category. Strained allenes are known to produce vinyl rather than allyl ethers on reaction with RO^-/ROH.[13]

Acknowledgment. We thank Dr. W. Dietrich for ^2H NMR spectra and Dr. O. Schnurr for preliminary experiments with diazocyclopentadiene.

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Catalysis of the Hydrolysis of Ethyl Benzoate by Inverted Micelles Adsorbed on Platinum

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In studies of electrooxidation of compounds in the presence of cationic surfactants, it was observed that the surfactant filmed the electrode, altering relative rates of electrode reactions.[1-3] The film, which was composed of a layer of anions on the platinum electrode ion paired to surfactant cations, excluded water from the surface. This allowed the obtaining of anodic voltammetric curves in aqueous solutions for many substances that normally do not give voltammetric curves in water.[3]

To obtain a better understanding of this film, a study was made of the catalysis of the hydrolysis of ethyl benzoate on the film adsorbed on platinum. The homogeneous kinetics of this system had been previously studied,[4,5] and it has been shown that the rate of hydrolysis of esters is affected by the presence of micelles.[6,7]

The kinetic runs were made in a beaker containing 100 mL of 0.0965 N sodium hydroxide, 6.8×10^{-3} mol of ethyl benzoate, and, unless otherwise stated, 2.46 mmol of the surfactant, Hyamine 2389 (predominantly (methyldodecylbenzyl)trimethylammonium chloride obtained from Rohm and Haas). The critical micelle concentration of the surfactant is 0.04% by weight of the active material.[8] (This corresponds to an approximately 1 mM solution.) The temperature was not controlled but was monitored and was 26 ± 0.5 °C. A comparison of rates determined at the two extremes of the temperature range showed that they had an average difference of only 1%.

The initial rate of disappearance of the hydroxide ion was measured by withdrawing 2.0-mL samples from the stirred solution at 10-min intervals and titrating with standard hydrochloric acid. Different area platinum foils were inserted in the solution.

The effect of potential on the rate was determined in an H cell with the compartments separated by sintered glass. The catalytic compartment contained the reaction mixture, a 9.5-cm² foil, and a saturated calomel reference electrode. The potentials which were controlled by an Anotrol Model 4700 potentiostat are referred to the calomel electrode. The other compartment contained a 16.5-cm² platinum counter electrode.

The reaction was found to be catalyzed by Hyamine 2389. There is a maximum in the rate at about 20 mM of Hyamine which is typical for micelle catalysis.[9]

Figure 1 shows the effect of suspending platinum foils of different areas in the solution. It can be seen that in the absence of surfactant, addition of platinum caused only small changes in rate, while in the presence of surfactant the rate increases linearly with increases in platinum area. Apparently the inverted micelle adsorbed on the platinum is a better catalyst than the normal micelle.

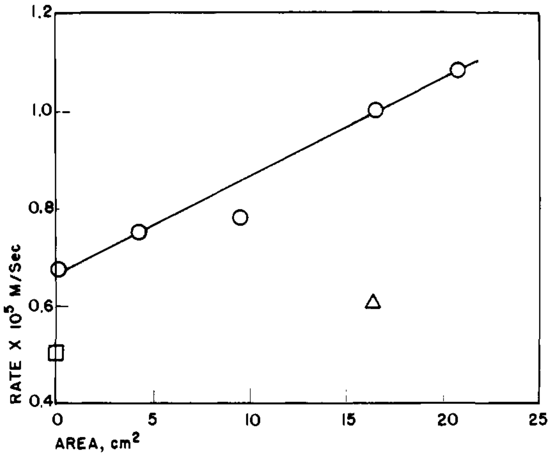

Figure 1. Effect of added platinum metal on the rate of hydrolysis of ethyl benzoate in the presence of Hyamine 2389 (4.87×10^{-2} M). (□) Rate in the absence of platinum or surfactant; (△) rate in the presence of platinum, without surfactant; (○) rate in the presence of platinum and surfactant.

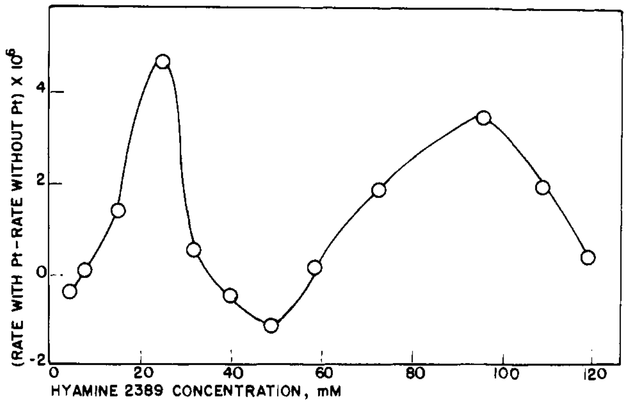

Figure 2. Effect of surfactant concentrations on the rate (×10^6 M/s) of the platinum–surfactant-film-catalyzed hydrolysis of ethyl benzoate (rate in the presence of platinum − rate in the absence of platinum).

Figure 2 shows the effect of different concentrations of surfactant on the acceleration of the rate by platinum as measured by subtracting the rate with surfactant from the rate with platinum and surfactant.

A reasonable explanation of this curve is that the first maximum in the rate occurs at the surfactant concentration that forms a monolayer which consists of an inverted micelle on the platinum surface. The decrease in rate beyond the maximum would then be caused by formation of a bilayer, with the minimum occurring on completion of the bilayer. That this explanation is correct is indicated by the fact that the concentration at the minimum is twice the concentration at the first maximum; however, this factor of 2 may be a coincidence. One would expect the third layer to be a good deal more diffuse. In agreement with this the second maximum is broader and occurs at 3.8 times the concentration of the first maximum rather than 3 times.

In the electrochemical studies[1-3] it had been observed that the Hyamine showed two oxidation waves and that this oxidation was important in the formation of the electrochemically active film. The catalysis of the hydrolysis reaction was studied on platinum potentiostatted at different potentials to determine whether Hyamine oxidation formed a film with different characteristics. No abrupt change in rate was observed, indicating that the oxidized film has essentially the same catalytic characteristics as the unoxidized film. As previously shown,[10] there is only a slight

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change of rate at low anodic potentials where Faradaic currents are negligible. At higher anodic potential there is a rise in rate caused by an increased adsorption of chloride accompanied by formation of the ion paired quaternary chloride. On the cathodic side there is also a rise which can be attributed to direct adsorption of the quaternary cation. Similar results have been obtained in other types of experiments.[11,12]

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Hexapus, a New Complexing Agent for Organic Molecules

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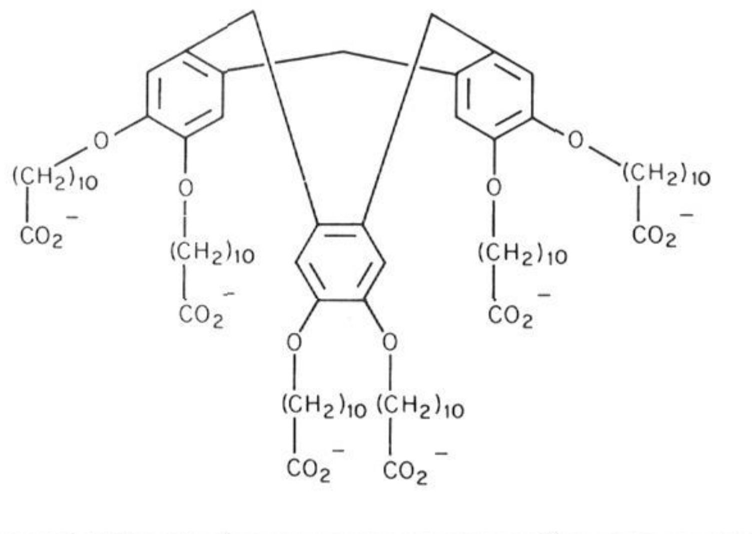
Enzymes function by assembling their catalytic groups and substrates in "cavities" or "grooves" located on the protein surface; proper orientation of the reactive functionalities within the small volumes of space greatly accelerates reaction rates. In an attempt to model enzyme action, chemists are synthesizing cavity-bearing compounds such as cyclodextrins,[1-3] crown ethers,[4-6] crosslinked polymers,[7,8] macrocycles,[9] and "tweezer" molecules.[10,11] We now report a new kind of space-encompassing compound, the hexa-10-carboxydecyl ether of 10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]-cyclononene-2,3,7,8,12,13-hexol, called "hexapus".[12] Six chains, projecting from a crescent-like cyclotriveratrylene framework, terminate with carboxylate groups that solubilize the compound in mildly basic water (solubility > 60 g/L or 0.04 M at pH 8.6, 25 °C). Hydrophobic association can gather together the six chains and create an adjustable "cavity" capable of incorporating small organic molecules (Figure 1). Hexapus thus resembles a micelle except that its six chains are covalently linked and prevented from participting in complex departure–entry equilibria found in micellar aggregates.[13]



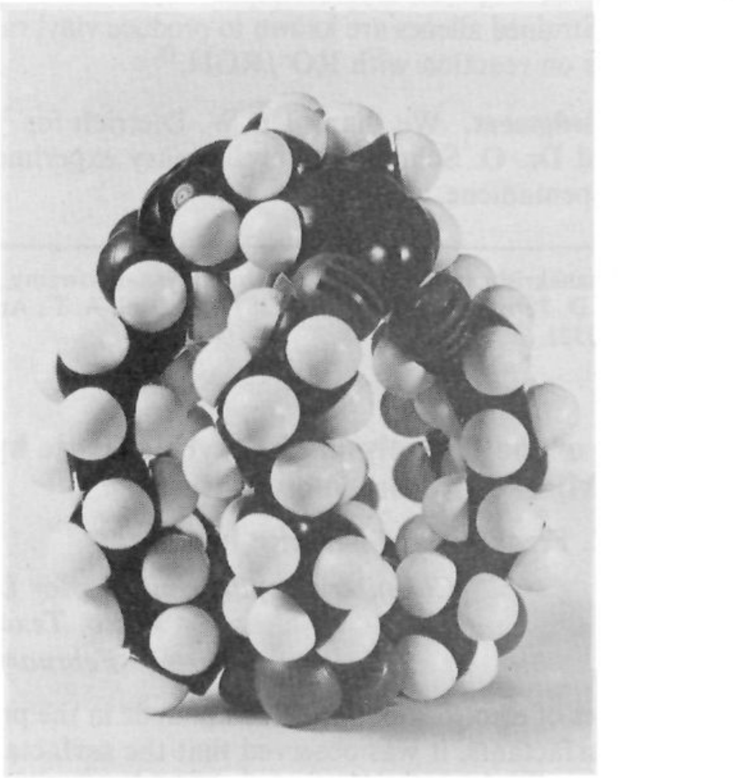


Figure 1. CPK model of hexapus having its six hydrophobic chains associated to minimize hydrocarbon–water contact.

Hexapus was synthesized by first reacting veratrole and formaldehyde in aq. HCl to form cyclotriveratrylene. This was demethylated with BBr_3 according to a literature procedure.[14] The resulting hexahydroxy compound (5.0 g, 0.014 mol) in DMF under N_2 was converted into its salt with NaH (2.5 g, 0.10 mol); the salt was then heated with ethyl 11-bromoundecanoate (33 g, 0.11 mol) at 90–100 °C for 3 h and 70 °C for 16 h. Removal of the solvent under reduced pressure, addition of CH_2Cl_2, filtration through Celite, and flash evaporation of the filtrate gave hexaester which was purified by column chromatography (SilicAR CC-7 Special/heptane–benzene eluant). Purified material (a light yellow syrup) weighed 10.6 g (46%). Hexaester (10.6 g, 0.0065 mol) in 50 mL of THF was added to 50 mL of 30% aqueous NaOH and boiled under reflux for 18 h. Standard workup produced yellowish crystals that were crystallized once from ether/benzene and four times from ether/hexane to yield 4.2 g (44%) of hexapus (colorless crystals, mp 99–100 °C). Structure proof consisted of the usual spectral and chemical analyses. In particular, the ^{13}C NMR spectrum showed only three aromatic carbons (two quaternary and one tertiary); the neutral equivalent was 245 (calc. 245); a correct molecular weight was obtained by field desorption mass spectrometry.[15] Thus the key alkylation step provides a satisfactory yield of product free from impurities with fewer than six chains.

Hexapus exhibits much less surface activity than single-chained fatty acid salts. Solutions do not foam even at 0.02 M hexapus. The surface tension of water mainfests a constant 61.0 ± 0.4 dyn/cm (pH 9.5 at 24 °C) in the presence of $4.0 \times 10^{-4} - 1.0 \times 10^{-2}$ M hexapus. In contrast, 1.0×10^{-2} M potassium laurate at pH 10.0 lowers the surface tension of water to 34 dyn/cm[16] Apparently, the tendency of hexapus to absorb at the air–water

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