, $CHBr \ \delta = 53.12$. Anal. Calcd for $C_{10}H_{20}Br_2$: C, 40.03; H, 6.72; Br, 53.26. Found: C, 40.00; H, 6.68; Br, 53.32. ¹³C NMR: CH₃ δ = 14.10, CH₂Br δ = 36.26, CHBr δ = 53.02. Anal. Calcd for $C_{12}H_{24}Br_2$: C, 43.93; H, 7.37; Br, 48.70. Found: C, 43.84; H, 7.31; Br, 48.85. ¹³C NMR: CH₃ δ = 14.14, CH₂Br δ = 36.34, CHBr δ = 53.13. Anal. Calcd for C₁₀H₁₄Br₂O₄: C, 33.55; H, 3.94; Br, 44.64. Found: C, 33.51; H, 3.96; Br, 44.60. ¹³C NMR: CH₃ $\delta = 52.79, 51.89$, carboxilic carbons $\delta = 172.29, 172.08$, CH $\delta =$ 40.92, 39.85, CH₂ δ = 32.76, 32.72, CHBr δ = 51.94, 51.52.

Product Isolation and Identification. Reaction was carried out both in conditions that matched those of the kinetic experiments $(2.50 \times 10^{-2} \text{ M CTAB}, 2.00 \times 10^{-4} \text{ M alkene}, 1.00 \times 10^{-4} \text{ M Br}_2, 5.00 \times 10^{-3} \text{ M HCl}, 25.0 ^{\circ}\text{C})$ and in preparative conditions $(5.00 \times 10^{-2} \text{ M CTAB}, 1.00 \times 10^{-2} \text{ M alkene}, 1.00 \times 10^{-2} \text{ M Br}_2, 5.00 \times 10^{-3} \text{ M HCl})$. The reaction mixture was extracted with Et_2O , avoiding hard shaking in order to prevent emulsion formation; the ether fraction was washed with brine, dried over Na_2SO_4 , and concentrated by rotary evaporation. The concentrated solution was analyzed by GLC by comparison with standards. The two bromohydrins were in a ratio of 5/1, the larger being 1-bromo-2-hydroxyalkane.

Bromination in Methanol. Bromine (0.50 mmol) was added dropwise to 10^{-2} M alkene in 50 mL of MeOH. Removal of MeOH by rotary evaporation yielded a pale yellow oil that contained three products (one of which was the dibromide, 4%) by GLC analysis. After separation on silica gel using a mixture of petroleum ether (40-70 °C) and Et₂O (7/3) as eluent, the two remaining products were identified by elemental analysis and ¹³C NMR as the 1-

⁽²⁰⁾ Duynstee, E. F. J.; Grunwald, E. J. Am. Chem. Soc. 1959, 81, 4540.

⁽²¹⁾ Dalton, D. R.; Hendrickson, J. B.; Jones, D. Chem. Commun. 1966, 591.

bromo-2-methoxy- and 1-methoxy-2-bromoalkanes in a ratio of 1/1. The same experiment was also carried out in the presence of 0.10 M NaBr and yielded 36% dibromide. Anal. Calcd for C₇H₁₅BrO: C, 43.09; H, 7.75; Br, 40.96. Found: C, 43.01; H, 7.78; Br, 40.98. ¹³C NMR: CH₃O δ = 58.65, OCH₂ δ = 76.72, CHBr $\delta = 53.27$, CH₃ $\delta = 13.69$, CH₃O $\delta = 57.06$, CH₂Br $\delta = 34.34$, OCH $\delta = 80.02$, CH₃ $\delta = 13.81$. Anal. Calcd for C₈H₁₇BrO: C, 45.95; H, 8.19; Br, 28.21. Found: C, 45.90; H, 8.20; Br, 28.12. ¹³C NMR: CH₃O δ = 58.79; OCH₂ δ = 76.82; CHBr δ = 53.00; CH₃ δ = 13.94; $CH_{3}O \delta = 57.19$; $CH_{2}Br \delta = 34.49$; $OCH \delta = 80.12$; $CH_{3} \delta = 13.90$. Anal. Calcd for C₉H₁₉BrO: C, 48.44; H, 8.58; Br, 35.81. Found: C, 48.40; H, 8.49; Br, 35.78. ¹³C NMR: CH₃O δ = 58.44, OCH₂ $\delta = 76.62$, CHBr $\delta = 52.97$, CH₃ $\delta = 13.69$; CH₃O $\delta = 56.87$, CH₂Br $\delta = 34.03$, OCH $\delta = 79.95$, CH₃ $\delta = 13.71$. Anal. Calcd for $C_{11}H_{23}BrO: C, 52.59; H, 9.23; Br, 31.81.$ Found: C, 52.37; H, 9.30; Br, 31.60. ¹³C NMR: CH₃O δ = 58.78; OCH₂ δ = 76.86; CHBr $\delta = 52.99$; CH₃ $\delta = 14.01$; CH₃O $\delta = 57.19$; CH₂Br $\delta = 34.43$; OCH $\delta = 80.15$; CH₃ $\delta = 14.01$. Anal. Calcd for C₁₃H₂₇BrO: C, 55.91; H, 9.74; Br, 28.61. Found: C, 55.86; H, 9.71; Br, 28.59. ¹⁸C NMR: $CH_3O \delta = 58.65, OCH_2 \delta = 76.77, CHBr \delta 53.20, CH_3 \delta = 13.95;$

 $CH_3O \delta = 57.07$, $CH_2Br \delta = 34.24$, $OCH \delta = 80.11$, $CH_3 \delta = 13.95$. Bromination Kinetics. Solution of alkenes in CTAB were prepared by mixing stock solutions of 0.20 M alkene in MeOH (the percentage of alcohol in the final solution was <0.10 %), 0.05 M CTAB in water, and 5.00 M NaBr in water. The kinetic runs were performed on a Durrum-Gibson stopped-flow spectrophotometer at 25.0 ± 0.1 °C. Each run was performed six times, and the reproducibility was $\pm 3\%$ or better.

One syringe contained micellized alkene $(2.00 \times 10^{-4} \text{ M})$ and NaBr (when used), the other bromine and HCl (0.01 M). The acid was used in order to suppress HOBr formation and consequently the presence of another brominating agent. However, runs performed in absence of HCl agreed with those performed in its presence. Bromine concentration after mixing was $1.30 \times$ 10^{-5} M, and first-order conditions were maintained.

The kinetics of the bromination reaction of 1-hexane with 2 \times 10⁻⁴ M added *n*-decane were performed under the same conditions. For bromination of cis-4-cyclohexene-1,2-dicarboxylic acid dimethyl ester in water, one syringe contained 4.60×10^{-4} M alkene in water and the other 3.00×10^{-5} M Br₂, NaBr, and 1.00×10^{-2} M HCl. Reactions were followed by monitoring the decrease in absorbance at 270 nm. First-order rate constants were calculated by using the kinetic equation

$$\ln\left(\frac{A_{\infty}-A_{0}}{A_{\infty}-A_{t}}\right)=kt$$

The initial absorbance of Br₃⁻ in CTAB at 270 nm did not increase on addition of NaBr and for CTAB > cmc did not increase with added CTAB.

Competitive Kinetics. Bromine (40 mg, 0.25 mmol) was added dropwise to 25 mL of CHCl₃ containing 42 mg (0.50 mmol) 1hexene and an equimolar amount of another 1-alkene (1-octene, 1-decene, or 1-dodecene). The product composition was compared with standard solutions of dibromides by GLC. The same experiment was performed in CHCl_3 in the presence of 5.00×10^{-3} M Bu₄NBr and in MeOH with and without NaBr. Reaction of Br₂ was quantitative and equimolar products were isolated.

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Semiempirical Study of Electron Exchange Interaction in Organic High-Spin π Systems. Classifying Structural Effects in Organic Magnetic Molecules

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A semiempirical AM1 molecular orbital plus configuration interaction model is applied to π -conjugated organic open-shell molecules in order to understand qualitatively the manner and degree to which they are spin-coupled by various electronic mechanisms, either in simpler open-shell systems or, in some examples, in larger polyradicals. A "library" of spin-coupling spacer groups (X in radical-X-radical or nitrene-X-nitrene) is delineated with relative exchange interaction strengths and natures described, including alkenes and polyalkenes, alkynes, phenyl rings, heteroatoms, and nonalternant pseudoaromatic systems. Example systems in which ferromagnetic (high-spin) coupling is observed in diradical models are predicted to remain high-spin as higher oligomeric species with like connectivity. The implications of these semiquantitative computational predictions in relation to simple qualitative models of radical-radical spin coupling are discussed in several cases. Overall, the semiempirical MO-CI method is shown to be both conceptually useful and highly cost effective for semiquantitative study and classification of broad classes of electron exchange coupling effects in non-Kekulé molecules.

Introduction

Recently, there has been much interest in the synthesis of organic materials with magnetic properties for potential information storage purposes.^{1,2} Different groups have aimed variously at the synthesis of charge-transfer organometallic mixed-crystal materials,3 high-spin molecular ferromagnetic materials based upon ground-state paramagnetic crystalline materials,4,5 nonconjugated polynitroxide radicals,^{6,7} and π -conjugated polyradicals⁸⁻¹⁰ and

⁽¹⁾ Cf. the various papers in: Proceedings of the Symposium on Ferromagnetic and High-Spin Molecular Based Materials, 197th Na-tional Meeting of the American Chemical Society, Dallas, TX, Fall 1989; Miller, J. S., Dougherty, D. A., Eds.; American Chemical Society: Washington, DC, 1989, Mol. Cryst. Liq. Cryst. 1989, 176, 1ff. Some of

<sup>these are cited variously in the following references.
(2) Cf. Proceedings of Symposium Q, Materials Research Society</sup> Meeting, Boston, MA, Nov 1989; Chiang, L. Y., Chaikin, P. M., Cowan, D. O., Eds.; Materials Research Society: Pittsburgh, PA, 1990. Mater. Res. Soc. Symp. Ser. 1990, 173, 1 ff.

⁽³⁾ Miller, J. S.; Epstein, A. J.; Reiff, W. M. Chem. Rev. 1988, 88, 201;

 ⁽d) Millet, S. S., Elsteini, A. S., Nelli, W. M. Chem. Rev. 1985, 35, 201,
 (d) Breslow, R. Pare Appl. Chem. 1982, 54, 927; Mol. Cryst. Liq. Cryst.
 1985, 125, 261. Breslow, R.; Jaun, B.; Klutz, R.; Xia, C.-Z. Tetrahedron
 1982, 38, 863. LePage, T. J.; Breslow, R. J. Am. Chem. Soc. 1987, 109,
 6412. Thomaides, J.; Maslak, P.; Breslow, R. J. Am. Chem. Soc. 1988,

 <sup>110, 3970.
 (5)</sup> Awaga, K.; Maruyama, Y. J. Chem. Phys. 1989, 91, 2713. Awaga,
 K.; Inabe, T.; Maruyama, Y. Mater. Res. Soc. Symp. Ser. 1990, 173, 33.