treatment was applied only to the region of detergent concentration in which the initial sigmoid dependence of k_{obsd} on detergent concentration was seen. It did not include the region at very high detergent concentration where k_{obsd} often decreases in bimolecular reactions due to dilution of one reactant in the micellar phase. A number of representative plots are shown in Figure 1; they include various types of reactions using a wide variety of detergents and conditions. The general linearity of these plots indicate that the quantitative expression which describes them (eq 8) describes, at least empirically, a large number of micelle catalyzed reactions.

The slopes of the plots range from approximately 1 to 5. These values are far less than the number of 10 to 100 detergent molecules which are found in micelles[3] and which would be predicted on the basis of eq 3. Such low exponential terms in eq 4 have previously been interpreted as being the number of surfactant molecules per substrate molecule in a catalytically productive pre-micelle.[5] The low values of n and their nonintegral nature may also suggest multiple equilibria in the formation of catalytically productive micelles.

The model described by eq 3 does not require distinct conformational forms of the catalyst which are the basis of the Monod–Wyman–Changeux[10] and the Koshland–Nemethy–Filmer[11] models for enzymatic homotropic interactions. Nevertheless, it is probable that catalytic micelles have different shapes in the absence of and in the presence of substrates, since both ionic and nonionic solutes are known to induce changes in the shapes of micelles.[12] Thus, the kinetics of micellar catalysis could be treated analogously to either of the two enzymatic conformational models,[10,11] although such a treatment would be extremely complex.

An apparent shortcoming of the alternative mechanism of micellar catalysis (eq 3) as a model for enzymatic positive homotropic interactions is that the phenomenon results from cooperativity in association of the subunits of the micelle, the detergent molecules, rather than association of the substrate to the detergent. This apparent shortcoming is reconcilable, at least in a qualitative sense, with a model proposed by Frieden.[13] Frieden has noted that many enzymatic homotropic interactions can be related to the degree of aggregation of a polymeric enzyme. One form of the enzyme, either dissociated or aggregated, would have the greater catalytic activity. He also noted that his model was analogous to the Monod–Wyman–Changeux model,[10] the only difference being that the two conformational forms which exist in equilibrium are monomer and oligomer.

The occurrence of homotropic interactions in enzymatic reactions has often been associated with the fact that enzymes catalyzing these reactions are always composed of subunits. A causal relationship between the association of subunits to form functional aggregates which show homotropic interactions has been inferred.[14] Micellar systems which catalyze chemical reactions are simple models of such systems. The model differs from the enzyme in that the subunit is a simple detergent molecule rather than a complex polypeptide chain. Thus, the causes of positive homotropic interactions in enzymatic and micelle catalyzed reactions are related; they can be traced to self-assembly of subunits in both cases.

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Long-Lived Radical Cations from Mesocyclic Dithioethers

Sir:

We wish to report that long-lived, nonaromatic, sulfur radical cations are formed by treatment of eight- and nine-membered mesocyclic dithioethers with one-electron oxidizing agents such as $Cu(CH_3CN)_4(BF_4)_2$, nitrosyl tetrafluoroborate, $NOBF_4$, or nitrosyl hexafluorophosphate, $NOPF_6$, in either acetonitrile or nitromethane.

The radical cation from 1,5-dithiacyclooctane (DTCO) is usually prepared by mixing solutions of 0.01 M $Cu(CH_3CN)_4(BF_4)_2$[1] and 0.03 M DTCO in dry nitromethane. A yellow colored solution with $\lambda_{\max}$ of 412 nm is formed instantly. At room temperature the solution gives an ESR spectrum consisting of a complex multiplet with a g value of 2.012 and showing no saturation at high microwave power. The ESR spectrum of the radical is observable for at least 72 h at room temperature. This g value and the splitting pattern suggests that the unpaired electron is localized on sulfur rather than carbon and is coupled to the α-hydrogens. The same spectrum is observed when DTCO is allowed to react with 1 mol of solid $NOBF_4$ or $NOPF_6$ in acetonitrile.

Since monothioethers (dimethyl sulfide, tetrahydrothiophene), acyclic dithioethers (2,5-dithiahexane), and mesocyclic dithioethers with six-, seven, and ten-membered rings (1,4-dithiane, 1,4-dithiacycloheptane, and 1,6-dithiacyclodecane) *do not give stable radicals* under conditions of the reaction, the transannular sulfur atom in the eight- and nine-membered mesocyclic rings appears to be responsible for the stability of the radical.

Aliphatic sulfur radical cations have been reported recently by treatment of some thioethers (e.g., tetrahydrothiophene, dimethyl sulfide) either with hydroxyl radicals generated by Ti^{III} and H_2O_2 in a flow system[2] or by pulse radiolysis in water.[3] During the studies it was found that when thioethers are oxidized with hydroxyl radicals, a monomeric cation radical, $R_2S\cdot^+$ is not observed. The initially formed monomer apparently reacts further with a neutral thioether molecule to form a dimeric radical cation, $R_2\dot{S}\text{–}S\text{–}R_2^+$, which is observed

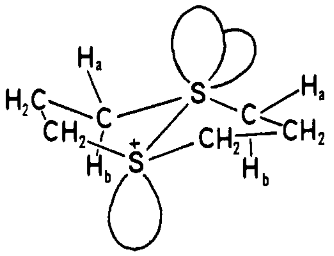

Figure 1. A possible structure[4] of DTCO·$^+$

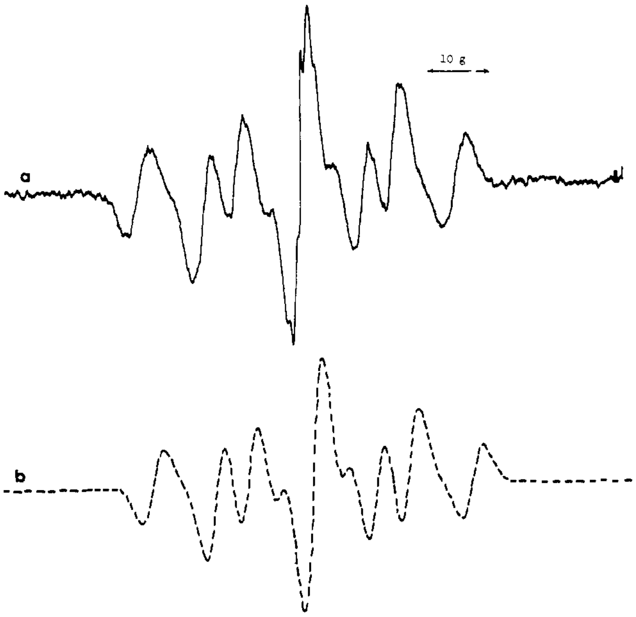

Figure 2. (a) ESR spectrum of DTCO·$^+$ at −25° in CH_3NO_2. (b) Simulated ESR spectrum of DTCO·$^+$.

by ESR.[2] The lifetime of these radicals is very short ($t_{1/2} \sim 10^{-4}$ s). Thus the enhanced stability of mesocyclic cation radicals can be attributed to the transannular interaction between the neutral thioether group and radical cation *within the same molecule.*

The ESR spectrum of the dimeric dimethylsulfide radical cation ($g = 2.0103$) formed by oxidation of dimethyl sulfide by hydroxyl radicals in water consists of a 13-line multiplet due to the delocalization of the electron over both sulfur atoms and coupling to 12 equivalent protons.[2] However, the ESR spectrum of the mesocyclic radical cation at low temperature (−25 °C) in CH_3NO_2 does not correspond to a nine-line spectrum resulting from coupling of the electron with eight equivalent protons but the spectrum is consistent with a spin localized preferentially on only one sulfur atom and split by the α-hydrogens into a triplet which is further split into another triplet (Figure 2a). The observed spectrum has been simulated[5] (Figure 2b) by assigning a coupling constant of $A = 15.2$ G to one triplet and $A = 10.4$ G to the other triplet with a line width of 3.6 G. By considering the bonding in the mesocyclic radical cation the spectrum may be rationalized. Counting both the lone pairs and the unpaired electron as substituents, the sulfur which contains the lone pair and the unpaired electron is five-coordinated and trigonal bipyramidal; the sulfur with the positive charge is four-coordinated and angular. Thus, the two sulfurs are not equivalent in this fused [3.3.0]mesocyclic ring system and interconversion appears to require appreciable steric reorganization.

The four α-hydrogens adjacent to the trigonal bipyramidal sulfur are divided into two inequivalent sets and the electron will interact with each set in a different manner to give the two triplets. In nonfused dimer radical cations little, if any, steric barrier prevents the two sulfur atoms from becoming equivalent and delocalization of the electron on both sulfurs is to be expected. When the solution containing the mesocyclic radical cation is heated in an attempt to speed up electron transfer between the sulfurs and give a nine-line ESR spectrum, the spectrum broadens and then disappears indicating that the radical decomposes at elevated temperature. The radical cation is also extremely susceptible to water; the yellow color and the ESR spectrum disappear instantly when moisture is admitted to the system. DTCO·$^+$ has been reduced back to DTCO with zinc amalgam in acetonitrile.

Although $Cu(CH_3CN)_4{}^{2+}$ and NO^+ react with both DTCO and thianthrene[9] to give long-lived radical cations, we have been unable to observe radicals with tetrahydrothiophene[2] with these reagents under similar conditions. To our knowledge, DTCO·$^+$ has the longest lifetime of any nonaromatic cation radical known. Amine[6] and phosphine[7] cation radicals have been reported but they have short lifetimes. Tetraalkylhydrazine radical cations[8] are only stable in solution for several minutes.

The nine-membered mesocyclic dithioether, 1,5-dithiacyclononane (DTCN), behaves similar to DTCO but gives a more complex ESR signal due to the nonequivalence of all α-hydrogens. Once the size of the mesocyclic ring-system reaches ten, the favorable transannular interaction no longer exists and the radical cation is not observed. Likewise, with the seven-membered ring, stabilization of the radical is decreased due to the ring strain involved in the fused [3.2.0] ring system.

Other aliphatic sulfur radical cations may be able to be stabilized by electron-pair donors besides a thioether sulfur as long as the donor is within the same molecule and no steric or electronic effects prevent cyclization. Further work is in progress.

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