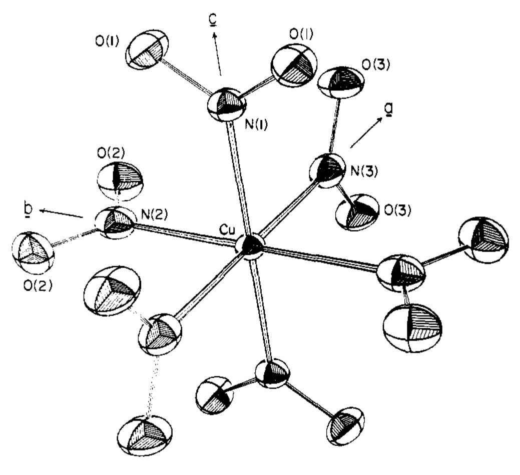

Figure 1. Hexanitrocuprate(II) anion showing atom numbering, thermal motion, and crystal axes. (Drawing produced by the computer program ORTEP; C. K. Johnson, Oak Ridge National Laboratory Report ORNL-3794, Oak Ridge, Tenn., 1965.)

prate(II),[1] barium hexafluorocuprate(II),[2] and bis(diethylenetriamine)copper(II) nitrate.[3] However, these are of limited value for studying Jahn-Teller effects since the Cu(II) ligands are not equivalent.[4]

In the fluoride complexes, K_2CuF_4 and $(BaF)_2CuF_4$, the long Cu-F distances are for four fluoride ions which bridge two Cu(II) ions while the short Cu-F distances are for nonbridging fluoride ions. The corresponding Ni(II) compounds K_2NiF_4[5] and $(BaF)_2NiF_4$[2] also show four long and two short Ni-F distances and, since six-coordinate Ni(II) is not a Jahn-Teller ion, the distortions observed in the Cu(II) complexes cannot be attributed to Jahn-Teller effects alone.

The bis(diethylenetriamine)copper(II) nitrate structure is not a good example of Jahn-Teller distortion since the ligands are tridentate and the $Cu^{(II)}$-N distances are determined in part by constraints imposed by the ligand geometry. The four long Cu-N bonds range from 2.17 (1) to 2.26 (2) Å, the two short Cu-N bonds average 2.01 Å, and all intraligand N-Cu-N angles are approximately 80°. The two short Cu-N distances correspond to the secondary amine nitrogen atoms and the four long bonds to primary amine atoms,[3] thus the ligands are again not equivalent. The corresponding Ni(II) compound shows a similar geometry with two short Ni-N (secondary) bonds and four long Ni-N (primary) bonds.[6] The same authors report the bis[di-(3-aminopropyl)amine]nickel(II) compound[6] which has two long and four short Ni-N bonds. They conclude that the Ni-N distances are strongly influenced by the ligand geometry.

In 1939 Van Vleck[7] stated, "It would be interesting if a physical case could be found where the cluster $X \cdot 6H_2O$ resonates through a variety of Jahn-Teller configurations, as then we would have a nice example of a characteristic quantum mechanical effect." We have sufficient evidence now to indicate that the cluster $Cu(NO_2)_6^{4-}$ is such an example since the presence or absence of a static distortion as well as the type of distortion depends on the counterion and on the temperature.

For example, both $K_2BaCu(NO_2)_6$[8] and $K_2CaCu(NO_2)_6$[9] crystallize in the same space group as $Rb_2PbCu(NO_2)_6$, but the CuN_6 environment is *elongated* tetragonal rather than *compressed* tetragonal in the presence of the K^+ counterion. A further example is provided by the observation that $K_2PbCu(NO_2)_6$ undergoes a reversible phase change from the cubic space group *Fm*3 with equal Cu-N distances[10] to the orthorhombic space group *Fmmm* with nonequivalent Cu-N distances below 280°K. Preliminary structural data for the orthorhombic phase indicate that the CuN_6 environment is *compressed* tetragonal with Cu-N distances of 2.07, 2.13, and 2.15 Å.[11] The corresponding nickel(II) compound, $K_2PbNi(NO_2)_6$, is cubic over the range of temperatures measured (130-295°K).[11] Thus, the changes in $M_2M'Cu(NO_2)_6$ structures can be attributed to the Jahn-Teller effect. Work is in progress which should provide precise structural data for $K_2PbCu(NO_2)_6$ below 280°K and for other crystals containing $Cu(NO_2)_6^{4-}$ and $Ni(NO_2)_6^{4-}$ clusters with various counterions.

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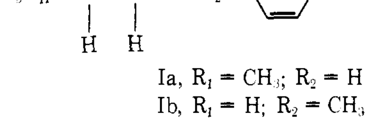
Effect of Micelles on the Rate and Stereochemistry of Solvolytic Displacement Reactions

Sir:

We wish to report the synthesis of a series of unusually reactive water soluble sulfonates (Ia-c) which has allowed us to study, for the first time, the effect of micelle formation[1] on the rate and stereochemistry of simple solvolytic displacement reactions. We have found that cationic micelles show little or no effect on the displacement reaction; in contrast, micelles formed from anionic surfactants bind Ia-c strongly, retard their rate of aqueous solvolysis by at least two orders of magnitude, and change the observed stereochemistry of displacement in Ib from 100% net inversion to 56% net inversion.[2]



Ia, $R_1 = CH_3$; $R_2 = H$
Ib, $R_1 = H$; $R_2 = CH_3$
Ic, $R_1 = R_2 = H$

We chose I as the system for study[3] because these compounds are water soluble as well as structurally similar to the water insoluble sulfonates more traditionally used in solvolytic studies.[4] Also, sulfonates of structure I are surface active[5] and thus self-micellize and should bind well to micelles composed of other surfactants.

The nonmicellar solvolytic behavior of sulfonates I in water can be summarized as follows: (1) they exhibit conve-

Table I. Rates of Solvolysis of Alkyl *p*-Trimethylammonium Benzenesulfonate Esters in Water with and without Added Surfactants

Substrate	Concn[a] × 10^3	Additive (cmc × 10^3)	Concn × 10^3	Temp (°C)	k(sec^{-1}) × 10^5	$t_{1/2}$ (min)
Ia	2.75			30	3.9[c]	300
	8.25			30	3.9[c]	
	1.27	CTAB (0.7)	1.27	30	3.9[c]	
	3.84	SLS (8.3)	17	30	($\leq 10^{-4}$)[c]	
Ib	0.21			25	1600[b]	0.7
	4.2	SLS (8.3)	17	25	23[c]	50
Ic	1.0			40	29[b]	40

[a] Molar units. [b] Determined by titration. [c] Determined by Fourier transform nmr.

nient first-order rates of solvolysis even near room temperature (Table I); (2) the system shows an unusually large[6] primary:secondary rate ratio (*ca.* 5 × 10^2 at 25°); (3) a typical product mixture from, for example, Ib is 2-octanol (80%), *trans*-2-octene (10%), *cis*-2-octene (5%), 1-octene (3%), and 3-octanol (2%).

We have studied the stereochemistry of this reaction using optically active Ib.[7] This material gives 2-octanol with 100% inversion of configuration, but there is essentially no difference in rate and stereochemistry[2] above or below its critical micelle concentration or in the presence of micellar hexadecyltrimethylammonium bromide (CTAB). However, in the presence of micellar concentrations of sodium lauryl sulfate (SLS) the reaction is strongly inhibited and there is a significant change in stereochemistry. The half-life for solvolysis of Ib increases to 50 min at 30° (*vs.* 40 sec at 25°); Ia undergoes <5% reaction in 10 hr at 30°. The 2-octanol produced from Ib in the presence of SLS is now formed with 56% (rather than 100%) inversion of configuration. These effects are not observed when SLS is replaced by sodium methanesulfonate, even at relatively high concentrations (0.03 *M*).

These results require strong binding of I to the anionic micelles and a surfactant-induced change in solvolytic displacement mechanism, even when molar amounts of I and SLS are nearly equivalent; *i.e.*, mixed micelles, containing alternately charged components, are responsible for the effect observed here. Although catalysis by a number of mixed micelles has been investigated,[8] in nearly all cases the components have been either similarly charged or charged and uncharged surfactants.[9] For this reason, we have investigated a range of substrate and catalyst concentrations in the SLS-inhibited reaction of Ib.

As can be seen from Table II, our results are surprisingly regular. They show, first, that at concentrations of Ib ≤1.5 × 10^{-2} *M*, the concentration of SLS must be greater than or similar to its critical micelle concentration[10] (cmc) in order to drastically modify the reaction's stereochemistry. The micellar reaction mechanism is not greatly changed even when the mixed micelles contain similar amounts of SLS and Ib. Furthermore, the results in Table II allow us to determine that under these conditions solvolysis in the presence of micellar SLS-Ib is taking place on the micelle rather than as a combination of (a) a highly inverting fast solvolysis of a small instantaneous concentration of unbound, monomeric Ib plus (b) a highly retaining (but slower) micellar reaction. If the latter were true, the total observed stereochemistry would depend on the total concentration of SLS above the cmc. The results show it does not; a plateau effect at 56% inversion is observed. At higher concentrations of ester, however, the stereochemistry returns to 100% inversion.

Table II. Dependence of Stereochemistry of Solvolytic Displacement of Ib on Concentration of Ib and Added Sodium Lauryl Sulfate (SLS) in Water at 25°

Qualitative conditions	SLS × 10^2	Ib × 10^2	Stereochemistry[a]
High [SLS]; low-to-moderate [Ib]	2.8	1.1	56
	2.8	1.5	57
	2.1	0.61	55
	1.7	1.0	54
Moderate [SLS]; moderate [Ib]	1.6	1.6	63
Moderate [SLS]; high [Ib]	1.7	2.1	81
Low [SLS]; low-to-moderate [Ib]	0.7	1.0	88
	0.7	1.6	93
No [SLS]	0	1.7	101
	0	0.63	99
	0	0.60[b]	99

[a] Determined by optical rotation on isolated 2-octanol (after purification by vapor phase chromatography) at five wavelengths, and confirmed using the fluorine nmr method developed by J. A. Dale, D. L. Dull, and H. S. Mosher, *J. Org. Chem.*, **34**, 2543 (1969). Error limits are ±2%. [b] 1.4 × 10^{-3} *M* (2 × cmc) cetyl trimethylammonium bromide (CTAB) added.

These results show that there are three above-cmc concentration regions of catalytic significance. When [SLS] ≫ [Ib], the micelles formed are predominantly composed of anionic surfactant molecules with a smaller amount of Ib molecules dispersed in each micelle. Under these conditions we believe electrostatic attraction reinforces the hydrophobic bonding which holds Ib to the micelle, and the ester binds very closely to neighboring SLS molecules. This "squeezes out" solvent water in this region,[11] and solvent assistance to the ionization is made more difficult; thus rate inhibition and significant stereochemical randomization are observed.[12] When [SLS] ≅ [Ib], this tight binding of Ib and SLS apparently persists. However, as the ratio of ester to SLS increases, the micelles increasingly resemble cationic aggregates. Here the positively charged head groups repel one another, so there is need for molecules of solvent to be incorporated between surfactant head groups. Under these conditions the reaction returns to its aqueous-like rate and stereochemistry.

The strong binding and stereochemical modification observed here have interesting implications for the long-sought use of micelles in asymmetric induction;[13] investigation of these implications is under way.

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(10) 8.3×10^{-3} M; *cf.* ref 5.

(11) Moss and coworkers (ref 2f) have observed that cationic micelles *do* affect the rate of 2-octylamine deamination, but alter the stereochemistry only in the presence of "hydrophobic" counterions such as ClO_4^-. Formation of "less aqueous micelles" resulting from strong binding of the poorly hydrated counterions was invoked to explain this; a prediction was made that the ClO_4^- effect might be too weak to perturb the stereochemistry of solvolytic displacement reactions. We have found that the presence of ClO_4^- does not, in fact, alter the inability of cationic micelles to change the rate and stereochemistry of the reactions studied here. However, one can think of SLS molecules (applying the Moss terminology) as extremely hydrophobic "counterions" which bind much *more strongly to micelles (and exclude more water) than does* ClO_4^- Thus there is a certain analogy between Moss' observations and those observed here under conditions where [SLS] ≃ [I]. Our effect has no counterpart, however, in the micellar effect on rates of deamination reactions (which are accelerated by cationic micelles, even in the presence of ClO_4^-), or under conditions of high anion/substrate ratio ([substrate] < cmc), where the ClO_4^- amine deamination effect disappears but the SLS solvolytic displacement effect persists.)

(12) We cannot rigorously determine, using data presently in hand, whether or not the tight binding of SLS to micelles formed from I results in an actual covalent intermediate; *i.e.*, whether the retention component arises from a "double displacement" process involving a neutral dialkyl sulfate intermediate. However, we believe it unlikely that double displacement would result in the sort of saturation effect observed here; the reasons are basically those outlined by Moss and coworkers in ref 2f. In any case, experiments are under way aimed at resolving this question.

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Synthesis of a 1,5-Naphthoquinone

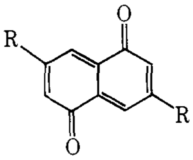
Sir:

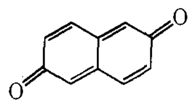
We wish to report the synthesis of an unequivocal 1,5-naphthoquinone, the 3,7-di-*tert*-butyl-1,5-naphthoquinone (**1a**). Of the three possible extended naphthoquinones, **1–3**, only **2** was known.[1] The synthesis of **1** seemed of interest with respect to the structure of naphthazarin (1,4- *vs.* 1,5-quinoid)[2-4] and to recent calculations on quinones.[5,6]

Table I. Calculated[15] Electron Affinities ($-E_A$) (eV) of Naphthoquinones

	Naphthoquinone					
	1,2-	1,4-	1,5-	1,7-	2,6-	2,3-
$-E_A$	2.98	3.09	3.62	3.61	3.75	3.66

Attempts to prepare **1** electrochemically[7] or under conditions suitable for the preparation of **2** failed,[8] indicating the higher reactivity of **1**. Oxidation experiments of 1,5-dihydroxynaphthalene with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in dioxane or lead tetraacetate in acetic acid carried out in our laboratories yielded brown amorphous substances and no compound with the tentative properties (uv, reduction) of **1**.


1, R = H
1a, R = *t*-Bu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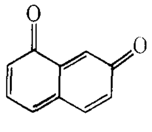
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In order to decrease the high reactivity of **1** we introduced a shielding group into positions, 3 and 7, namely *tert*-butyl. As is known and has recently been shown by the synthesis of highly reactive ring systems, *e.g.*, pentalene[9] and cyclobutadiene,[10] *tert*-butyl groups exert a high stabilizing effect with only minor changes of the π-electron system.[11]

Dehydrogenation of 1,5-dihydroxy-3,7-di-*tert*-butylnaphthalene by DDQ under nitrogen in methylene chloride yielded in a nearly quantitative reaction after evaporation red crystals of **1a**. The structure follows from the easy reduction to the conjugate hydroquinone and from spectral data: nmr ($CDCl_3$) 1.27 (s, 18 C $(CH_3)_3$), 6.52, 7.67 (2d, 2 × 2, H 2, 6 and H 4, 8, $J \approx 2$ Hz); ir (CCl_4) 2970 (CH_3), 1620 (C=C), 1625 (C=O), 1594 cm^{-1} (C=C); uv_{max} (CCl_4) 475, 462 nm sh; mass spectrum (70 eV) *m/e* (rel intensity) $[M^+ + 2]$ 272 (3), 257 (4), 201 (1). As in other cases[12] the mass spectrum of this quinone shows only a very small peak at the molecular mass (*m/e* 270). The existence of a molecular ion *m/e* (found) 270.1614, (calcd for $C_{18}H_{22}O_2$ 270.1619) could be shown by high resolution mass spectrometry,[13] tlc R_F ($CHCl_3$, silica gel) 0.2. **1a** is stable at room temperature under anhydrous conditions, however, with moisture 5-hydroxy-3,7-di-*tert*-butyl-1,4-naphthoquinone is slowly formed.

We have already shown for the anthraquinone series[14] that the calculated energy of the LUMO's (electron affinities)[15,16] seems to be a good measure for the stability[17] of quinones. As can be seen from Table I the easily obtainable naphthoquinones possess E_A values of nearly −3 eV whereas the values of **1–3** are found to be in the range from −3.6 to −3.75 eV. 1,5-Dihydroxy-3,7-di-*tert*-butylnaphthalene (mp 230–232° dec) was prepared by 1,5-dichlorosulfonation[19] of 2,6-di-*tert*-butylnaphthalene (10% yield) followed by fusion with KOH (65%).

1a possesses an unusually low C=O stretching frequency (1625 cm^{-1}, CCl_4) as compared with 1,4-naphthoquinone (1675 cm^{-1}, CCl_4)[20] and other para one-ring quinones (1690–1660 cm^{-1}). This observation can be explained by the extended conjugated π-electron system of **1a**, which correlates to the value of another two-ring quinone, 4,4′-diphenoquinone (1634 cm^{-1}, CCl_4),[20] and is a strong argu-