The behavior of the stilbene–viologen system in DPL/DCP at lower temperatures is somewhat more complicated. The actual *increase* in stilbene probe fluorescence in the presence of viologen in the phase-transition region is probably attributable to a "tightening" of the vesicle structure brought about by interaction of the added cation with the anionic head groups of the assembly. The quenching of stilbene fluorescence observed at lower temperatures is more difficult to understand. As pointed out above, the sharp increase in stilbene fluorescence in DPL alone at low temperatures is best attributed to location of the stilbene probe in a highly ordered environment in which the effective "microviscocity" is very high. Studies with other probes more hydrophilic than stilbene also suggest that the functionalized surfactants should be retained in the hydrocarbon portion of the vesicles. The contrast between the behavior of the stilbene probes in DPL alone and in DPL/DCP (Figure 6) may indicate that in the mixed vesicles the stilbene occupies a "different" site at low temperatures. This could explain the quenching by MV^{2+}. Alternatively, if we assume the stilbene remains "within" the bilayer interior, the observed quenching could be due either to a static phenomenon whereby the viologen is also incorporated into a relatively hydrophobic site such that some stilbene–viologen contacts are possible or to a quenching over greater distances such as has been proposed for other vesicle systems.[36] Studies are currently under way to distinguish between these possibilities.

The overall results of this study emphasize the variability of the structures of different surfactant assemblies. Moreover, they indicate how controlled modulation can be obtained, especially in the case of charged micelles, by the use of additives. Thus SLS micelles can be adjusted from loose aggregates with little separation of hydrophobic from hydrophilic regions to well-organized assemblies capable of sequestering nonpolar solubilizates in a hydrophobic interior, much less accessible to polar solutes. This ability to modify the sequestering action of surfactant assemblies should be especially useful in developing surfactant systems for control and modification of reactivity.

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Registry No. SDS, 151-21-3; MV^{2+}, 4685-14-7; *trans,trans*-DPB, 538-81-8; S_4, 77814-46-1; S_6, 77814-47-2; S_{10}, 77824-98-7; S_{12}, 77814-49-4; S_{16}, 74392-06-6; heptyl alcohol, 111-70-6; dicetyl phosphate, 2197-63-9; *trans*-stilbene, 103-30-0.

Monte Carlo Study of Macrocyclization To Form Benzo-Crown Ethers

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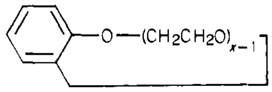
Abstract: A Monte Carlo study has been conducted of the formation of benzo-crown ethers (**1**) from an acyclic precursor.



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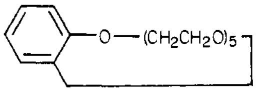

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The range of x is 2 to 16 inclusive. Limiting behavior is obtained at $x \geq 7$. As x falls below 7, calculated cyclization constants fall below the extrapolation of the limiting behavior. The cyclization constants pass through a minimum when x is about 4. The major features of the computed cyclization constants are in harmony with trends observed in kinetic constants reported recently by Illuminati et al.[11] The presence of an ortho-fused benzo moiety has a marked effect on the relative ease of cyclization to form $(CH_2CH_2O)_6$ and **2**.

Calculations based on a rotational isomeric state model[1-3] for unperturbed poly(oxyethylene) have provided insight into configuration-dependent properties of macrocycles formed from this polymer. The model that predicts cyclization to form $(OCH_2CH_2)_{2y}$, $y = 2–10$, is most readily achieved with $(OCH_2CH_2)_6$,[4] a conclusion which stands in harmony with experiment.[5,6] Among the most favored conformations calculated[4] for $(OCH_2CH_2)_6$ is the one seen in its complex with potassium ion.[7,8] The most favorable conformation calculated[4] for $(OCH_2CH_2)_8$ is the one found experimentally in the crystalline state.[7] Larger poly(oxyethylene) macrocycles are sufficiently flexible so that no one conformation dominates the configuration partition function. Cyclization of the larger poly(oxyethylene) chains is found to require a contraction in the average distribution of chain atoms along the major principal axis of the gyration tensor, with little change perpendicular to this axis.[4,9]

Origin of the large macrocyclization equilibrium constants for $(OCH_2CH_2)_6$ and $(OCH_2CH_2)_8$ becomes clear upon comparison with macrocyclization equilibrium constants for the formation of $(SCH_2CH_2)_{2y}$ from poly(thiaethylene).[10] Macrocyclization equilibrium constants are found to be smaller in the sulfur series. Furthermore, the macrocyclization equilibrium constants calculated for the members of the sulfur series with $y = 3$ and 4 follow the trend established by molecules with higher y, but the molecules with $y = 3$ and 4 in the oxygen series have significantly higher macrocyclization equilibrium constants than the results predicted by this trend. The special behavior of $(OCH_2CH_2)_6$ and $(OCH_2CH_2)_8$, as opposed to the unremarkable behavior of $(SCH_2CH_2)_6$ and $(SCH_2CH_2)_8$, might conceivably be attributed to either of two factors: (a) geometric constants (bond lengths and bond

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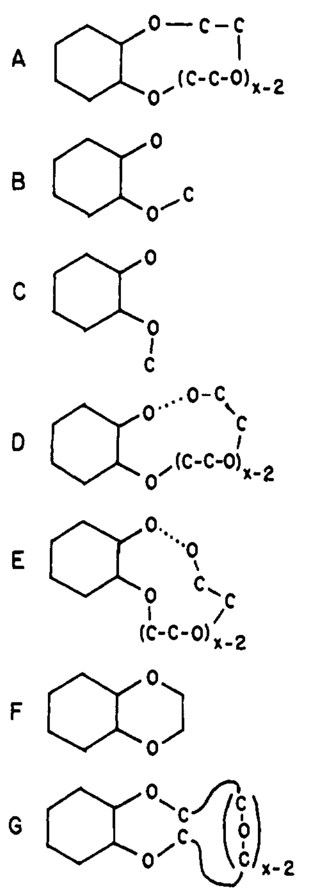

Figure 1. Benzo-crown ethers with hydrogen atoms omitted. Fragments are depicted in B–E. The dashed line in D and E connects oxygen atoms which define the "end-to-end distance" discussed in the text.

angles) differ in the two series, and (b) statistical weights arising from first- and second-order interactions are significantly different for poly(oxyethylene) and poly(thiaethylene). The former effect has been shown to be dominant.[10] The C–C and C–X bond lengths, as well as the C–C–X and C–X–C bond angles, conform more closely to those required for a tetrahedral lattice when X is oxygen than when X is sulfur, giving rise to the special ease of cyclization to form $(OCH_2CH_2)_6$. Geometrical modification of a small fragment in $(OCH_2CH_2)_6$ might therefore be expected to have severe consequences for the propensity of its formation from the acyclic precursor.

A means of achieving such a change in geometry would be incorporation of a fused benzo moiety (Figure 1A). As a consequence a cis conformation is imposed on that C–C bond, and the C–C–O angle is enlarged by about 10°. These changes markedly reduce the ability of the ring to conform to a tetrahedral lattice. Kinetic data for formation of such rings have recently been reported.[11] The rate of cyclization may, of course, depend on considerations other than the propensity for adoption of compact configurations by the acyclic precursor. Nevertheless, it is of interest to ascertain whether this propensity, as established using rotational isomeric state calculations, might be a dominant factor in dictating the chain-length dependence of the observed cyclization rate constants. The rotational isomeric state calculations have already been shown to be capable of rationalizing an unusual temperature dependence for the NMR coupling constants in poly(oxyethylene) macrocycles which incorporate a heteroaromatic system.[12] Here we reported that this model also correctly reproduces the major features found in the rate constants for cyclization. In particular, the 18-member ring system for the compound depicted in Figure 1A is predicted to *not* have any unusual propensity for cyclization. This prediction is in harmony with experiment[11] and in contrast to the behavior seen in the aliphatic $(OCH_2CH_2)_x$ series.[4,10]

Calculations

Geometry. Bond lengths used were 136, 140, 143, and 153 pm for C^{ar}–O, C^{ar}–C^{ar}, C–O, and C–C, respectively, where C^{ar} denotes an aromatic carbon atom.[4,13] Bond angle supplements were 60° for C^{ar}–C^{ar}–C^{ar} and C^{ar}–C^{ar}–O, and they were 68.5° for the remaining angles.

Representative Chains. Growth of representative poly(oxyethylene) chains was started from one of the oxygen atoms in the planar ortho $C_6H_4(O)O$ fragment. The first methylene group was assigned one of the two locations in the plane of the aromatic system (Figure 1B,C). A representative polyoxyethylene chain of the desired length (Figure 1D,E) was then grown from this methylene group using Monte Carlo methods and the rotational isomeric state model described by Abe and Mark.[3] This model correctly reproduces the unperturbed dimensions and dipole moments, as well as their temperature coefficients, for linear poly(oxyethylene). The resulting configuration was judged to contribute to the propensity for cyclization if the "end-to-end distance" (dashed line in Figure 1D,E) was within a specified tolerance.

Approximate adherence of the chain to a tetrahedral lattice permitted use of quite strict tolerances in our earlier study of macrocyclization of poly(oxyethylene).[4] In the case of $(CH_2CH_2O)_6$, for example, 0.12% of the precursor acyclic chains generated had $\Delta r < 55$ pm and $\Delta\theta < 2°$. Here Δr is the end-to-end distance and $\Delta\theta$ is the deviation from 110° of the bond angle formed upon ring closure. In contrast, not a single poly(thiaethylene) chain in a sample of 99 000 could satisfy these strict tolerances in our study of macrocyclization to form $(CH_2CH_2S)_6$.[10] The difference in behavior of poly(oxyethylene) and poly(thiaethylene) in this regard arises because the geometry of the latter chain is poorly approximated by a tetrahedral lattice. Criteria for cyclization had to be severely relaxed in the study of macrocycle formation of poly(thiaethylene) in order to provide for a significant number of surviving chains.

Chains of current interest are poorly described by a tetrahedral lattice because of the imposed rigidity of the benzo moeity. They therefore present a difficulty similar to the one encountered with poly(thiaethylene). Representative samples of chains with x = 2, 3, or 4 were found to have no chains with $\Delta r < 100$ pm. A more relaxed criteria must be used for identification of cyclic chains if the results are to be in harmony with the known ring formation.[11] We have examined chains which satisfy the criteria $\Delta r < 200$, 300, 400, and 500 pm. With *any* of these criteria, we find (a) cyclization is predicted for all chain sizes (x = 2–16) examined, (b) cyclization probabilities go through a local minimum at x = 3 or 4, and (c) there is no special ease of macrocycle formation at x = 6. If the criteria adopted is $\Delta r < 500$ pm, the macrocycle with the smallest probability of formation is that with x = 16. In contrast, use of $\Delta r < 200$, 300, or 400 pm produces the smallest probability at x = 3 or 4 rather than at x = 16. Since the experimental kinetic constants are found to be smaller at x = 16 than at x = 3–4, we have adopted $\Delta r < 500$ pm in preparation of Figure 2.

The orientations depicted in Figure 1B,C must both be included in the ensemble if the objective is to treat cyclization of all molecules with $x \geq 2$. When x = 2 (Figure 1F), the starting conformation in Figure 1B is clearly preferred. The situation is less clear for molecules with larger x. The starting conformation depicted in Figure 1B may then lead to cyclic structures which possess severe steric interactions (Figure 1G). Repulsive interaction of the methylene groups in the $-CH_2$–O–C^{ar}–C^{ar}–O–CH_2- fragment cannot occur if the starting conformation is the one depicted in Figure 1C. Representative chains, 2×10^5 in number, were generated using each starting conformation for each x in the range 2 to 16. Let $p_{x,B}$ and $p_{x,C}$ denote probabilities that an

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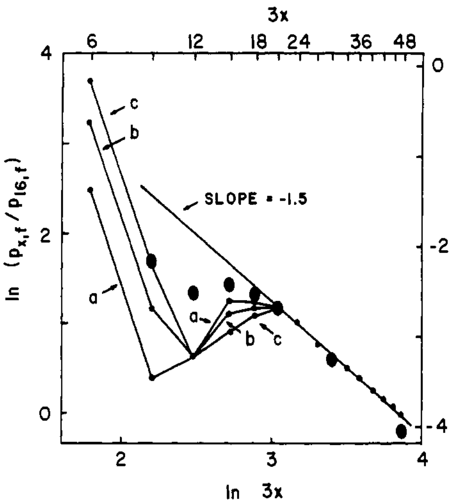

Figure 2. Chain length dependence of normalized cyclization probabilities ($p_{x,f}/p_{16,f}$) and experimental kinetic constants (EM). The values of f used are 0.1, 0.3, and 0.5 for curves a, b, and c, respectively. A straight line of slope −1.5 is drawn through the curves at high x. Kinetic constants are from Illuminati et al.[11] They are depicted as filled ovals.

"end-to-end distance" of 500 pm or less is observed for a chain of specified x when the starting conformation is that depicted in Figure 1B or 1C, respectively. The desired probability, $p_{x,f}$, is then formulated as $p_{x,f} = fp_{x,B} + (1 - f)p_{x,C}$. The most important conclusions reached in this study can be obtained with any physically sensible assignment of f.

Results and Discussion

Figure 2 depicts calculated cyclization propensities using f = 0.1, 0.3, and 0.5. Our concern here is with trends seen upon changes in x. In order to facilitate comparison, the vertical scale in Figure 2 has been adjusted so that points obtained at all f are coincident for the largest molecule studied (x = 16). This objective is obtained by multiplying each $p_{x,f}$ by a constant, $1/p_{16,f}$. The resulting curves are essentially coincident for $x \geq 7$. They are well described by a straight line with slope -1.5, as is shown in Figure 2. This is the slope expected for any sufficiently large flexible chain.[14] The large filled circules in Figure 2 denote the kinetic constants (designated[11] as EM) obtained experimentally by Illuminati et al.[11] for formation of the macrocycles of the type depicted in Figure 1A. Kinetic constants for formation of the larger rings are also described by the straight line of slope -1.5 when x is larger than about 7. Thus the Monte Carlo calculations correctly identify the value of x at which the limiting behavior is obtained. This identification can be obtained with any reasonable assignment for f.

None of the experimental kinetic constants plotted in Figure 2 lie above the extrapolation of the line whose slope is -1.5. Kinetic constants for the shorter chains fall significantly below this line. The three Monte Carlo curves for x between 3 and 6 also fall below the extrapolation of the line whose slope is -1.5. Thus the calculation correctly identifies the direction in which chains of this size deviate from the trends established by the behavior of long chains. Futhermore, the direction in which this deviation occurs is *opposite* to that seen in the absence of the aromatic system. The point for $(OCH_2CH_2)_6$ has been found to lie significantly *above* the trend established by $(OCH_2CH_2)_x$ of large x.[10] Incorporation of the benzo moiety into the crown ether eliminates the enhanced propensity for cyclization to form $(OCH_2CH_2)_6$. This benzo moiety prohibits approximate description of $(OCH_2CH_2)_6$ conformations using a tetrahedral lattice, just as does substitution of sulfur for the oxygen atoms in the macrocycle.[10] Either change therefore abolishes the special ease of formation of the 18-member ring.

The experimental kinetic constants pass through a shallow minimum when x is 4. Monte Carlo calculations also find a minimum near x = 4, although the calculated minimum is somewhat deeper than that found experimentally. The minimum located by the Monte Carlo calculation occurs precisely at x = 4 if f lies between 0.14 and 0.80. A small macrocyclization equilibrium constant was also calculated for $(OCH_2CH_2)_4$[4] and $(SCH_2CH_2)_4$.[10]

In conclusion, the Monte Carlo calculations based on a rotational isomeric state model for unperturbed acyclic poly(oxyethylene) reproduce the following features of the kinetic constants for formation of the ring system depicted in Figure 1A. (1) The limiting behavior is obtained when x is about 7. (2) Cyclization constants at smaller x (x = 2 possibly excepted) fall *below* the prediction based on extrapolation of the limiting behavior. (3) Cyclization constants pass through a minimum when x is near 4. We can therefore infer that the probability for adoption of a conformation with a small "end-to-end distance" makes a dominant contribution to the cyclization rate for these molecules.

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Gas-Phase Reactions of Rh^+ with Alkanes

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Abstract: The gas-phase reactions of laser-desorbed Rh^+ with various alkanes are examined using Fourier transform mass spectrometry (FTMS). The secondary reactions of these product ions are also reported. In contrast to the first-row group 8 transition metal ions whose reactions with alkanes show extensive cleavage of C–C bonds, Rh^+ shows few products resulting from C–C cleavage, and dehydrogenation is the major process in all reactions. Evidence is given that suggests the existence of a π-allylic intermediate, and some dehydrocyclization is indicated in our results. Ligands with molecular formulas corresponding to trienes bound to rhodium show no further reaction which may be caused by either steric or electronic effects.

The gas-phase reactions of transition metal ions with various hydrocarbons have been the focus of recent investigations by ion cyclotron resonance (ICR) spectrometry[1-3] and ion beam techniques.[4-7] The results of these experiments have provided many

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