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

D_2O^a			oxygen ^b		
		%		% DCA loss	
[D ₂ O], 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, $[DCA] = 5 \times 10^{-4} \text{ M}$, $[DMH] = 3.5 \times 10^{-3}$ 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- <i>d</i> ₁ ^{<i>b</i>}	
CH3CN	DMH-d ₁₂	50	
CD_3CN	$DMH-d_{12}$	60	
CD_3CN	DMH	30	

^a Degassed solutions at 30 °C, $[DCA] = 8 \times 10^{-4} \text{ M}$, [diene] = 1×10^{-2} M. Solvent and diene were dried (CaH₂) and handled under vacuum. ^b See footnote d in Table I.

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

Deuterium incorporation results using CH₃CN-D₂O 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 CD₃CN 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 CH₃CN predominant protonation by DMH⁺ is inferred, Table II, eq 2.

$$DCA^{-} \xrightarrow[or DMH^{+}]{} \longrightarrow MCA + Cl \qquad (2)$$

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-lived¹⁴ DCA⁻ is the MCA precursor since electron transfer from DCA⁻. to oxygen is expected to be diffusion controlled $(E_{1/2}(R/R^-) \simeq -1.5 \text{ and } -0.57 \text{ V vs. SCE for DCA}^{15}$ and $O_{2,16}^{16}$ 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⁻ · lifetime in the microsecond range.¹⁴ The decreasing O₂ quenching efficiency above 0.1 M DMH, Table I, can be ascribed to O₂ 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 photooxidation¹⁶ and photocycloaddition of methyl 1,2-diphenylcyclopropene-3-carboxylate to 9,10-dicyanoanthracene.17

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References and Notes

- Presented in part at the meeting of the Florida Section of the American Chemical Society, May 1976, Jacksonville, Fla. Abstract No. 39, and the Rocky Mountain regional meeting of the American Chemical Society, June 1978, Boulder, Colo., Abstract No. 16.
- (a) T. Latowski, Z. Naturforsch. A, 23, 1127 (1968); (b) T. Tosa, C. Pac, and
 H. Sakurai, Tetrahedron Lett., 3635 (1969); (c) L. L. Miller and R. S. Narang,
 Science, 169, 368 (1970); (d) M. Ohashi, K. Tsujimoto, and K. Seki, J. (2)Chem. Soc., Chem. Commun., 384 (1973); (e) N. J. Bunce, S. Safe, and L. O. Ruzo, *J. Chem. Soc., Perkin Trans. 1*, 1607 (1975); (f) N. J. Bunce and L. Ravanal, *J. Am. Chem. Soc.*, **99**, 4150 (1977); (g) B. Chittim, S. Safe, N. J. Bunce, L. O. Ruzo, K. Olie, and O. Hutzinger, Can. J. Chem., 56, 1253 (1978).
- (a) L. O. Ruzo, N. J. Bunce, and S. Safe, Can. J. Chem., 53, 688 (1975); (3)(b) L. O. Ruzo and N. J. Bunce, *Tetrahedron Lett.*, 511 (1975); (c) N. J. Bunce, P. Pilon, L. O. Ruzo, and D. J. Sturch, *J. Org. Chem.*, **41**, 3023 (1976)
- (a) Y. Y. Kulis, I. Y. Poletaeva, and M. G. Kuz'min, *Zh. Org. Khim.*, 9, 1214 (1973); (b) O. M. Soloveichik and V. L. Ivanov, *ibid.*, 10, 2404 (1974); (c) O. M. Soloveichik, T. M. Grigor'eva, and V. L. Ivanov, *ibid.*, 12, 2200 (1976); (d) O. M. Soloveichik, V. L. Ivanov, and M. G. Kuz'mín, *ibid.*, 12, 859 (1976).
- J. Saltiel and D. E. Townsend, *J. Am. Chem. Soc.*, **95**, 6140 (1973). (a) N. C. Yang, D. M. Shold, and J. K. McVey, *J. Am. Chem. Soc.*, **97**, 5004 (1975); (b) N. C. Yang, K. Srinivasachar, B. Kim, and J. Libman, *ibid.*, **97**, (6)5006 (1975).
- J. Saltiel, D. E. Townsend, B. D. Watson, and P. Shannon, J. Am. Chem. Soc., 97, 5688 (1975).
- (a) The photolability of this system in acetonitrile has been noted.^{6a,7} (b) (8) Identified by comparison with an authentic sample. Quantitative MCA formation is evidenced by maintenance of isosbestic points in the UV spectra of solutions irradiated (404 nm; [DMH] $\simeq 10^{-2}$ M) to 90% conversion. (c) Benzophenone-trans-stilbene actinometry (366 nm): D. Val-entine, Jr., and G. S. Hammond, J. Am. Chem. Soc., 94, 3449 (1972).
 (9) Since ¹E* formation appears not to be freely reversible in acetonitrile,⁷
- little change in k_eT_m is expected between 23 and 30 °C.
 (10) For reviews, see B. Stevens, Adv. Photochem., 8, 161 (1971); M. Ottolenghi, Acc. Chem. Res., 6, 153 (1973).
- (11) (CD₃)₂CCHCHC(CD₃)₂: ~99% isotopic purity by mass spectroscopy. Synthesis of DMH-d₁₂ will be reported in the full paper.
 (12) Irradiation of DCA-DMH in CH₃OD afforded 82% MCA-d₁.
- (13) For reviews on aromatic anion radicals, see (a) N. L. Holy, *Chem. Rev.*, 74, 243 (1974); (b) L. M. Dorfman, *Acc. Chem. Res.*, 3, 224 (1970).
 (14) DCA⁻• is labile at room temperature but stable at -40 °C; see T. Matsu-
- moto, M. Sato, and S. Hirayama, *Chem. Lett.* (*Jpn.*), 603 (1972).
 M. E. R. Marcondes, V. G. Toscano, and R. G. Weiss, *J. Am. Chem. Soc.*, 97, 4485 (1975); T. Matsumoto, M. Sato, and S. Hirayama, *Bull. Chem. Soc.* Jpn., 46, 369 (1973).
- (16) J. Eriksen, C. S. Foote, and T. L. Parker, J. Am. Chem. Soc., 99, 6455 (1977)
- (17) K. A. Brown-Wensley, S. L. Mattes, and S. Farid, J. Am. Chem. Soc., 100, 4162 (1978).
- (18) N. M. Hasty and D. R. Kearns, J. Am. Chem. Soc., 95, 3380 (1973)
- (19) Cf. K. Mizuno, C. Pac, and H. Sakurai, J. Am. Chem. Soc., 96, 2993 (1974);
 J. J. McCullough, R. C. Miller, D. Fung, and W. S. Wu, *ibid.*, 97, 5942 (1975);
 J. Libman, J. Chem. Soc., Chem. Commun., 361, 363 (1976); K. Mizuno, R. Kaji, H. Okada, and Y. Otsuji, ibid., 594 (1978).

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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% H₂SO₄.¹ 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% H₂SO₄ where aggregation, not monolayer formation, predominates. During the course of this work, a micelle of carbonium ions was observed for the first time.



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

1-Methoxydodecane, normally surface inactive, dissolves in 95.2% H₂SO₄ 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% H₂SO₄ (pK_a = -3 to -4).⁵ Thus, micelles of 1-methoxydodecane in 95.2% H₂SO₄ 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 acid⁶) 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 10²-fold decrease in cmc cannot be explained by a change in the RCONR₂:RCOHNR₂⁺ 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% H₂SO₄, whereas micelles abound in concentrated H₂SO₄. Ionic surfactants tend to dissolve in pure water, form insoluble monolayers on moderately concentrated aqueous acid, and finally regain solubility in concentrated acid.⁸

p-Dodecyloxybenzoic acid was esterified and treated with methylmagnesium iodide to give *p*-dodecyloxy- α -methylstyrene. When this compound was added to 95.2% H₂SO₄, it produced micelles of *p*-dodecyloxycumyl cation with a cmc of 0.01 M (Figure 2). Spectrometric data confirm the presence



Figure 2. The surface tension in dynes/centimeter (uncorrected) of p-dodecyloxycumyl cation in 95.2% H₂SO₄ as a function of concentration.

of carbonium ions within the micelles: the ¹H NMR spectrum has peaks at δ 2.90 (C⁺-CH₃), 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% H₂SO₄ 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 H₂SO₄ much like they do in water. For example, heptane was found to dissolve in H₂SO₄ 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 HNO₃-H₂SO₄ and perhaps modifying the ratios of isomeric nitration products.¹⁰ Mixtures of 95% H₂SO₄ (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 HNO₃. 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 HNO₃-H₂SO₄ 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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References and Notes

- (1) E. M. Arnett, J. Chao, B. Kinzig, M. Stewart, and O. Thompson, J. Am. Chem. Soc., 100, 5575 (1978).
- (2) See J. Steigman and N. Shane, J. Phys. Chem., 69, 968 (1965), for a discussion of micelle formation by long-chain fatty acids in concentrated H₂SO₄.
- (3) Each point in Figure 1 represents an average of 10 surface tension measurements. cmc values are estimated to be accurate to ±25% unless indicated otherwise.
- (4) R. L. Burwell, Jr., Chem. Rev. 54, 615 (1954).
- (5) N. C. Deno and J. O. Turner, J. Org. Chem., 31, 1969 (1966).
- (6) M. Liler, Adv. Phys. Org. Chem., 11, 267(1975).
 (7) K. Yates and J. B. Stevens, Can. J. Chem., 43, 529 (1965).
- (8) For example, stearic acid forms micelles in basic water and in concentrated H₂SO₄, whereas N-α-methylbenzylstearamide exists as monolayers on 15–50% H₂SO₄. The water levels at which insoluble monolayers predominate depend crucially, no doubt, on the chain length of the surfactant.
- (9) G. Fraenkel and D. G. Farnum in "Carbonium Ions", Vol. 1, G. A. Olah and P. v. R. Schleyer, Eds., Interscience, New York, 1968, p 237.
- (10) Effects of micelles on electrophilic aromatic substitution products have been reported only once previously: D. A. Jaeger and R. E. Robertson, J. Org. Chem., 42, 3298 (1977).
- (11) At present this explanation is highly speculative.

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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 electron⁴ 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.

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 CIDNP⁶ by a mechanism analogous to those of most previously reported cases of radical-



Figure 1. 60-MHz ¹H 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.

ion-pair-induced polarization.^{2,3} This mechanism involves electron transfer from c-PP to the triplet state of the sensitizer, ³TCB, generating the radical ions, TCB⁻ (g = 2.0056) and c-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-PP⁺ have hyperfine coupling constants of opposite sign, a_{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" polari-



zation 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