for the rod-shaped merocyanine molecules is much higher. Further, the large change in S, in going from **1** to **2**, is indicative of the significant molecular motion required during the reaction. Therefore, the constraints offered by the local order encountered by **1** in the aggregate cannot be ignored. Since rates of **1** → **2** isomerization are lowest in the N_L phase, it is obvious that the bilayer nature of the disc-like aggregate offers the most constraint to ring closure. This could most probably arise because of the rod-like merocyanine molecules being effectively "incorporated" within the bilayer matrix preventing facile ring closure. In fact, a similar explanation has been advanced to explain the retardation of isomerization rates of **1** in the smectic B phase of *n*-butyl stearate.[20]

The kinetics of merocyanine to spiropyran isomerization have been studied in three polybutadiene oligomers[20] and in a variety of polymeric media.[21-23] Although no clear-cut dependence of isomerization rates on viscosity has been established, it appears that isomerization rates are not significantly altered by the bulk viscosity of the solvent. However, the internal or microviscosity arising from restricted segmental motions of the hydrocarbon chains in the vicinity of merocyanine molecules does appear to play a significant role in determining the rates and mechanism of the isomerization.[20-23] The bulk viscosities for KL and SDS lyomesophases have been determined.[24,25] No significant changes in viscosity at the $N_L \rightarrow N_C$ transitions are observed, but viscosity decreases drastically at the $N_C \rightarrow I$ transitions.

Lower bulk viscosity in the isotropic micellar phase (I) could enhance freedom for molecular motion in **1** and consequently isomerization rates are expected to be and are higher in the I phase as compared to N_L or N_C phases. The microviscosities of the bilayer and cylindrical aggregates are not known. Depending upon the site where **1** is solubilized in the disc-like and cylindrical aggregates, the microviscosity encountered by **1** could be quite different, and this could contribute significantly to the reactivity of **1**.

Conclusions

The rates of the unimolecular rearrangement of a merocyanine to a spiropyran in nematic lyophases are dependent on the nature of the surfactant aggregate. The lowest rates are encountered in the disc-like N_L phase. Since the wavelength of absorption maximum for the merocyanine does not change through the phase transitions, the polarity of N_C, N_L, and I phases appear to be identical. There is a large change in the order parameters of reactant and product indicative of the significant molecular motion required during the reaction. Although the bulk viscosities of N_L and N_C phases are not very different, microviscosities are probably quite different. This difference coupled with the changes in local order encountered by **1** are the most likely explanations for the rate changes at the phase transitions.

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Reaction Path Analysis of Hydrogen Abstraction by the Formaldehyde Triplet State[1]

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Abstract: The fully optimized transition state for hydrogen abstraction from methane by the formaldehyde excited triplet state has been determined by using ab initio theory and UHF/3-21G calculations. The most noteworthy feature of the transition state is that the methane hydrogen approaches the oxygen at an angle of 108.9° rather than at the 90° normally assumed for this reaction. Steric factors are suggested as the most likely source of this observation.

I. Introduction

Theoretical analysis of the preferred trajectory for attack on a carbonyl group by nucleophiles has become a powerful tool for understanding a wide array of ketone and aldehyde *ground-state* chemistry.[2] By comparison, relatively little computational effort has been devoted to defining the preferred mode of approach of reactants toward the carbonyl *excited-state*. For example, theoretical discussions have generally assumed that θ (Figure 1) for the prototypical hydrogen abstraction reaction by a formaldehyde $^3n-\pi^*$ state is 90° [3] (as would be expected for the initial approach of a hydrogen donor to the nonbonding p-orbital of the sp hybridized oxygen[4,5]). There is a corresponding paucity of excited-state *experimental data* vis-a-vis the ρ, θ, and ϕ parameters of Figure 1. What is available is derived from intramolecular chemistry and limited by the constraints thus imposed.[6] We have therefore undertaken a theoretical study of hydrogen abstraction by the formaldehyde triplet state in order to define the preferred transition state for approach by methane. This is the first treatment of this reaction which involves full optimization to give the saddle point geometry.

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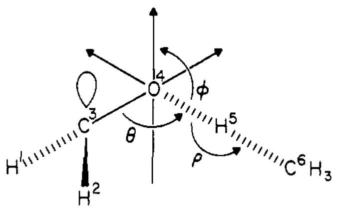

Figure 1. Geometrical parameters used in the analysis of $^3CH_3{=}0^* + CH_4 \rightarrow {}^{\bullet}CH_2OH + {}^{\bullet}CH_3$.

Table I. Saddle Point Geometry for Hydrogen Abstraction from Methane by the Formaldehyde $^3n,\pi^*$ State

geomtrcl paramtrs[a]	$^3CH_2{=}O^* + CH_4$	saddle point[d]	$^{\bullet}CH_2OH + {}^{\bullet}CH_3$
θ		108.9°	112.2°
ϕ[b]		9.2°	
ρ		176.0°	
out-of-plane bend	34.8°	31.3°	29.7°
r_{13}[c]	1.0733	1.0723	1.0696
r_{23}	1.0733	1.0732	1.0753
r_{34}	1.3835	1.3941	1.3920
r_{45}		1.1769	0.9645
r_{56}	1.0829	1.3503	

[a] See Figure 1. [b] Calculated from the two HCOH dihedral angles by using $\phi = 2345 - (180 - \angle 1345)$. [c] In Å. [d] A complete description of the transition state is as follows. Bond lengths: $r_{45} = 1.1769$, $r_{34} = 1.3941$, $r_{23} = 1.0732$, $r_{13} = 1.0723$, $r_{46} = 2.5270$, $r_{67} = 1.0775$, $r_{68} = 1.0780$, $r_{69} = 1.0777$. Bond angles: $\angle_{345} = 108.9$, $\angle_{234} = 119.1$, $\angle_{134} = 112.2$, $\angle_{346} = 106.5$, $\angle_{467} = 103.9$, $\angle_{468} = 103.1$, $\angle_{469} = 104.4$. Dihedral angles: $\angle_{2345} = 25.9$, $\angle_{1345} = 172.4$, $\angle_{2346} = 25.6$, $\angle_{3467} = 69.6$, $\angle_{3468} = -50.3$, $\angle_{3469} = 189.9$.

II. Methods of Calculation

The location of the transition was determined by ab initio molecular orbital calculations by using a version of the GAMESS[7] program modified to run on the Cyber 205 computer. A 3-21G basis set[8] was employed for the saddle point computations within the unrestricted Hartree–Fock (UHF) formalism. The saddle point was calculated by using initial optimized geometries for the methane ground state and for the $^3n{-}\pi^*$ state of formaldehyde. The latter had an out-of-plane, bending angle[9] of 35° (experimental = 38°)[10] and a C–O bond length of 1.38 Å (experimental = 1.31 Å).[10,11] The purity of the triplet was evidenced by $\langle S^2 \rangle = 2.0001$.[12] The fully optimized transition state was located by using the methodology of Schlegel[13] and was confirmed by a subsequent force constant calculation which yielded one negative eigenvalue. The transition state had $\langle S^2 \rangle = 2.0010$. The search was initiated with $r_{45} + r_{56} = 2.5$ Å, $\theta = 109°$, $\rho = 180°$, and $\phi = 0°$ based on preliminary calculations.

III. Results and Discussion

Our results are summarized in Table I, which contains the geometrical data describing the transition state computed for formaldehyde and methane as well as that of the reactants and products. As is evident from this table, the optimized transition state has the expected virtually colinear arrangement of CH_2-$O{\cdots}H{\cdots}CH_3$ ($\rho = 176°$), but both ϕ (9.2°) and θ (108.9°) deviate from a strictly "n-orbital approach" (i.e., $\phi = 0°$ and $\theta = 90°$).[14]

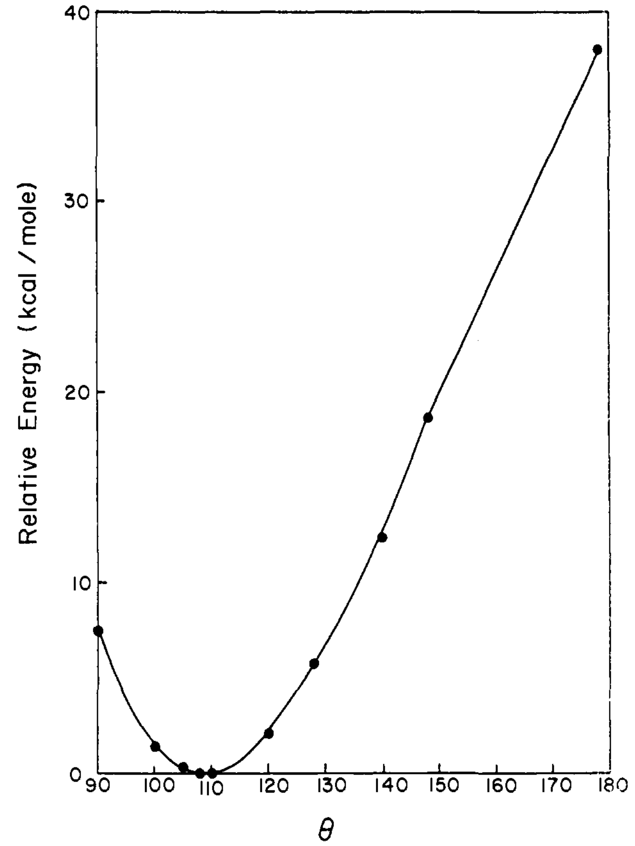

Figure 2. Energy dependence on θ, with the other transition-state parameters held constant (cf. Table I) and $\rho = 180°$.

The shape of the energy dependence on θ was of particular interest, and therefore we calculated the energy as a function of θ given fixed values for the rest of the geometric parameters. This was done in a series of single-point computations (by using the 3-21G basis set and GAMESS as described above), with the same geometry as the transition state except that θ was varied over the range 90–180°, and ρ was set to 180°. The results are plotted in Figure 2 and show a relatively steep increase in energy upon significant modification of the transition state angle.

Examination of the nonbonded interatomic distances for the transition-state geometry, but with $\theta = 90°$, reveals several distances which lie well within the sum of the van der Waals radii (for example, r_{35}, 1.8; r_{36}, 2.9; r_{26}, 2.6 Å). These interactions are eased appreciably at the actual transition state with $\theta = 109°$ (r_{35}, 2.1; r_{36}, 3.2; r_{26}, 3.1 Å). It has proven useful to characterize reaction and rotational barriers by factoring total energy into the one-electron ($T + V_{ne}$) and "pure" repulsive ($V_{nn} + V_{ee}$) component terms.[15-17] Such a treatment for the dependence of energy on θ is presented in Figure 3, where relative one-electron and individual repulsive coulombic terms are plotted normalized to 0 when $\theta = 90°$. We recognize that the energy units in Figure 3 are orders of magnitude larger than those in Figure 2. Nevertheless, the *trends* one observes for the several curves show the repulsive (i.e., steric) interactions progressively diminishing as θ increases thus partially compensating for the increase in energy caused by the

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(11) Calculations at the 6-31G* level give a bond length and out-of-plane bending angle of 1.34 Å and 40°, respectively; cf. *Carnegie-Mellon Quantum Chemistry Archive*, 3rd edition; 1983; sequence no. 1031. The best fit by ab initio methods has been obtained by using "many-body perturbation theory", with 1.33 Å and 37°; cf. Adams, G. F.; Bent, G. D.; Bartlett, R. G.; Purvis, G. D. *J. Chem. Phys.* **1981**, *75*, 834–842. See, also: Sannigrahi, A. B.; Mukherjee, D. C.; De, B. R. *Int. J. Quantum Chem.* **1983**, *22*, 1695–1705.

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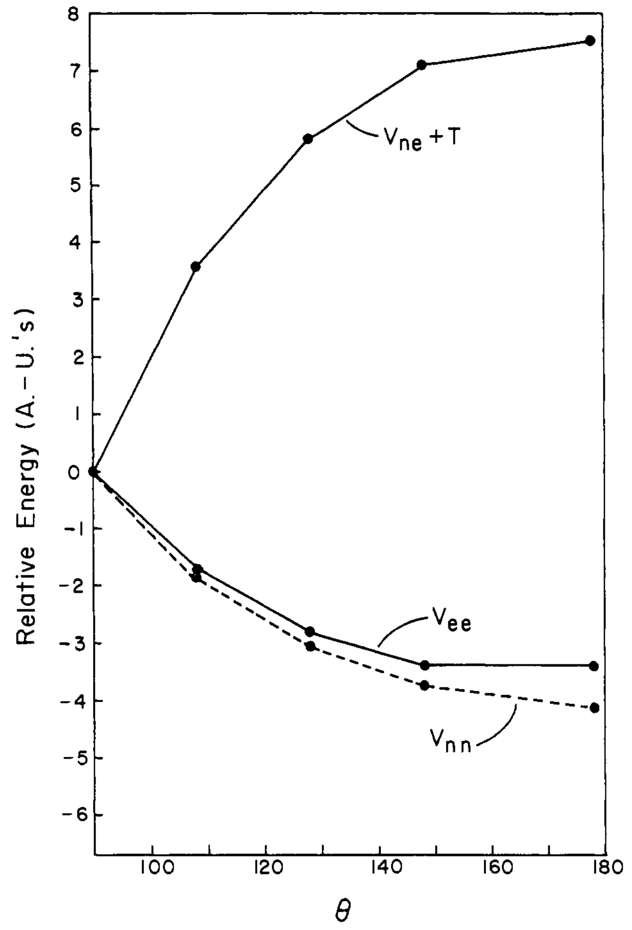

Figure 3. Breakdown of the θ plot (Figure 2) into component terms and normalized to 0 at 90°. The component terms are the one-electron coulombic interactions between the electrons and nuclei (V_{ne}), the total electronic kinetic energy (T), the two-electron coulombic interactions between all pairs of electrons (V_{ee}), and the coulombic interactions between all pairs of nuclei (V_{nn}).

reduced one-electron interactions at wider θ angles. The net consequence of these countervailing effects is to minimize the transition-state energy at a $\theta > 90°$. Since in Figure 3 r_{46} remains constant at all values of θ, these steric effects presumably derive from methane interacting with the formaldehyde CH_2 unit (see above).[18] It is possible that the (upward) deviation of ϕ from 0° has a similar origin.[19] One would expect such effects to be accentuated with larger carbonyl and hydrocarbon reactants.[20,21]

The O–H bond distance (r_{45} = 1.18 Å) in the transition state is comparable to that estimated by Salem[22] (1.16 Å) from a surface crossing analysis, and $r_{45} + r_{56}$ (2.53 Å) compares favorably to the value (2.6) calculated by Bigot[3a] from the potential energy surface of a 90° approach. The activation energy for the process was determined by single-point UMP3/6-31G*//3-21G calculations[23,24] by using the GAUSSIAN82 series of programs.[25,26] The transition state is found to lie 22.2 kcal/mol above the reactants.[27] Specific values, all with MP3/6-31G*//3-21G are −40.348 44 au for CH_4,[28] −114.057 26 au for formaldehyde triplet,[26] and −154.370 25 au for the transition state.[26] An MP3/6-31G*//3-21G calculation for formaldehyde ground state[26] gives −114.172 49 au, thus placing the triplet at this level of computation at 72.3 kcal/mol (experimental value = 80 kcal/mol).[29]

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[18] Such a steric effect has been noted previously; cf. ref. 3a.

[19] A ϕ plot analgous to Figure 2 shows a relatively shallow minimum between 0 and 45° with energy then increasing rapidly towards 90°. See also ref. 3b.

[20] Our elongated (C–O) (r_{34}) bond length has undoubtedly dampened these effects, and to the extent that they play a major role in determining the transition state, θ at r_{34} = 1.31 Å would be displaced yet further from 90°.

[21] Other factors which might influence θ are rehybridization of the oxygen in the isolated formaldehyde triplet (we see such rehybridization, but it does not appear to involve the n_O-orbital) and the potential interaction of the methane C–H orbital with oxygen orbitals other than n_O.

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[26] We thank James Blake and Prof. William Jorgensen for carrying out these calculations.

[27] Bigot[3a] obtained a value of 27 kcal/mol. Our calculated value, using the 3-21G basis set without correlation, is 33.4 kcal/mol. There are no published experimental activation parameters for intermolecular hydrogen abstraction by an aliphatic ketone or aldehyde.

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