and a term including an electronic coupling matrix element squared (V^2). The rate ratio k_{-et}/k_{sep} is thus described as the product of FC and a term P which is a dimensionless adjustable scaling parameter that includes the separation rate (eq 3c). The dependence of the rate ratio on ΔG_{-et} and the solvent and vibrational reorganization energies, λ_s and λ_v, are contained in FC. The reorganization energies are adjustable, as is a final parameter, ν, which is a single averaged frequency taken as representative of the rearranged vibrational modes. In fitting the data it is assumed that values for λ_v and ν of 0.3 eV and 1500 cm^{-1}, respectively, are appropriate for both sets of data.[4] The fitting procedure thus involves finding the best values for P and λ_s. The value of λ_s which gives the best fit to the CSH data, 1.4 eV, is smaller than that for the CR data, 1.6 eV.[10]

It is clear from Figure 1 that both sets of data can be described very well by the same semiclassical formalism in which the effects of solvent dielectric saturation are not included.[11] Indeed, in the free energy range in which the data are obtained (ca. −2.0 to −2.6 eV, Figure 1) the decrease in rate with increasing exothermicity of the CSH reaction is even *more pronounced* than that of the CR reaction, although the fitting procedure reveals that this is due to the somewhat smaller λ_s for the CSH reaction. Thus, the present study demonstrates that when CR and CSH reactions in geminate pairs are compared directly using similar chemical systems, the prediction[3] that the inverted region for the CSH reactions should be less pronounced than that for the CR reactions is not sustained. This finding for solvent-separated pairs is in agreement with similar conclusions obtained by Marcus[12] for electron-transfer reactions in contact ion pairs based upon comparisons between absorption and emission spectra of CT complexes.

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(10) Although the difference in λ_s of 0.2 eV may not be very accurate due to limitations in the electron-transfer model and the assumptions involved in the fitting procedure, the total reorganization energy for the CSH reaction is clearly somewhat smaller than that for the CR reaction.

(11) A referee points out that a more pronounced inverted region would be predicted for the CSH reaction if both MA$^+$ and the MA radical were similarly solvated. We feel that this is unlikely in the polar acetonitrile solvent.

(12) Marcus, R. A. *J. Phys. Chem.*, in press.

Variational Transition State for the Reaction of Cl_2C: with Ethylene and the Thermodynamics of Carbene Additions

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According to conventional transition state theory, the transition state for a reaction is located at the potential energy maximum along the minimum energy reaction path (MERP). However, this definition can lead to serious errors in computed rate constants.[1] The most relevant point is actually the maximum in the free energy of activation curve or "variational transition state" (VTS).[1] Many of the dynamical consequences of free energy of activation maxima have been studied for atom-transfer reactions using mostly semiempirical potential energy surfaces[1] and a few ab initio surfaces.[2] Houk and co-workers[3] have now proposed that differences in the locations of the conventional and variational transition states can rationalize two intriguing aspects of carbene additions to alkenes: observations of negative activation energies[4] and entropy control of selectivity.[5] Their proposals stemmed from results of ab initio 3-21G calculations, particularly for $^1CCl_2$ plus ethylene, which indicated that π-complexes are not intermediates in reactions of relatively reactive halocarbenes with alkenes.[3] The use of the 3-21G basis set in this context raises concern since it does not include d-orbitals which are accepted as critical to the electronic structure of small rings.[6] Accordingly, in order to better test the basis of their model and to provide a more reliable gas-phase energy surface, ab initio calculations have been carried out for $^1CCl_2 + H_2C{=}CH_2$ including d-orbitals and electron correlation in the geometry optimizations. Subsequent calculations of vibrational frequencies yielded the free energy of activation curve and VTS.

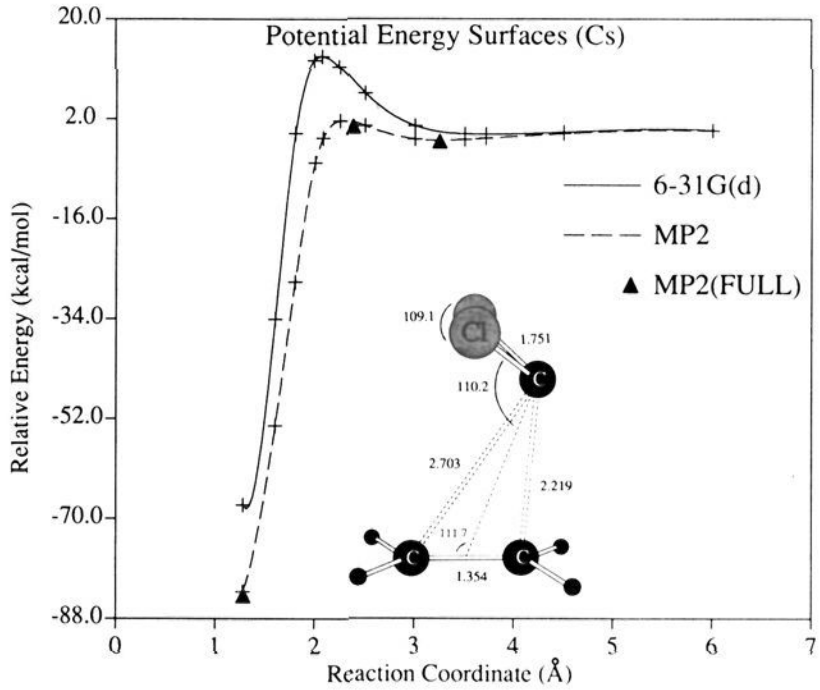

Figure 1. Computed potential energy surfaces. Inset: key geometrical parameters for the MP2(FULL)/6-31G(d) optimized transition state.

The reaction coordinate, r_c, is defined as the distance between the carbene carbon and the center of the CC bond in ethylene.[3] A MERP was obtained by geometry optimizations in C_s symmetry with the 6-31G(d) basis set at fixed values of r_c.[6,7] Four stationary points (reactants, π-complex, transition state, and product) were located and confirmed by frequency calculations. The effect of electron correlation was then estimated by single-point calculations with MP2 theory in the frozen core approximation for each 6-31G(d) optimized geometry.[6] In view of the pronounced correlation effects, the stationary points were reoptimized including the correlation energy at the MP2(FULL)/6-31G(d) level[6] on a Cray XMP. Frequency calculations were carried out for nine of the 6-31G(d) optimized points to compute the zero-point corrections, enthalpies, and entropies needed to construct the free energy of activation profile.[6,8]

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(1) (a) Truhlar, D. G.; Garrett, B. C. *Acc. Chem. Res.* **1980**, *13*, 440. (b) Truhlar, D. G.; Hase, W. L.; Hynes, J. T. *J. Phys. Chem.* **1983**, *87*, 2664. (c) Kreevoy, M. M.; Truhlar, D. G. In *Investigations of Rates and Mechanisms of Reactions*; Bernasconi, C., Ed.; Wiley: New York, 1986; Vol. 6, Part 1, p 13. (d) Truhlar, D. G.; Garrett, B. C. *J. Chim. Phys.* **1987**, *84*, 365.

(2) (a) Truhlar, D. G.; Isaacson, A. D.; Skodje, R. T.; Garrett, B. C. *J. Phys. Chem.* **1982**, *86*, 2252. (b) Isaacson, A. D.; Truhlar, D. G. *J. Chem. Phys.* **1982**, *76*, 1380. (c) Garrett, B. C.; Truhlar, D. G.; Wagner, A. F.; Dunning, T. H., Jr. *J. Chem. Phys.* **1983**, *78*, 4400. (d) Truhlar, D. G.; Grev, R. S.; Garrett, B. C. *J. Phys. Chem.* **1983**, *87*, 3415. (e) Doubleday, C.; McIver, J.; Page, M.; Zielinski, T. *J. Am. Chem. Soc.* **1985**, *107*, 5800.

(3) (a) Houk, K. N.; Rondan, N. G.; Mareda, J. *J. Am. Chem. Soc.* **1984**, *106*, 4291. (b) Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 4293. (c) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555.

(4) (a) Zupancic, J. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 944. (b) Turro, N. J.; Lehr, G. F.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W. *J. Am. Chem. Soc.* **1982**, *104*, 1754.

(5) (a) Skell, P. S.; Cholod, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 7131. (b) Giese, B.; Lee, W.-B.; Neumann, C. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 310.

(6) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(7) Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; Defrees, D. J.; Schlegel, H. B.; Frisch, M. J.; Pople, J. A.; Kahn, L. R. GAUSSIAN 82, Release H; Carnegie-Mellon University: Pittsburgh, PA, 1982.

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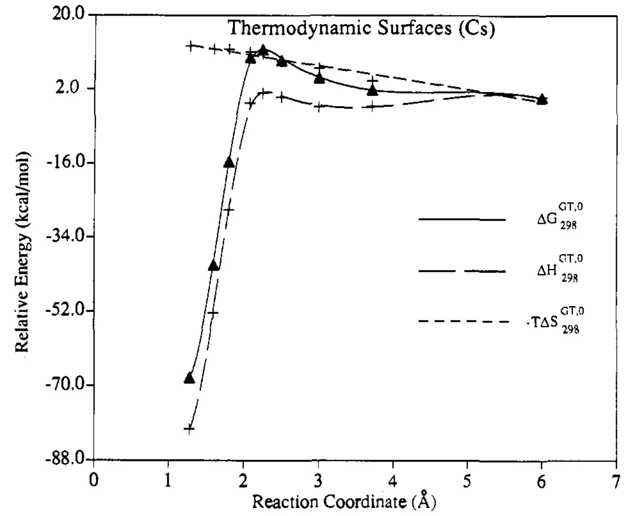

Figure 2. Computed activation profiles.

The results for the potential energy in Figure 1 at the 6-31G(d) level reveal a shallow minimum (−0.8 kcal/mol) at 3.71 Å for the π-complex and the transition state at 2.08 Å, 13.3 kcal/mol above the reactants. The MP2 corrections dramatically flatten the barrier to only 1.7 kcal/mol at 2.25 Å and deepen the minimum to −1.7 kcal/mol at 3.5 Å. Optimization at the MP2(FULL)/6-31G(d) level yields a barrier of only 0.6 kcal/mol shifted to 2.38 Å and a π-complex in a 2.0 kcal/mol depression at 3.25 Å. Fortuitously, Houk's 3-21G results are qualitatively similar to the MP2/6-31G(d) curve owing to an apparent cancellation in the strong basis set and correlation dependencies. The 3-21G TS is shifted in to 2.01 Å with a height of −1.3 kcal/mol, and the minimum for the π-complex occurs at 2.65 Å with a depth of −2.2 kcal/mol.[3]

The computed activation profiles[1,2] for $\Delta G^{GT,0}$, $\Delta H^{GT,0}$, and $-T\Delta S^{GT,0}$ are shown in Figure 2 using the MP2/6-31G(d)//6-31G(d) energies and 6-31G(d) derived frequencies. The enthalpy curve is quite flat to the 1.1 kcal/mol maximum at 2.25 Å, while the $-T\Delta S^{GT,0}$ curve rises nearly linearly along the reaction path. Loss of translational entropy is largely responsible for the substantial free-energy barrier of 11.7 kcal/mol. Interestingly, the abrupt drop in the enthalpy profile near 2.25 Å causes the positions of the variational and conventional transition states to essentially coincide; the enthalpy and free energy are both lower at 2.08 and 2.50 Å than 2.25 Å, so the inward shift for the VTS appears to be less than ca. 0.1 Å. It is reasonable to assume that this is a general feature for carbene additions and, consequently, a weakness in Houk's model.[3]

The present results suggest the following modified explanation of the experimental data. For halocarbene reactions with alkenes, π-complexes are not free-energy minima, though they may have broad, shallow wells in the enthalpy profiles. Such wells are more likely for monosubstituted than polysubstituted alkenes. The VTS occurs at the onset of covalent bonding where the enthalpy curve exhibits a precipitous drop. For alkenes more reactive than ethylene and carbenes comparable to or more reactive than CCl_2, this point will usually be at negative enthalpies and lead to negative activation energies. Furthermore, the entropy control of selectivity arises from the comparatively flat $\Delta H^{GT,0}$ profile approaching the VTS in comparison to the more strongly variant $T\Delta S^{GT,0}$ curve. Consequently, change in the position or looseness of the VTS typically has a greater effect on $T\Delta S^{GT,0}$ than $\Delta H^{GT,0}$.[9]

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(8) Translations and rotations were projected out before diagonalization of the hessian matrix. Vibrations with imaginary or low (<500 cm^{-1}) frequencies were treated as rotations (E_v = 1/2 RT). In addition, for computing the free energy of activation profile an additional degree of freedom was removed from the hessian matrix for motion along the reaction coordinate.[1,2] This amounted to neglecting one of the low-frequency vibrations.

(9) Gratitude is expressed to the National Science Foundation for support of this work.

Registry No. CCl_2, 1605-72-7; $H_2C{=}CH_2$, 74-85-1.

Supplementary Material Available: Full geometrical specifications for the stationary points (6 pages). Ordering information is given on any current masthead page.

Spontaneous Solid-State [8 + 8] Dimerization of Cycloheptatrienethione: The First Example of a Nontopochemically Controlled Reaction in the Ground State

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Solid-state organic chemistry[1,2] and particularly the field of topochemically controlled reactions have recently been developed in photoinduced reactions.[1d] This paper describes a newly discovered example of a ground-state nontopochemically controlled reaction of cycloheptatrienethione (**1**) in the crystalline state leading to a novel [8π + 8π] cyclodimer with a specific stereochemistry.

We have recently reported the synthesis,[3] properties,[3,4] and X-ray structural analysis (performed at −40 °C) of **1**,[5] a deep red crystalline but appreciably labile substance (mp 20 °C). Although crystalline **1** can be stored below −40 °C for many days, it was found that **1** dimerizes slowly at 0 °C in the solid state in the dark within a few days.

The initially formed product is obtained as amorphous solid (powder X-ray diffraction) which gives pale yellow prisms, mp 73 °C dec, on recrystallization (ether, 98%) without any change in the IR and NMR spectra. Combustion analysis and mass spectra indicate the molecular formula $C_{14}H_{12}S_2$ for the product **2**. The NMR (^1H and ^{13}C) spectra are fully consistent with its being a head-to-tail type of [8 + 8] dimer,[6] **2**. The stereochemistry of **2** was established to be the syn configuration based on X-ray diffraction method (Figure 1).[7] Monitoring the solid-state re-

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(1) For reviews see: (a) Paul, I. C.; Curtin, D. Y. *Acc. Chem. Res.* **1973**, *6*, 217–225. (b) Curtin, D. Y.; Paul, I. C.; Duesler, E. N.; Lewis, T. W.; Mann, B. J.; Shiau, W. *Mol. Cryst. Liq. Cryst.* **1979**, *50*, 25–42. (c) Cavezzotti, A.; Simonetta, M. *Chem. Rev.* **1982**, *82*, 1–13. (d) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433–481. (e) *Organic Chemistry in Anisotropic Media*; Scheffer, J., Ed.; Tetrahedron Symposia-in-Print No. 29, Pergamon: Oxford, 1987.

(2) (a) Kitaigorodsky, A. I. In *Physical Chemistry: Molecular Crystals and Molecules*; Loebl, E. M., Ed.; Academic: New York, 1973; Vol. 29. (b) Thomas, J. M.; Morsi, S. E.; Desvergne, J. P. In *Advances in Physical Organic Chemistry: Topochemical Phenomena in Organic Solid-State Chemistry*; Gold, V., Bethell, D., Eds.; Academic: London, 1977; Vol. 15, pp 63–151. (c) *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, 1987.

(3) Machiguchi, T.; Otani, H.; Ishii, Y.; Hasegawa, T. *Tetrahedron Lett.* **1987**, *28*, 203–206.

(4) Machiguchi, T.; Hasegawa, T.; Otani, H.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1375–1376.

(5) Machiguchi, T.; Mizuno, H.; Hasegawa, T.; Ishii, Y.; Otani, H. *Chem. Lett.* **1987**, 1893–1896.

(6) Cf. Oda, M.; Kayama, Y.; Kitahara, Y. *J. Chem. Soc., Chem. Commun.* **1971**, 505–506.

(7) Crystal data for **2**: monoclinic, space group = *C*2/*c*, a = 16.836 (2) Å, b = 9.534 (1) Å, c = 16.499 (1) Å, β = 114.25 (1)°, V = 2414.7 (4) Å^3, Z = 8, D_{cald} = 1.345 g cm^{-3}. Reflections (2037) were measured of which 1624 were classed as observed. The structure was solved by the direct method using MULTAN84:[8] R = 0.068.

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