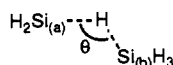


dependent at all temperatures, showing the typical variation corresponding to a third-body-mediated association. Table I shows the rate constants obtained in SF₆ at 10 Torr total pressure and at infinite pressure (obtained by extrapolation). We note that the rate constants at infinite pressure are close to the collisional limit (the Lennard-Jones collision number is estimated to be $4.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K) in support of a very loose type of transition state, although it should be added that there is a discrepancy of ca. a factor of 2 with Jasinski and Chu³ (at 298 K). Figure 1 shows the pressure-dependent rate constants as a function of temperature. For simplicity only the SF₆ data are shown. The rate constants in Ar showed similar trends but were smaller (as expected for a weaker collision partner). It is clear from the data that *k*_i decreases with increasing temperature. The average activation energy at the high-pressure limit is ca. -3 kJ mol⁻¹; however, the Arrhenius plot is slightly curved. RRKM calculations using a variational transition state have been carried out and fitted to these rate constants. These are also shown in Figure 1. To obtain reasonable fits it is necessary (i) to tighten the activated complex structure (increase the magnitude of low-frequency vibrations) with increasing temperature and (ii) to assume SF₆ removes an average of 10.8 kJ mol⁻¹ in a down collision ($(\Delta E)_{\text{down}}$, stepladder model).

These results are qualitatively similar to earlier findings for the Si-H insertion reactions of SiMe₂,⁷ PhSiH,⁸ and MeSiH,⁹ where negative activation energies are also found. One possible explanation for these results is the occurrence of an intermediate complex in the pathway leading to products. This prompted us to re-examine the potential energy surface for reaction 1 using ab initio methods. Calculations of the geometry of the interacting SiH₂ + SiH₄ species during the reaction have been carried out at the MP2/6-31G(d,p)^{10,11} and the MP2/6-311G(d,p)^{10,12} levels of theory. A minimum energy configuration has been found at both levels of theory, corresponding to an intermediate complex of the type



With the smaller basis set, we find $\theta = 120.5^\circ$, with Si_(a)-H = 1.686 Å and Si_(b)-H = 1.569 Å. This C₁ structure has been verified to be a minimum on the potential energy surface by calculating and diagonalizing the matrix of energy second derivatives (Hessian) and demonstrating that the Hessian is positive definite. With the larger basis set, θ closes to 86.2° with the corresponding bond distances of 1.525 and 2.046 Å, respectively. At the latter level of theory (MP2/6-311G(d,p)), the complex is found to be 51.5 kJ mol⁻¹ lower in energy than separated SiH₂ + SiH₄ (not including zero-point vibrational corrections). This intermediate is separated from the global minimum (disilane) by a barrier of less than 6.5 kJ mol⁻¹. Thus, the energy required to move from the local minimum to disilane is well below that available from the reactants. This means that the surface in the region of the intermediate represents an extremely "shallow" minimum and should probably be thought of as rather flat. Although detailed dynamic calculations have yet to be performed, this is just the kind of potential surface likely to give rise to a reaction free energy bottleneck, the location of which will vary with system total energy (and therefore temperature), as supported by the kinetic findings.

Acknowledgment. We thank the following: (i) the Reading University Research Endowment Fund for the award of a stu-

(7) Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Walsh, R. *J. Am. Chem. Soc.* **1990**, *112*, 8337.

(8) Blitz, M. A.; Frey, H. M.; Tabbutt, F. D.; Walsh, R. *J. Phys. Chem.* **1990**, *94*, 3294.

(9) Becerra, R.; Frey, H. M.; Mason, B. P.; Walsh, R. Manuscript in preparation.

(10) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.

(11) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(12) (a) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. (b) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3261.

dentship to B.P.M.; (ii) the Anglo-Spanish Research Collaboration Fund (Acciones Integradas) for financial support (R.B., H.M.F., and R.W.); and (iii) the National Science Foundation (Grant CHE89-11911) and the Air Force Office of Scientific Research (Grant 90-0052) for partial support of M.S.G. The calculations were performed on the North Dakota State University IBM 3090, obtained in part by a joint study agreement with IBM.

Origin of the Nonstereospecificity in the Ring Opening of Alkyl-Substituted Cyclobutenes

Fernando Bernardi,*[†] Massimo Olivucci,[‡]
Ioannis N. Ragazos,[‡] and Michael A. Robb*[‡]

Dipartimento di Chimica "G. Ciamician"
dell'Università di Bologna, Via Selmi 2
40126 Bologna, Italy

Department of Chemistry, King's College, London
Strand, London WC2R 2LS, U.K.

Received October 21, 1991

The rule that photochemical ring opening in cyclobutenes occurs stereospecifically according to a disrotatory pathway¹ has recently been challenged by careful experimental work^{2a,3} in which a mixture of all possible diene isomers is obtained from the direct photolysis of alkyl-substituted cyclobutenes.² In particular, the direct photolysis³ (193 nm) of a single stereoisomer of 7-methylbicyclo[4.2.0]oct-7-ene (1) yields a mixture of cis,cis (c,c), cis,trans (c,t) and trans,cis (t,c) products (Scheme I). This example is a good candidate for a theoretical study because all possible products can be detected.

Using ab-initio CAS-SCF (complete active space) computations (using Gaussian 91⁴) at the 4-31G level, we have demonstrated that the occurrence of three products in the photochemistry of 1 can be rationalized via a reaction path that passes from the excited state to the ground state via three different transition points which correspond to conical intersections⁵ or touchings of the ground and excited states, shown as CI1, CI2, and CI3 in Figure 1 (CI is the parent butadiene). The three different conical intersections have almost equal energies and contain the same basic twisted tetradicaloid butadiene moiety (shaded) with all the

[†] Dipartimento di Chimica "G. Ciamician" dell'Università di Bologna.
[‡] Chemistry Department, King's College, London.

(1) (a) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781-853. (b) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin Publishing: Reading, MA, 1978. (c) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; Blackwell Scientific Publications: Oxford, 1991. Coxson, J. M.; Halton, B. *Organic Photochemistry*; Cambridge University Press: London, 1974; pp 47-57. (d) Van der Lugt, W. Th. A. M.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 6042. (e) Grimbert, D.; Segal, G.; Davaquet, A. *J. Am. Chem. Soc.* **1975**, *97*, 6629. (f) Welscher, T. L.; Seitz, W. A.; Yurke, B.; Gonzales, R. A.; Matsen, F. A. *J. Am. Chem. Soc.* **1977**, *99*, 8389. (g) Morihashi, K.; Kikuchi, O.; Suzuki, K. *Chem. Phys. Lett.* **1982**, *90*, 346. (h) Morihashi, D.; Kikuchi, O. *Theor. Chim. Acta* **1985**, *67*, 293.

(2) (a) Clark, K. B.; Leigh, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 6086. (b) Dauben, W. G.; Haubrich, J. I. *J. Org. Chem.* **1988**, *53*, 600. (c) Leigh, W. J.; Zheng, K. *J. Am. Chem. Soc.* **1991**, *113*, 2163. (d) Leigh, W. J.; Zheng, K.; Clark, K. B. *J. Org. Chem.* **1991**, *56*, 1574. (e) Leigh, W. J.; Zheng, K.; Clark, K. B. *Can. J. Chem.* **1990**, *68*, 1988.

(3) Leigh, W. J.; Zheng, K.; Nguyen, N.; Werstiuk, N. H.; Ma, J. *J. Am. Chem. Soc.* **1991**, *113*, 4993.

(4) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Wong, M. W.; Replege, E. S.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Baker, J.; Martin, R. L.; Stewart, J. J. P.; Pople, J. A. *Gaussian 91* (Revision C); Gaussian, Inc.: Pittsburgh, PA, 1991.

(5) (a) Gerhartz, W.; Poshusta, R. D.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 4263. (b) Bonacic-Koutecky, V.; Koutecky, J.; Michl, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 170-189. (c) Bernardi, F.; De, S.; Olivucci, M.; Robb, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 1737-1744. (d) Davidson, R. E.; Borden, W. T.; Smith, J. *J. Am. Chem. Soc.* **1978**, *100*, 3299-3302. (e) Mead, C. A. The Born-Oppenheimer approximation in molecular quantum mechanics. In *Mathematical frontiers in computational chemical physics*, Truhlar, D. G., Ed.; Springer: New York, 1987; Chapter 1, pp 1-17. (f) Blais, N. C.; Truhlar, D. G.; Mead, C. A. *J. Chem. Phys.* **1988**, *89*, 6204-6208. (g) Manthe, U.; Koppel, H. *J. Chem. Phys.* **1990**, *93*, 1658-1669.

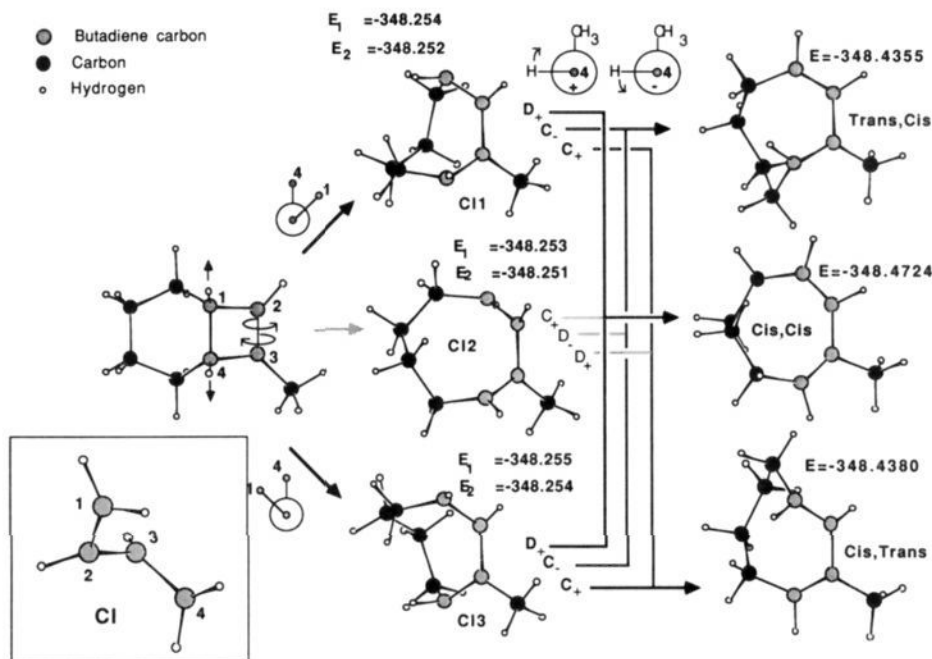
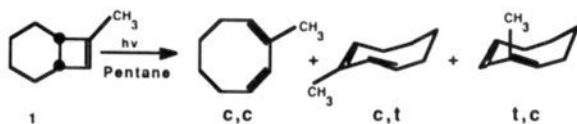


Figure 1. CAS-SCF/4-31G optimized geometries and energies (E_h) for three conical intersections, CI1, CI2, and CI3, and three ground-state minima, trans,cis; cis,cis, and cis,trans. The geometry of the conical intersection for butadiene is shown as CI. C_+ , C_- , D_+ , and D_- refer to positive and negative conrotatory and disrotatory motion. The energies of the ground and excited states are given in the case of the conical intersections.

Scheme I

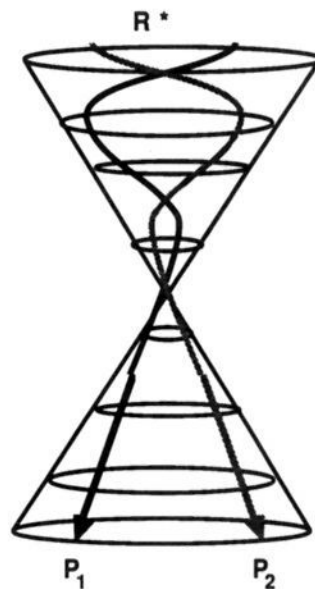


double bonds broken. The photochemical reaction is divided into two stages. The first stage, which occurs on the excited-state surface before the transition point, corresponds to *ring opening*, involving primarily C_2-C_3 rotation. The *conrotatory or disrotatory motion* occurs in the second stage of the reaction, on the ground-state surface after the transition point, and there are three possible ground-state paths from each conical intersection (e.g., return from CI1 along C_- , C_+ , and D_+ to three possible products: t,c; c,t; and c,c). Thus the stereochemistry is decided in the second stage of the reaction by the nature of the path which is actually followed from the conical intersections to the products. The possibility of these different relaxation routes from each conical intersection provides a mechanistic rationalization of the observed fact that the ring opening of **1** is nonstereospecific.

The geometries of the three transition points (conical intersections) were obtained by geometry optimization using CAS-SCF wave functions with a 4-31G basis. (Note that we have only optimized the geometries of the transition points so that information about the details of the reaction path itself is not obtained.) In each case a four-electron, four-orbital active CAS space was used comprising the four π orbitals of the butadiene fragment. The two states involved in the conical intersection would correspond to the covalent $1A_g$ and $2A_g$ in butadiene itself.

A conical intersection, where ground- and excited-state surfaces touch, provides the transition point for a photochemical reaction because the system must assume the specific geometry of the conical intersection or the probability of radiationless decay is very small. However, the existence of a mechanism involving a conical intersection has another, more important implication: *several equally probable downhill paths exist, each leading to different products as the reacting system emerges on the ground-state potential energy surface after passing through the conical intersection.* A very simplified illustration of the situation for two variables is illustrated in Scheme II. In general, the excited system R^* will follow oscillatory trajectories traversing the conical intersection region several times before emerging onto the ground

Scheme II



state. Depending on the direction of these trajectories at the instant that the system crosses to the ground state, the system will follow a different path on the ground state, leading to different products such as P_1 or P_2 . The efficiency of the reaction will be controlled by *dynamical effects* that may make certain trajectories on the excited state more probable and thus ensure that a given ground-state path is preferred. Further, *steric effects* may block certain pathways on the ground state. However, the very existence of a mechanism involving a conical intersection guarantees that several products will always be formed in general. Of course with more than 2 degrees of freedom there are more possibilities, as seen in the example reported in this work.

The geometric structures of the butadiene fragment at the conical intersections given in this paper are all very similar to the structure of butadiene itself (Figure 1, CI). Thus one might be able to design photochemical reactions of this type that are stereospecific by controlling the excited-state dynamics or ground-state steric effects by suitable substitution. The introduction of

a strained double bond⁶ in the reactant, which results in a stereospecific reaction, may be an example of dynamic control in the excited state, but only detailed dynamics computations could confirm this.

Acknowledgment. This work was supported by the SERC (U.K.) under Grants GR/F 48029, 465452, and GR/G 03335.

(6) (a) Leigh, W. J.; Zheng, K. *J. Am. Chem. Soc.* **1991**, *113*, 4019. (b) Leigh, W. J.; Zheng, N., errata in press.

The Gas-Phase Macrocyclic Effect: Reaction Rates for Crown Ethers and the Corresponding Glymes with Alkali Metal Cations

Hong Zhang and David V. Dearden*

The University of Texas at Arlington
Department of Chemistry, Box 19065
Arlington, Texas 76019-0065

Received December 9, 1991

The macrocyclic effect,¹ well-known in solution,² is manifested by higher binding constants and greater guest selectivity for cyclic as opposed to acyclic ligands. This effect is dramatically evident when the chemistry of the macrocyclic crown ethers is compared to that of their acyclic polyether analogues, the glymes.² For example, 18-crown-6 has binding constants in methanol 3–4 orders of magnitude higher for Na⁺, K⁺, and Ba²⁺ than does its acyclic analogue, pentaglyme.^{3,4} Two factors are believed to be responsible.⁵ First, the configurational entropy is more favorable for the cyclic ligands, since their donor groups are preorganized to interact favorably with a guest species, while acyclic ligands must undergo more extensive rearrangement to adopt a favorable conformation for guest binding. Second, because desolvation of both the ligand and the metal cation precedes complex formation, ΔH for the complexation process is more favorable for cyclic ligands, since they are less well-solvated than their acyclic counterparts. For nitrogen macrocycles in solution, the solvation effects dominate,⁵ but it has proven difficult to generalize this observation for polyethers.^{2,4} To eliminate the role of the solvent in such interactions and thereby observe the *intrinsic* reactivity of macrocyclic ligands, we have undertaken a study of the reactions of crown ethers and glymes with alkali metal cations in the gas phase. We report herein the observation of a strong gas-phase macrocyclic effect, which is evident in the kinetics of formation of metal cation-bound ligand dimer species.

Our studies build upon a number of earlier investigations of crown ether-cation interactions in the gas phase, which employed fast atom bombardment⁶ (FAB) and plasma desorption⁷ mass spectrometry, as well as studies of the mass spectrometry of crown ethers⁸ and their gas-phase reactions^{9,10} with Fe⁺ and Co⁺. The

(1) Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 6540–6541.

(2) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271–339.

(3) Frensdorff, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 600–606.

(4) Haymore, B. L.; Lamb, J. D.; Izatt, R. M.; Christensen, J. J. *Inorg. Chem.* **1982**, *21*, 1598–1602.

(5) Hinz, F. P.; Margerum, D. W. *J. Am. Chem. Soc.* **1974**, *96*, 4993–4994. Hinz, F. P.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2941–2949.

(6) (a) Johnstone, R. A. W.; Lewis, I. A. S.; Rose, M. E. *Tetrahedron* **1983**, *39*, 1597–1603. (b) Johnstone, R. A. W.; Rose, M. E. *J. Chem. Soc., Chem. Commun.* **1983**, 1268–1270. (c) Bonas, G.; Bosso, C.; Vignon, M. R. *Rapid Commun. Mass Spectrom.* **1988**, *2*, 88–89. (d) Laali, K.; Lattimer, R. P. *J. Org. Chem.* **1989**, *54*, 496–498.

(7) Malhotra, N.; Roepstorff, P.; Hansen, T. K.; Becher, J. *J. Am. Chem. Soc.* **1990**, *112*, 3709–3710.

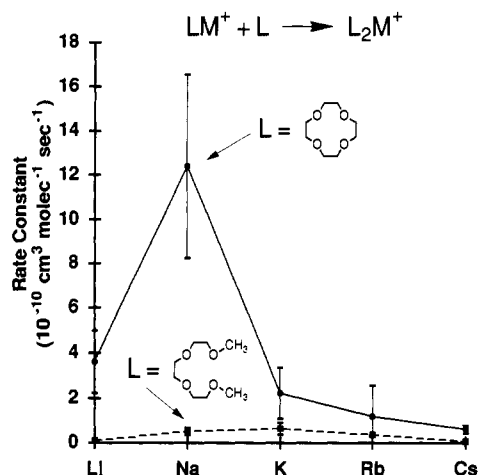


Figure 1. Mean rate constants for formation of alkali metal cation-bound dimers of 12-crown-4 and triglyme. Error bars are ± 1 standard deviation.

transition metal experiments are particularly interesting in that they exhibit a “mechanistic” macrocyclic effect: 12-crown-4 reacting with Fe⁺ gave nine products, but triglyme gave only one.^{9,10} Likewise, Cr⁺ gave five products with 12-crown-4 but only three with triglyme.¹⁰ These results clearly warrant further investigation.

Our experiments were performed using a Fourier transform ion cyclotron resonance mass spectrometer (Extrel FTMS-1000). Alkali metal cations were introduced into the trapping cell via laser desorption using an excimer pumped dye laser (Lambda Physik LPX 205i/FL 3002). A variable leak valve was used to admit neutral ligands into the vacuum chamber. The compounds employed were used as purchased, except that each was subjected to successive freeze–pump–thaw cycles prior to introduction into the leak valve. Pressures were measured with a Bayard-Alpert ionization gauge, which was calibrated by measuring rates for the self-chemical ionization of acetone and comparing the results to literature values.¹¹ Ligand pressures were typically in the range 5×10^{-8} – 5×10^{-7} Torr. Rate constants were measured by monitoring reactant and product ion intensities as a function of time and applying pseudo-first-order kinetic analysis.

The largest likely source of error in the *absolute* rate measurements is in the pressure determinations. However, the *relative* rate constants determined using these methods are conservatively estimated to be correct within better than about $\pm 33\%$ based on the reproducibility of repetitive measurements. The pressure variable is essentially eliminated in the relative rate determinations, because up to four different alkali metal ions were simultaneously introduced into the trapping cell (by mixing their salts on the sample probe) and studied together under identical neutral pressures.

Subsequent to the laser shot, 1:1 ligand–alkali metal cation complexes were observed to form rapidly in the trapping cell. These complexes are probably radiatively stabilized.¹² Since the metal cations and the neutral ligands were introduced into the cell separately, this provides conclusive evidence that complex formation can occur as a gas-phase process, as had been suggested by earlier FAB experiments.^{6,7} The observed complexation rates are within an order of magnitude of the ion–molecule collision

(8) Lee, Y. C.; Popov, A. I.; Allison, J. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *51*, 267–277.

(9) Huang, S. K.; Lee, Y. C.; Allison, J.; Popov, A. I. *Spectrosc. Lett.* **1983**, *16*, 215–219.

(10) Huang, S. K.; Allison, J. *Organometallics* **1983**, *2*, 883–890.

(11) Sieck, L. W. *Rate Coefficients for Ion-Molecule Reactions*; U.S. Department of Commerce, National Bureau of Standards: Washington, DC, 1979.

(12) As a referee has pointed out, radiative stabilization has been invoked before for similar metal–ligand complexation reactions: Dunbar, R. C.; So-looki, D.; Tessier, C. A.; Youngs, W. J.; Asamoto, B. *Organometallics* **1991**, *10*, 52–54.