217-219 °C (from ethyl acetate). The spectral properties of this compound were identical with those of the urazole isolated above.

Conversion of 14 to 16. A mixture of **14**[14] (101 mg, 0.316 mmol), *N*-bromosuccinimide (63.7 mg, 0.358 mmol), and a little AIBN in dry carbon tetrachloride (25 mL) was irradiated as before for 4 h. The cooled reaction mixture was filtered, washed with saturated sodium bicarbonate solution (3 × 10 mL), dried, filtered, and evaporated to give a beige foam which was not further purified.

The above solid was dissolved in dry tetrahydrofuran (25 mL), DBU (520 mg, 3.4 mmol) was added, and the reaction mixture was stirred under nitrogen for 24 h. After dilution with dichloromethane (25 mL), water (10 mL) was added and the aqueous phase was removed and extracted with dichloromethane (2 × 10 mL). The combined organic layers were washed with 10% hydrochloric acid (2 × 5 mL), 0.5 N sodium hydroxide solution (2 × 5 mL), and water (10 mL) prior to drying and solvent evaporation.

The resultant brown oil (**15**) was heated to reflux in ethyl acetate (25 mL) under nitrogen for 18 h. After solvent removal, the residue was subjected to preparative layer chromatography on silica gel (elution with 15% ethyl acetate in hexane) to give 33.8 mg (34%) of **16** as a white foam: IR ($CDCl_3$) 3100-2820, 1770, 1710, 1460, 1400, 1200, 775 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.33-7.20 (series of m, 6 H), 6.17 (d, J = 3.9 Hz, 1 H), 5.49 (d, J = 3.9 Hz, 1 H), 3.72-3.50 (m, 2 H), 2.76 (s, 3 H); *m/e* calcd 319.1290, obsd 319.1279.

Conversion of 17 to 20. A mixture of **17**[13] (171 mg, 0.535 mmol), *N*-bromosuccinimide (87.5 mg, 0.491 mmol), and a little AIBN in dry benzene (15 mL) was irradiated as before for 1.5 h. The reaction mixture was cooled, treated with DBU (0.75 g, 4.9 mmol) in dry tetrahydrofuran (5 mL), and stirred overnight at room temperature. The reaction mixture was passed through a short silica gel column. Medium-pressure liquid chromatography on silica gel (elution with 45% ethyl acetate in petroleum ether) of the residue after evaporation afforded 99.4 mg (59%) of **20**. The analytical sample was prepared by recrystallization from ethyl acetate: white solid; mp 198-200 °C; IR (KBr) 3100-2800, 1775, 1710, 1460, 1400, 1205, 1135, 880, 780, 765, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.97-7.35 (m, 6 H), 5.73 (s, 2 H), 5.60-5.43 (m, 2 H), 3.72-3.55 (m, 2 H), 2.80 (s, 3 H); ^{13}C NMR ($CDCl_3$) 156.6, 138.6, 133.68 129.7, 128.3, 126.6, 123.5, 57.9, 42.3, 25.2 ppm; *m/e* calcd 317.1164, 317.1171.

Anal. Calcd for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76. Found: C, 71.74; H, 4.84.

Hydrolysis-Oxidation of 20 to Naphthocyclooctatetraene 21. A slurry of **20** (29.8 mg, 0.094 mmol) and sodium hydroxide (0.14 g, 3.5 mmol) in 2-propanol was heated at reflux for 1.5 h. The reaction mixture was cooled, made acidic with 10% hydrochloric acid, basified (pH ~9) with ammonium hydroxide solution, and extracted with dichloromethane (4 × 5 mL). The combined organic phases were dried, filtered, and evaporated. The residue was taken up in dichloromethane (10 mL) and Attenburrow manganese dioxide (132 mg) was added. The reaction mixture was stirred overnight under nitrogen and filtered through Celite. The filtrate was evaporated and the residue was chromatographed on silica gel (elution with carbon tetrachloride). There was obtained 16 mg (83%) of **21** as a white solid, mp 91-97 °C. Recrystallization from pentane raised the melting point to 111-113 °C (lit.[16] mp 113-114 °C): IR (KBr) 3100-2800, 890, 760, 730, 680, 640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.8-7.25 (m, 6 H), 6.76 (d, J = 5.3 Hz, 2 H), 6.07 (br d, J = 6.8 Hz, 2 H), 5.8-5.7 (m, 2 H); *m/e* calcd 204.0939, obsd 204.0944.

Acknowledgment. This research was supported in part by a grant (CA-12115) from the National Cancer Institute.

Registry No. 6, 38310-36-0; **6** dibromide adduct, 77416-62-7; **7**, 77400-32-9; **8**, 77400-33-0; **9**, 265-49-6; **10**, 77400-34-1; **11**, 77400-35-2; **12**, 77400-36-3; **13**, 77416-63-8; **14**, 77400-37-4; **15**, 77400-38-5; **16**, 77400-39-6; **17**, 63079-33-4; **18**, 77400-40-9; **20**, 77400-41-0; **21**, 262-83-9; 2,3-benzo[4.4.2]propella-2,7,9,11-tetraene, 65140-12-7; (−)-*endo*-bornyltriazolinedione, 73462-83-6; (−)-*endo*-bornyltriazolidine 2,3-benzo[4.4.2]propella-2,7,9,11-tetraene addition product, 77400-42-1.

Kinetics of the Acid-Catalyzed Hydration of Allene and Propyne

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The kinetics of the conversion of allene and propyne to acetone in aqueous sulfuric acid have been measured. The solvent isotope effects k_{H^+}/k_{D^+} and the dependence of the rates on acidity are consistent with the Ad$_E$2 mechanism of rate-limiting protonation at the terminal carbons leading to the intermediate 2-propenyl cation $CH_3C^+H{=}CH_2$ in each case, followed by hydration to the enol and isomerization to acetone. This route is strongly favored by published theoretical studies.

The hydration of allene to acetone in concentrated sulfuric acid (eq 1) has been known since 1888.[1] However,

$$CH_2{=}C{=}CH_2 \xrightarrow[H_2O]{H_2SO_4} CH_3C(O)CH_3 \tag{1}$$

even though there has been great interest in electrophilic additions to substituted allenes[2,3] and alkynes,[4,5] including a variety of kinetic studies, there do not appear to have been any rate studies of hydration of allene itself (eq 1). Similarly, there are no published studies on the acid hydration of the isomer propyne, which also gives acetone (eq 2).

$$CH_3C{\equiv}CH \xrightarrow[H_2O]{H_2SO_4} CH_3C(O)CH_3 \tag{2}$$

Examination of the protonation of allene and propyne in the gas phase[6] led to the conclusion that either of these

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Table I. Rates of H_2SO_4-Catalyzed Hydration of Allene and Propyne at 25.0 °C

substr	$[H_2SO_4]$, M[a]	H_0[b]	$10^3 k_{obsd}$, s^{-1}
allene[c]	10.39	−5.15	5.06
	9.98	−4.95	1.92
	9.83	−4.85	1.58
	9.69	−4.76	1.18
	9.58	−4.70	1.11
	9.12	−4.45	0.546
	8.32	−4.03	0.111
propyne[d]	11.23	−5.66	6.13
	10.39	−5.15	1.32
	9.98	−4.95	0.434
	9.58	−4.70	0.259
	9.12	−4.45	0.0961

[a] Concentrations measured by titration. [b] Acidity functions were calculated by conversion of measured molarities to weight percentages by using data in: "Handbook of Chemistry and Physics", 51st ed.; Weast, R. C., Ed.; CRC Press: Cleveland, OH, 1970–1971; p F-7. The values of H_0 were calculated as a function of weight percent reported by: Jorgenson, M. J.; Hartter, D. R. *J. Am. Chem. Soc.* **1963**, *85*, 878–83. Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions", Butterworths: London, 1959. [c] $\log k_{obsd} = -1.405 H_0 - 9.589$, and $r = 0.994$; eq 9 gives $\phi = -0.44$, $\log k_0 = -9.31$, and $r = 0.93$. [d] $\log k_{obsd} = -1.591 H_0 - 11.171$, and $r = 0.992$; eq 9 gives $\phi = -0.53$, $\log k_0 = -10.32$, and $r = 0.95$.

substrates gives a mixture of the 2-propenyl cation **1** and the allyl cation **2** (eq 3), but in different proportions from

$$CH_3C{\equiv}CH \text{ or } CH_2{=}C{=}CH_2 \xrightarrow{BH^+} \underset{\mathbf{1}}{CH_3C^+{=}CH_2} + \underset{\mathbf{2}}{CH_2{=}CHC^+H_2} \quad (3)$$

the two precursors. These individual ions were long lived in the gas phase, and formation of the more stable isomeric ion **2** was favored in more exothermic proton transfers, indicating a substantial barrier to formation of this species.

An effort was made to form stable ions that would be observable by NMR by protonation of allene in strong acid solution, but $CH_3CFCH_3^+$ was the product detected.[7]

Kinetic studies of the addition of HCl in acetic acid to arylallenes were interpreted[3d,e] in terms of rate-limiting protonation at the central carbon (eq 4), as evidenced by

$$ArCH{=}C{=}CH_2 \xrightarrow{H^+} ArC^+HCH{=}CH_2 \xrightarrow{Cl^-} ArCH{=}CHCH_2Cl \quad (4)$$

the ρ^+ value of −4.2, as well as the significant rate accelerations caused by methyl substitution at either position 1 or 3.

In view of this interest in protonation reactions of allene, as well as the fascinating question of the selectivity of the protonation site of this molecule, it appeared desirable to extend our continuing studies of the hydration reactions of unsaturated hydrocarbons[8] to this compound, as well as to the isomeric propyne.

Results

The conversion of allene to acetone (eq 1) in sulfuric acid solutions at 25 °C was monitored by observation of the disappearance of the UV end absorption[9] of allene at 214 nm. The conversion of propyne (eq 2) was monitored in the same fashion by observing the disappearance of the UV absorption at 205 nm. In both cases, the conversion to acetone was confirmed by observation of the UV spectrum of the product solution, which was the same as that of authentic acetone, λ_{max} 265 nm. The results for H_2SO_4 are reported in Table I. The rates were found to be linearly related to the acidity function H_0 with slope of −1.40 for allene and −1.59 for propyne. Rates were also measured in D_2SO_4 solution as reported in Table II, along with isotope effects k_{H^+}/k_{D^+} derived from rates interpolated for H_2SO_4 solutions of the same molarity.

Table II. Isotope Effects on H_2SO_4-Catalyzed Hydration of Allene and Propyne

substr	[sulfuric acid], M	H_0[a]	k_{obsd}, $[H_2SO_4]$[b]	k_{obsd}, $[D_2SO_4]$	k_{H^+}/k_{D^+}
allene	10.25	−5.08	3.53×10^{-3}	1.38×10^{-3}	2.56
	9.29	−4.54	6.17×10^{-4}	3.53×10^{-4}	1.75
propyne	11.10	−5.58	5.09×10^{-3}	1.68×10^{-3}	3.03
	10.25	−5.08	8.15×10^{-4}	4.85×10^{-4}	1.68

[a] H_0 for H_2SO_4 of the specified molarity. [b] Interpolated from $\log k_{obsd} = \gamma H_0 + \epsilon$.

Discussion

Of the various criteria[8,10] available for assignment of the mechanism of hydration of allene, the most definitive would appear to be the solvent isotope effect. As can be seen in Table II, the values for allene (2.56 and 1.75) are significantly greater than 1.0 and in the range usually considered[8,10] diagnostic of the Ad_E2 mechanism of rate-limiting protonation on carbon to give a carbocation intermediate (eq 3). The difference in the measured isotope effects at the two different acidities is rather substantial, but this may arise in part from the use of interpolated values for the H_2SO_4 rates. Comparative values of k_{H^+}/k_{D^+} for some unreactive alkenes interpreted as reacting by the Ad_E2 path are 2.62 ($CH_2{=}CH_2$) and 2.82 (propene).[8a] Smaller values were obtained for the isomeric 2-butenes ($k_{H^+}/k_{D^+} = 1.56$ for *Z* and 1.04 for *E*),[8b] so this criterion clearly must be applied with some discretion.

The magnitude of the slope of log *k* vs. H_0 has also been used as a criterion of mechanism in such reactions, and the values for allene (−1.40) and propyne (−1.59) are comparable to those found for unreactive alkenes interpreted[8a,b] as reacting by the Ad_E2 path: ethylene (−1.54), propene (−1.39), 2-butene (−1.49 for *Z*, −1.40 for *E*). The large magnitudes of these slopes can be plausibly interpreted as due to greater solvent stabilization of the intermediate unstable cations in the more acidic media which are also more polar and less nucleophilic. This positive response to solvent polarity and lack of dependence on solvent nucleophilicity are consistent with rate-limiting formation of $CH_3C^+{=}CH_2$ from allene and propyne.

In the interpretation of the reactivity of alkenes the effect of substituents has been most helpful.[8] Indeed, for the reaction of arylallenes with HCl in acetic acid[3d,e] the correlation of the rates with σ^+ values established the mechanism as the Ad_E2 pathway (eq 4). However, for allene itself this criterion is less useful, as there is a change in the site of protonation. Arylallenes (eq 4),[3d,e] $Me_2C{=}C{=}CHOAc$,[3f] and $CH_2{=}C{=}CHOEt$[3g] protonate on the central carbon, whereas allene itself undergoes protonation

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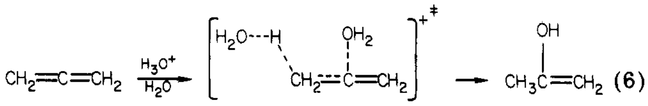
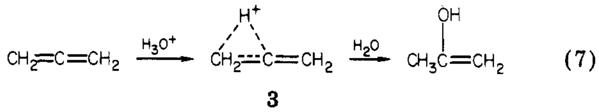
on the terminal carbon to eventually form acetone (eq 5).

$$\underset{2}{^{+}CH_2CH{=}CH_2} \overset{H^+}{\nleftarrow} CH_2{=}C{=}CH_2 \xrightarrow{H^+} \underset{1}{CH_3C^+{=}CH_2} \xrightarrow{H_2O} CH_3C(O)CH_3 \quad (5)$$

Ion **2** is more stable than **1** in the gas phase by 11 kcal/mol,[6] and presumably this difference is largely retained in solution, so formation of **2** followed by rearrangement to **1** to give acetone can be ruled out. Addition of hydrogen halides to allene and 3-alkylallenes also occurs by protonation of the terminal carbon.[2]

Thus, the kinetic data for allene are consistent with and suggestive of rate-limiting protonation at the terminal carbon, but other possible mechanisms should also be considered. Two alternative pathways for formation of acetone via its enol are concerted attack of the proton and water to give the product directly (eq 6), or formation of a π-complex intermediate which is attacked by H_2O (eq 7).



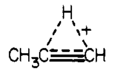


Comparison of the reactivity of allene with that of propyne allows further insight into the reaction. There appears to be agreement[4,11] that the hydrations of substituted alkynes involve Ad_E2 processes, giving vinyl cations (eq 8). The isotope effects and acidity dependence

$$RC{\equiv}CH \xrightarrow{H^+} RC^+{=}CH_2 \qquad (8)$$

observed for propyne are consistent with this latter path, and it can probably safely be assigned to propyne as well. The reactivity ratio k(allene)/k(propyne) varies with acidity because of the different dependences of log k_{obsd} on H_0 for the two substrates, but within the experimentally observed range of acidities it varies from 3.8 in 10.39 M H_2SO_4 to 5.7 in 9.12 M acid. The heat of formation of allene exceeds that of propyne by only 1.2 kcal/mol;[12b] so assuming the solvation energies of allene and propyne in the sulfuric acid solutions used are similar, these two reactions are very similar in their energies of ground states and transition states and in their activation energies. The principal difference in the formation of **1** from allene or propyne is that protonation would occur on an sp^2 carbon in the former case and on an sp carbon in the latter. However, since both reactions give the same product, acetone, and the evidence indicates that for propyne this occurs through the vinyl cation **1**, it appears reasonable to postulate this intermediate in the allene protonation as well. Inasmuch as these relatively unreactive substrates probably have rather late transition states, these are probably rather similar in structure as well as energy. A more refined comparison of k(allene)/k(propyne) would divide the allene rate by a statistical factor of 2 to account for the two equivalent protonation sites on allene. Inclusion of this factor would reduce the rate ratio cited above to the range 1.9 to 2.9.

Theoretical calculations for various isomeric $C_3H_5^+$ structures are highly revealing.[12] At the STO-3G level the energy of **1** exceeds that of **2** by 10.4 kcal/mol, in good agreement with experimental results.[12a] However, the bridged species **3** is higher in energy than the vinyl cation **1** by 31.1 kcal/mol and higher than the bridged ion **4**



4

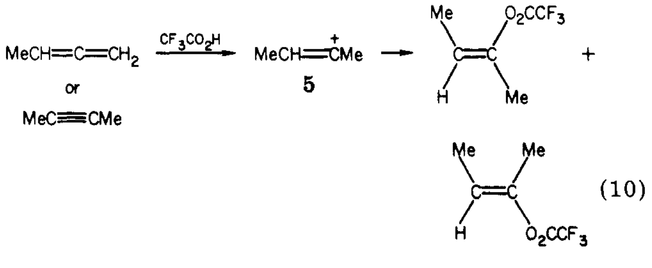
(which would be formed by attack on the triple bond of propyne) by 15.6 kcal/mol.[12a] Comparable results were obtained by MINDO/3 methods.[12b] This relative disfavoring of the bridged structures **3** and **4** is in sharp contrast to the situation for protonated ethylene and acetylene, for which calculations suggest that the bridged structures are of at least comparable stabilities to the open ions.[12a] The methyl substituent is evidently much more effective in the stabilization of the charge in the open ion **1** than in the bridged ion **4**.[12a] The instability of **3** may be related to the barrier for protonation at the central carbon of allene, which effectively prevents formation of the stable allyl cation **2** in solution. The bridged structures **3** and **4** are expected to be even less favored in solution as opposed to the gas phase, because solvent interacts best with localized charges.[13] Thus, to the extent that these calculated energy differences are reliable, they provide strong arguments against the intervention of bridged ions at any stage of these reactions.

A specific approach to the possible involvement of water in the rate-limiting transition state (eq 6) is the application of the Bunnett–Olsen equation (eq 9)[5e,14] to the reaction

$$\log k_{obsd} + H_0 = \phi(H_0 + \log [H_2SO_4]) + \log k_0 \quad (9)$$

of allene and propyne. It was proposed[5e,14] that the value of ϕ derived from eq 9 is diagnostic of the role of the solvent in the rate-limiting transition state. The ϕ values calculated for allene and propyne are −0.44 and −0.53, respectively, but the correlation coefficients are poor (0.93 and 0.95, respectively). These ϕ values are typical of those for reactions proposed not to involve solvent in the transition state, including hydrations of alkynes and alkenes,[5e] and argue against such a role for H_2O for allene (eq 6) and propyne.

A reaction which may be compared to hydration is the addition of trifluoroacetic acid, which has been proposed to involve the formation of intermediate vinyl cations in additions to alkynes[5e,15,16] and methylallene.[16] A rate ratio for CF_3CO_2H addition of $k(MeCH{=}C{=}CH_2)/k(MeC{\equiv}CMe)$ = 15 at 75.4 °C was observed,[16] and these substrates give the same isomeric ratio of vinyl trifluoroacetates, supporting the intervention of the same intermediate vinyl cation **5** in both reactions (eq 10). At 60 °C a rate ratio



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of 3-hexyne/1-butyne of 2.1 was observed,[15] and if the same ratio is applicable to 2-butyne/1-butyne, a rate ratio $MeCH{=}C{=}CH_2/EtC{\equiv}CH$ of 30 can be calculated, as compared to the $CH_2{=}C{=}CH_2/MeC{\equiv}CH$ ratio of 3.8–5.7 observed here. The enhanced rate for $MeCH{=}C{=}CH_2$ indicated by this comparison seems reasonable[17] and reinforces the conclusion that hydration and CF_3CO_2H additions are comparable reactions proceeding through formation of carbocation intermediates.

Another interesting comparison can be made between the reactivity of allene and that of propene. The latter compound was studied[8a] in sulfuric acid concentrations that overlap those reported here for allene, and the rate ratio k(propene)/k(allene) in 9.12 M H_2SO_4 is only 6.5, with an interpolated rate for propene. Thus these reactions, both of which are interpreted as involving rate-limiting protonation on sp^2-hybridized carbon, proceed at rates that are rather close even though the allene reaction involves formation of a vinyl cation.[18] The rate ratio k(propene)/k(propyne) at this acidity is 37, which is surprisingly significantly larger than the reported ratio of 3.6 for k(1-hexene)/k(1-hexyne).[11] The origin of this difference is under study.

In summary, the experimental evidence is consistent with the most simple explanation, namely, that protonation of allene and propyne occurs at carbon to form the same 2-propenyl cation 1 in each case. The theoretical studies strongly favor this route, so the Ad_E2 mechanism for acid-catalyzed hydration of allene and propyne may be considered to be firmly established.

Experimental Section

Allene was obtained from PCR, Inc., propyne from Matheson of Canada Ltd., and deuterated sulfuric acid from Aldrich. These reagents were used as received. Concentrations of acid solutions were measured by titration. Kinetics were measured by bubbling the gases into the acid solution in 1-cm UV cells and then tightly capping the cells so that no gas spaces were left. The decrease in the end absorption of the substrates was monitored with time at 214 nm for allene and 205 nm for propyne. Unicam SP 1800 and Cary 14 spectrophotometers were used. Duplicate runs were made in all cases.

Acknowledgment. Financial support for this research was provided by the National Sciences and Engineering Research Council (NSERC) of Canada.

Registry No. Allene, 463-49-0; propyne, 74-99-7.

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[17] The methyl group in $MeCH{=}C{=}CH_2$ would be expected to have a significant stabilizing effect on the developing vinyl cation 5 even though it is not directly substituted on the cationic carbon. When allenic methyls are on carbons where positive charge develops even larger effects are observed. Thus, the rate of protonation of $Me_2C{=}C{=}CHOAc$ at C_2 is about 100 times faster than the protonation at C_2 of $CH_2{=}CHOAc$.[3f]

[18] The rate ratio $k(EtOCH{=}CH_2)/k(EtOCH{=}C{=}CH_2)$ is only 1.5.[3g]

Kinetics of the Aminolysis of Ethyl *p*-Nitrophenyl Carbonate in the Presence of Dodecylammonium Diethylarsinate Aggregates in Chloroform. Complex Effects of Solubilized Water

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The kinetics of the aminolysis of ethyl *p*-nitrophenyl carbonate (ENPC) by dodecylamine (DA), dodecylammonium diethylarsinate (DADEA; dry aggregates and in the presence of solubilized water), and DA plus dry DADEA in chloroform were studied spectrophotometrically. Addition of 0.20 M of the surfactant enhances the rate of aminolysis by DA by a factor of 28.3 due to bifunctional catalysis by the former. In the aminolysis by 0.20 M DADEA, the rate constants were a function of the water/surfactant molar ratio R. Thus, they were insensitive to the presence of solubilized water up to $R = 0.55$, followed by a gradual decrease at higher R values. From the obtained activation parameters it could be seen that solubilized water affects both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, and these showed a series of quasi-mirror-imaged maxima and minima at different R values. These results were rationalized in terms of the effects of water on the rigidity of the micelle, on the micelle–substrate interactions, and on the stabilization of the reagent and transition states.

Alkylammonium carboxylates and halides dissolve in nonpolar solvents to form reversed micelles whose "core" contains the surfactant head ions.[1] Reversed micelles catalyze several types of reactions, e.g., ester aminolysis and hydrolysis,[1-4] and the hydration of carbonyl compounds.[5] In all these reactions, the rate constants depend on the concentration of solubilized water. This dependence was rationalized in terms of the hydration of the surfactant head groups which changes their catalytic efficiency and alters the substrate–surfactant interactions.[1-5] Additionally, water can alter the micellar parameters (e.g., shape and aggregation number)[7] and the properties of the substrates present in the micellar core (e.g., their pK_a values).[8]

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