Table I. Deuterium Incorporation and Oxygen Quenching, 30 °C

D_2O[a]			oxygen[b]		
				% DCA loss	
$[D_2O]$, M	ϕ_{-DCA}[c]	% MCA-d_1[d]	[DMH], M	degassed	air satd
0.00	0.057		0.23	21	5.0
0.055	0.057	84	0.12	20	1.1
0.14	0.058	91	0.097	19	0.4
0.28	0.055	95	0.075	20	0.0
0.55	0.057	97	0.034	17	0.0
1.4	0.056		0.011	11	0.0

[a] Degassed solutions, $[DCA] = 5 \times 10^{-4}$ M, $[DMH] = 3.5 \times 10^{-3}$ M. [b] From solutions irradiated (404 nm) in parallel, $[DCA] = 4 \times 10^{-4}$ M. [c] Irradiated at 366 nm to 11% conversion. [d] Irradiated to ~95% conversion at 404 nm. MCA was isolated by TLC and analyzed for deuterium content by mass spectroscopy.

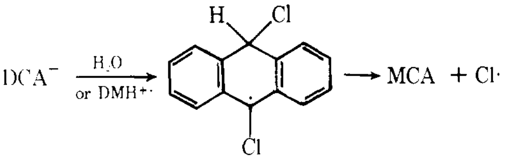
Table II. Deuterium Incorporation under Anhydrous Conditions[a]

solvent	diene	% MCA-d_1[b]
CH_3CN	DMH-d_{12}	50
CD_3CN	DMH-d_{12}	60
CD_3CN	DMH	30

[a] Degassed solutions at 30 °C, $[DCA] = 8 \times 10^{-4}$ M, $[diene] = 1 \times 10^{-2}$ M. Solvent and diene were dried (CaH_2) and handled under vacuum. [b] See footnote *d* in Table **I**.

nations.[2,3] While our observations implicate $DCA^{-}\cdot$, they do not support the free-radical pathway in eq 1.

Deuterium incorporation results using CH_3CN-D_2O appear in Table I, where MCA-d_1 is 9-chloroanthracene-*10-d*. Except under rigorously anhydrous conditions, Table II, attempts to effect deuteration from CD_3CN or DMH-d_{12}[11] failed. From these findings, it is evident that displacement of chlorine is a consequence of protonation and not hydrogen-atom abstraction.[12,13] Furthermore, since D_2O affects product structure but not the efficiency of DCA loss, Table I, all anion radicals formed give MCA regardless of the proton source. In anhydrous CH_3CN predominant protonation by $DMH^{+}\cdot$ is inferred, Table II, eq 2.



(2)

Spectroscopic observations in the presence of air rigorously exclude significant oxygen quenching of MCA formation owing to interception of any excited singlet state.[7] On the other hand large oxygen quenching effects can be accounted for if the longer-lived[14] $DCA^{-}\cdot$ is the MCA precursor since electron transfer from $DCA^{-}\cdot$ to oxygen is expected to be diffusion controlled ($E_{1/2}(R/R^-) \simeq -1.5$ and -0.57 V vs. SCE for DCA[15] and O_2,[16] respectively).[13b] Consistent with this mechanism, 1,2,4,5-tetracyanobenzene ($E_{1/2}(R/R^-) = -0.64$ V vs. SCE),[17] 10^{-3} M, also suppresses DCA loss. The known slow protonation of the anthracene anion radical[13b] and the effects of low concentrations of proton donors and quenchers (Tables I, II) are consistent with a minimum $DCA^{-}\cdot$ lifetime in the microsecond range.[14] The decreasing O_2 quenching efficiency above 0.1 M DMH, Table I, can be ascribed to O_2 scavenging by the diene.[16-18] Photodehalogenations occurring directly within the exciplex are insensitive to O_2.[4a-c]

Since spectroscopic observation of radical ions from olefin-arene exciplexes is lacking, this work strongly supports proposed mechanisms in several systems,[16,17,19] particularly those concerning olefin photooxidation[16] and photocycloaddition of methyl 1,2-diphenylcyclopropene-3-carboxylate to 9,10-dicyanoanthracene.[17]

Acknowledgment. This work was supported by National Science Foundation Grants No. CHE77-23582 and CHE76-024399.

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William K. Smothers, Kirk S. Schanze, Jack Saltiel*
Department of Chemistry, Florida State University
Tallahassee, Florida 32306
Received September 5, 1978

Aggregation in Strong Acid. A Micelle of Carbonium Ions

Sir:

Arnett et al. recently reported that a long-chain aliphatic amide, *N*-α-methylbenzylstearamide, forms monolayers on subphases composed of 15-50% H_2SO_4.[1] Racemic and (*S*)-(−) amide were shown to have different surface tension vs. [acid] curves. We describe here the behavior of a long-chain amide and related compounds in 70-95% H_2SO_4 where aggregation, not monolayer formation, predominates. During the course of this work, a micelle of carbonium ions was observed for the first time.

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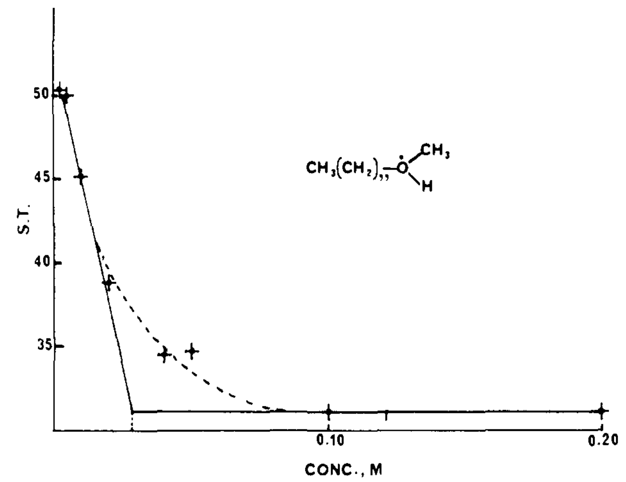


Figure 1. The surface tension in dynes/centimeter (uncorrected) of 1-methoxydodecane conjugate acid in 95.2% H_2SO_4 as a function of concentration.

1-Methoxydodecane, normally surface inactive, dissolves in 95.2% H_2SO_4 and displays surfactant-like properties. In particular, a biphasic surface tension-concentration plot (Figure 1) proves that the ether molecules assemble into micelles.[2] The critical micelle concentration obtained from Figure 1, 0.03 M, is three-four times higher than that of surfactants with the same chain length in pure water.[3] Micellization cannot be attributed to the ether cleaving into a surface active alcohol derivative for the following reasons: (1) Surface tension measurements, made less than an hour after preparing the solutions, showed no drift indicative of chemical reaction. (2) Ethers cleave but slowly in concentrated H_2SO_4 and can be recovered unaltered from this medium after several hours exposure.[4] Aliphatic ethers do, however, behave as weak bases which half-protonate at ~50% H_2SO_4 ($pK_a = -3$ to -4).[5] Thus, micelles of 1-methoxydodecane in 95.2% H_2SO_4 are comprised of oxonium ion head groups attached to hydrocarbon chains. In accord with this picture, the nitrogen analogue of the oxonium ion, *N,N*-dimethyldodecylammonium ion, has a similar cmc in H_2SO_4 of 0.02 M.

The fatty acid amide, *N,N*-dimethyldodecanamide, also forms micelles in 95.2% H_2SO_4 (cmc = 0.03 ± 0.01 M). Carbonyl protonation (a well-established reaction of simple amides in concentrated acid[6]) converts the long-chain amide into a surfactant. Aggregation depends critically on the water content of the acid: the cmc equals $6 \pm 2 \times 10^{-4}$ M in 80% H_2SO_4 and $2 \pm 0.5 \times 10^{-4}$ M in 70% H_2SO_4. This water effect is reminiscent of (but much larger than) that reported for lauric acid in acidic media.[2] Since the dodecanamide is fully protonated in all of our experiments (amides are half-ionized at only 11-23% H_2SO_4[7]), the 10^2-fold decrease in cmc cannot be explained by a change in the $RCONR_2$:$RCOHNR_2^+$ ratio. Apparently, the high concentration of hydronium ion present in 70% H_2SO_4 enhances the monomer activity and promotes the tendency to cluster.[2]

Destabilization of monomer with increasing water levels ultimately prevents the amide from dissolving in the aqueous acid. This helps clarify a fact alluded to above, namely that amide monolayers exist on 15-50% H_2SO_4, whereas micelles abound in concentrated H_2SO_4. Ionic surfactants tend to dissolve in pure water, form insoluble monolayers on moderately concentrated aqueous acid, and finally regain solubility in concentrated acid.[8]

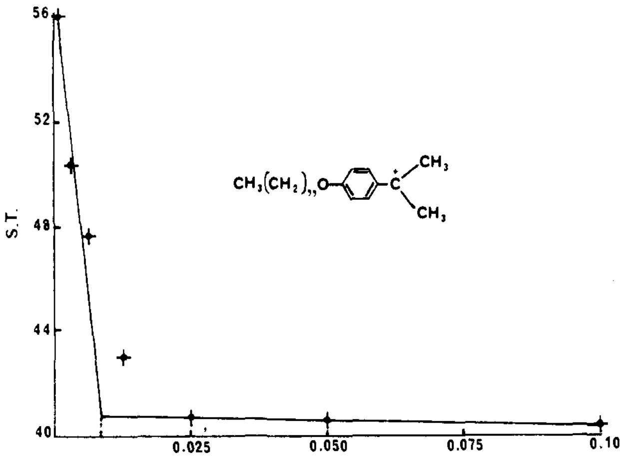
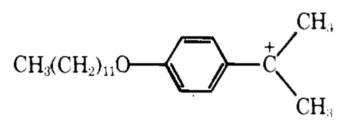


Figure 2. The surface tension in dynes/centimeter (uncorrected) of *p*-dodecyloxycumyl cation in 95.2% H_2SO_4 as a function of concentration.

p-Dodecyloxybenzoic acid was esterified and treated with methylmagnesium iodide to give *p*-dodecyloxy-α-methylstyrene. When this compound was added to 95.2% H_2SO_4, it produced micelles of *p*-dodecyloxycumyl cation with a cmc of 0.01 M (Figure 2). Spectrometric data confirm the presence of carbonium ions within the micelles: the ^1H NMR spectrum has peaks at δ 2.90 (C^+-CH_3), 7.20 (meta to C^+), and 8.55 (ortho) compared with δ 2.90, 7.15, and 8.44 reported previously for the *p*-methoxycumyl cation.[9] The similarity between the NMR spectra of the related micellar and monomeric carbonium ions suggests that the micelles are loose structures and that head to head interactions within the Stern layer play little role. This is supported by UV data on *p*-dodecyloxycumyl cation in 85% H_2SO_4 where the absorbance at 403 nm could be measured above and below the cmc. Obedience to Beer's law (i.e., the lack of a "break" as in the surface tension plots) indicates that micellization does not significantly perturb the environment of the chromophoric head group.



Surfactants can solubilize hydrophobic compounds in concentrated H_2SO_4 much like they do in water. For example, heptane was found to dissolve in H_2SO_4 solutions of lauric acid to the extent of one heptane molecule for every 11-13 surfactants. This suggested the possibility of solubilizing aromatic compounds in HNO_3-H_2SO_4 and perhaps modifying the ratios of isomeric nitration products.[10] Mixtures of 95% H_2SO_4 (40 g), lauric acid (4.0 g), and bromobenzene (0.50 g) were cooled to 0 °C followed by addition of 0.38 g of HNO_3. After stirring for 25 min, the reaction mixtures were poured on ice-water and extracted with ether. The ether was washed with water, dried, and analyzed by GLC. The para:ortho ratio was 2.1 ± 0.3 compared with 7.2 ± 0.9 for nitration without any lauric acid. If the bromobenzene orients itself in the micelle so that the bromine is pointed toward the external medium, then ortho substitution could be sterically favored.[11] Control experiments showed that neither fractionation during workup nor rearrangement of the nitrobromobenzenes can account for the substantial difference in product composition. Hopes for a practical synthetic procedure using micelles in HNO_3-H_2SO_4 faded when we found little effect with toluene as well as oxidation of surfactant under all but the mildest nitrating conditions. It remains to be seen whether reactions in H_2SO_4 alone, such as cyclizations, can be influenced by the presence of micelles.

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F. M. Menger,* J. M. Jerkunica
Department of Chemistry, Emory University
Atlanta, Georgia 30322

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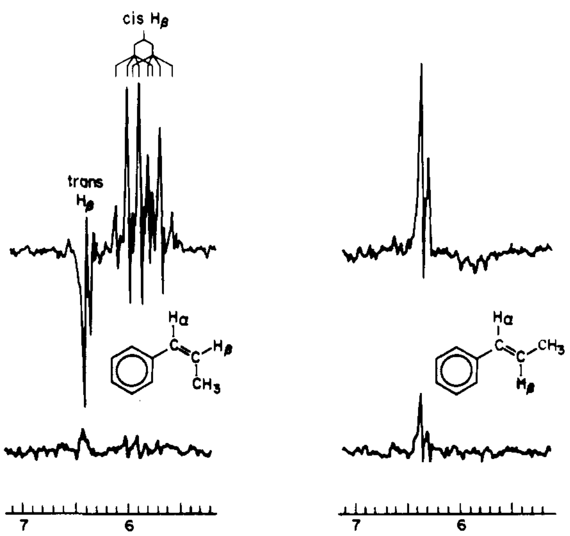
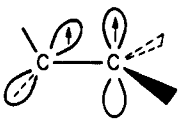


Figure 1. 60-MHz ^{1}H NMR spectra (olefinic region) observed during the irradiation of tetrachlorobenzoquinone (0.02 M) in acetonitrile-d_3 solutions containing 0.02 M *cis*- (left) or *trans*-1-phenylpropene (right). The reactant olefin and a dark spectrum are shown below each CIDNP spectrum. The aromatic and allylic regions are not shown.

Photosensitized Isomerization of Electron Donor and Acceptor Styrenes. Recombination of Radical-Ion Pairs in the Singlet and Triplet States

Sir:

The light-induced interactions between photosensitizers and olefins may involve a variety of mechanisms including (a) triplet energy transfer to populate the olefin triplet state (**1**), (b) electron transfer to generate olefin radical ions (e.g., **2**) paired with sensitizer derived ions, or (c) addition to form biradicals. (**3**). Magnetic resonance techniques are potentially useful for the study of these reactions; degenerate triplet energy transfer or degenerate electron exchange between a radical ion and its diamagnetic precursor may give rise to line broadening;[1-3] the interaction of radical-ion pairs may induce nuclear[2,3] or electron[4] polarization; finally, the magnetic interactions in biradicals may result in nuclear spin polarization effects.[5] In this communication we discuss CIDNP effects observed during the irradiation of suitable sensitizers in the presence of β-substituted electron donor or electron acceptor styrenes. The effects observed for donor and acceptor styrenes are different indicating two different mechanisms of isomerization.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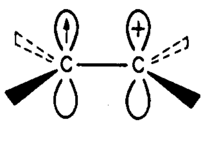
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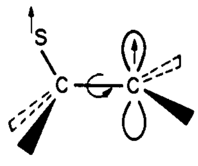

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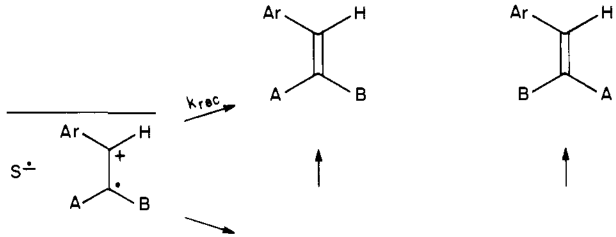
The mechanism of donor olefin isomerization is illustrated for the pair tetrachlorobenzoquinone (TCQ), *cis*-1-phenylpropene (*c*-PP). During UV irradiation of this system, the doublet of quartets representing the olefinic proton in the β position and the aromatic signal appear in strongly enhanced absorption (*A*), whereas the methyl doublet appears in emission (*E*); at the same time, the complex olefinic spectrum of the trans isomer (*t*-PP) shows *E* with approximately one third of the intensity of *c*-PP (Figure 1, left).

The effects observed for *c*-PP can be explained on the basis of the radical-pair theory of CIDNP[6] by a mechanism analogous to those of most previously reported cases of radical-ion-pair-induced polarization.[2,3] This mechanism involves electron transfer from *c*-PP to the triplet state of the sensitizer, ^{3}TCB, generating the radical ions, $TCB^{-\cdot}$ ($g = 2.0056$) and $c\text{-PP}^+$ ($g = 2.0027$), and reverse electron transfer in this pair to regenerate the reactants in their singlet ground states (μ, $\epsilon > 0$; $\Delta g < 0$). The opposite signal directions of the aromatic and olefinic protons on the one hand and the methyl group on the other hand suggest that the nuclei in the corresponding positions of $c\text{-PP}^{+\cdot}$ have hyperfine coupling constants of opposite sign, $a_{\text{ring}}, a_\beta < 0 < a_{CH_3}$, reflecting the spin density distribution of the radical cation.

The polarization of the isomerized olefin can be explained as originating in the same ion pair where that of *c*-PP is generated ($\mu > 0$; a_β, $\Delta g < 0$). However, the opposite signal direction of *t*-PP suggests an alternative mechanism of product formation ($\epsilon < 0$).[6] A plausible mechanism involves cis-trans isomerization of free-radical cations and electron exchange with the reactant olefin. In this reaction, the "escape" polarization is partitioned between reactant and rearranged olefin according to the extent of rearrangement. The unrearranged ions involved in this reaction will weaken the "in cage" polarization of the reactant styrene.



It follows that the rate of the radical-ion rearrangement (k_r) is crucial: it must be slower than the electron return (recombination) after intersystem crossing (k_{rec}) but competitive with the regeneration of reactant olefin from "escaped" radical ions. A decrease in k_r is expected to result in weaker enhancements of rearranged and reactant olefin: because of a smaller yield of rearranged olefin a larger fraction of the escape polarization would be transferred to the reactant olefin. This prediction is confirmed in the reaction of the trans isomer. Because the trans

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