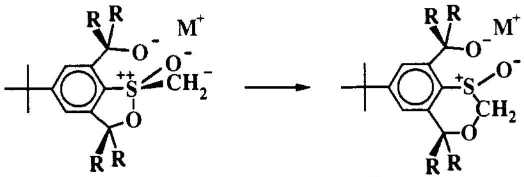
easily measured catalyzed kinetics. Exchange was much slower for **2** than for **1**, with catalysis by this weak base. It is clear that trifluoromethylated **2** is much less kinetically acidic than methylated **1**.

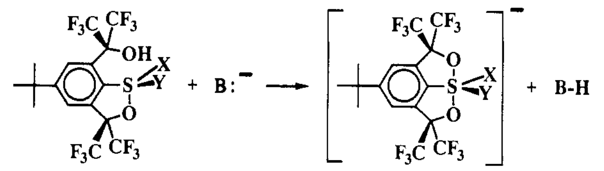
The two fluorine apical ligands of the 10-F-2 trifluoride anion (F_3^-) have a calculated[10] total negative charge of −1.03, more than the negative charge (−1.00) on the same two atoms of the precursor species (F_2 and F^-). It is clear for a wide range of hypervalent species, with center atoms more electropositive than the central F of F_3^-, that the trifluoromethyl groups of the tridentate ligands of **2**, more than the methyl groups of **1**, strongly stabilize the symmetrical species, relative to an unsymmetrical species obtained by cleaving one of the apical bonds. If the anions of the sulfurane oxides are unsymmetrical as **5** and **6**, there could be less total negative charge on the two alkoxy centers of the unsymmetrical anions than on both of the alkoxy centers of the symmetrical neutral sulfurane oxides. Stabilization of anions **5** or **6** would therefore be provided more by CH_3 groups than by CF_3 groups, since there is thought to be less total negative charge on the two alkoxy centers of unsymmetrical anion **5** (or **6**) than is expected on the same two alkoxy centers of the symmetrical hypervalent species **1** (or **2**).



5 (R = CH_3) **7** (R = CH_3)
6 (R = CF_3) **8** (R = CF_3)

The observation (by ^{1}H and ^{19}F NMR) of anions **5** and **6** revealed their unsymmetrical geometry.[11] It was necessary to use a stronger base to convert **2** to **6** (KO-*t*-Bu/CH_3Li, $pK_\alpha > 58$)[12,13] than to convert **1** to **5** (lithium tetramethylpiperidide, LiTMP, $pK_\alpha = 37.3$).[14] The weaker base (LiTMP) did not completely form **6** from **2**, providing evidence for the lower equilibrium acidity of **2** relative to **1**. Both **5** and **6** rearrange by transfer of an alkoxy oxygen from S to C to form **7** and **8**.[11]

It was established[5] (by low-temperature NMR and X-ray crystallography) that anions **10a–c** are symmetrical hypervalent anions (10-S-3, 10-S-4, and 10-S-5), while protonated species **9a–c** are unsymmetrical (8-S-2, 8-S-3, and 8-S-4). The destabilization of anions **10** by introduction of π-donor equatorial oxygens is seen by the acidities of **9a** ($pK_\alpha = 4.4$), **9b** (5.0), and **9c** (7.2). The sulfuranide dioxide anion (**10c**) is stable (2.6 kcal/mol), relative to the unsymmetrical anion formed by cleaving one of the apical S–O bonds, but considerably less stable than the sulfuranide anion **10a** (7.5 kcal/mol).[5] Replacement of one of the oxygens of **10c** by a more electropositive CH_2^- ligand makes unsymmetrical 8-S-4 **6** more stable than **10d**, which is not seen.[15] While equatorial π-donor ligands have usually been found[16] to have their electron-pair orbitals perpendicular to the 3c–4e bond, it is probable that the repulsive interaction between the equatorial CH_2^- and O^- ligands of **10d** would make the CH_2^- electron pair parallel to the 3c–4e bond. This would allow electron donation to the antibonding unoccupied hypervalent orbital of the 3c–4e bond, destabilizing **10d** to make it rearrange to **6**. Although **6** is an anion, its unsymmetrical geometry sufficiently reduces the negative charge on the two alkoxy oxygens, relative to the apical oxygens of symmetrical **2**. The CF_3 substituent effects, therefore, make **2** less acidic than **1**.



9 a, X = Y = electron pair (e.p.)
b, X = O; Y = e.p.
c, X = Y = O

10 a, X = Y = e.p.
b, X = O; Y = e.p.
c, X = Y = O
d, X = O; Y = CH_2

Further work on the reactions of **1** and **2**, as well as on the analogous species formed by replacing sulfur with selenium, is underway.

Acknowledgment. This research was supported in part by National Science Foundation Grant CHE-8910896.

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(8) The potassium salt was dried at 100 °C at 0.5 mmHg for 12 h prior to its use in a glove box. The CD_3OD was distilled from Mg, THF-d_8 from Na and benzophenone, and CD_2Cl_2 from CaH_2. A CD_3OD solution of base was added to a sulfurane oxide solution in CD_2Cl_2 or THF-d_8 frozen in liquid nitrogen. Samples thawed at −78 °C immediately prior to use were placed in a precooled NMR probe for kinetic studies.

(9) Ross, M. R. Ph.D. Thesis, University of Illinois, Urbana-Champaign, 1981.

(10) Cahill, P. A.; Dykstra, C. E.; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6359. A similar prediction is obvious from the MOs of the symmetrical 3c–4e bond suggested by J. Musher (*Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54).

(11) The ^{1}H aromatic singlet of **1** (7.49 ppm), upon the addition of lithium tetramethylpiperidide (LiTMP), became two signlets (7.43 and 7.58 ppm) at −60 °C in THF-d_8. A stronger base (KO-*t*-Bu/CH_3Li)[12] at −43 °C was needed to convert **2** (8.24 ppm) to **6** (8.06 and 7.48 ppm). Further evidence for this conversion was found in the ^{19}F NMR spectrum; the two quartets of **2** (−75.67 and −76.05 ppm) became the four equal-size quartets appropriate for **6** (−66.72, −71.03, −73.32, and −74.35 ppm). Quenching **5** and **6** by water reformed **1** (82%) and **2** (6%), together with sulfoxides **7** and **8**. (The rearrangement of **6** to **8** was fast enough to reduce the amount of **2** observed.)

(12) Schlosser, M.; Strunk, S. *Tetrahedron Lett.* **1984**, *25*, 741.

(13) Jaun, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741.

(14) Fraser, R. R.; Mansour, T. S. *J. Org. Chem.* **1984**, *49*, 3442.

(15) Although **6** is unsymmetrical, there may be a small bonding interaction between the alkoxide oxygen and the adjacent sulfur.

(16) For examples: Peak, S. C.; Schmutzler, R. *J. Chem. Soc. A* **1970**, 1049. Simon, A.; Peters, E.-M.; Lentz, D.; Seppelt, K. *Z. Anorg. Allg. Chem.* **1980**, *468*, 7. Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3047. Cowley, A. H.; Sprenger, G. H. *J. Fluorine Chem.* **1976**, *7*, 333.

Activation Parameters for a 1,2 Carbon Shift in a Carbene Rearrangement†

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Laser flash photolysis (LFP) has been extensively employed to determine the absolute rate constants and associated activation parameters for *intermolecular* carbene reactions.[1] Previously obscure aspects of these processes have thereby been highlighted. For example, the activation energies of certain carbene/alkene cycloadditions were found to be very low, or even negative, whereas the free energy barriers were controlled by highly unfavorable activation entropies.[2]

Less is known about the absolute rate constants and activation parameters of *intramolecular* carbene reactions. Experimental

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† Dedicated to Professor Wolfgang Kirmse on his 60th birthday.

(1) Reviews: Eisenthal, K. B.; Moss, R. A.; Turro, N. J. *Science* **1984**, *225*, 1439. Schuster, G. B. *Adv. Phys. Org. Chem.* **1986**, *22*, 311. Scaiano, J. C. In *Chemical Kinetics of Small Organic Radicals*; Alfassi, Z. B., Ed.; CRC Press: Boca Raton, FL, 1988, Vol. III, p 73 f. Moss, R. A.; Turro, N. J. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, in press. (See, also, other chapters in this book.)

(2) Turro, N. J.; Lehr, G. F.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W. *J. Am. Chem. Soc.* **1982**, *104*, 1754. Moss, R. A.; Lawrynowicz, W.; Turro, N. J.; Gould, I. R.; Cha, Y. *Ibid.* **1986**, *108*, 7028. Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555.

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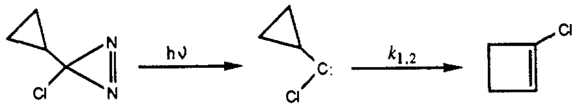
values have been estimated or measured for the 1,2 hydride shifts of dialkylcarbenes,[3] benzylhalocarbenes,[4,5] methylchlorocarbene,[6,7] and other alkylchlorocarbenes.[6,8] Reported values of E_a ranged from 1–2 kcal/mol in the dialkylcarbenes[3] to 6–7 kcal/mol for benzylbromocarbene.[4]

Absolute kinetic parameters for 1,2 alkyl migrations in carbenes are nearly unknown; there is a kinetic measurement for the decay of *tert*-butylchlorocarbene,[9] and we,[10] and others,[8] reported $k_{1,2}$ $\sim$4–9 × 10^5 s^{-1} for the 1,2-carbon migration in the rearrangement of cyclopropylchlorocarbene (CyCCl) to chlorocyclobutene (**2**); eq 1. Of all the measured 1,2 intramolecular carbene rearrangements, this is the slowest, slightly slower than the hydride shift in CH_3CCl ($k_{1,2} \sim 1.3 \times 10^6$ s^{-1}).[6] It has been suggested that the cyclopropyl group "stabilizes" CyCCl;[8,11] but how is this effect expressed? To help answer this question, we measured the activation parameters for the CyCCl → **2** reaction, and we present our findings here. While our work was in progress, Liu and Bonneau communicated their results for reaction 1.[12] The significantly different outcomes of the two studies have important implications for intramolecular carbene reactions.



(1)

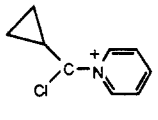
1 CyCCl **2**

Activation parameters for CyCCl → **2** were determined in four different ways: (1) direct observation; (2) an ylide method; (3) competition against an alkene and (4) product analysis.

(1) Direct Observation. Cyclopropylchlorodiazirine (**1**)[13] in isooctane, absorbance $\sim$1.0 at 348 nm, was flashed with a 14-ns, 70–80-mJ, 351-nm pulse from a XeF excimer laser.[10] CyCCl decay, monitored at 255 nm, obeyed good first-order kinetics over the first 90% of reaction; at 20 °C, $k_{1,2} = (8.5 \pm 0.5) \times 10^5$ s^{-1} (five runs) agreed with out previously published value [$(9.0 \pm 1.0) \times 10^5$ s^{-1}].[10] Rate constants were determined as mean values of five runs at each of five temperatures, $309 \geq T \geq 245$ K, with reaction temperature monitored by an indwelling thermocouple and calibrated digital voltmeter. An Arrhenius analysis gave $E_a = 2.7 \pm 0.1$ kcal/mol, log $A = 8.0$ s^{-1}, $r > 0.99$. Average deviations in the rate constants ranged from 4 to 10%.[14] An independent, duplicate set of measurements afforded $E_a = 2.8 \pm 0.2$ kcal/mol, log $A = 8.0 \pm 0.1$ s^{-1}, $r > 0.99$.

Liu et al. reported[8,12] that dimerization of CyCCl interfered with kinetic studies of CyCCl decay at 250 nm. Their detection of CyCCl dimer as a significant product[15] followed preparative laser pulsing of diazirine **1** at 300 mJ/pulse, although their kinetic measurements were made at 30 mJ. We pulsed $CDCl_3$ solutions of distilled **1** at ≤80 mJ (corresponding to our kinetic conditions) at both −18 °C and 21 °C. NMR studies at 200 MHz, relative to internal decane, CH_2Cl_2, or $CHCl_3$ standards, showed the formation of >90% of **2** at either temperature, and <10% *possible* dimer (i.e., residual cyclopropyl protons *not* associated with **1**. Similar results were obtained in conventional photolyses of **1** at 21 or −21 °C. In parallel experiments, **1** was pulsed in pentane solutions containing isooctane as an internal standard. Capillary GC analyses confirmed 85–92% yields of **2**, with no evidence of carbene dimer. We thus conclude that dimerization is not a problem under our kinetic conditions.[16]

(2) Ylide Method.[9] As before,[10] pulsed photolysis of **1** in pyridine–isooctane solution gave ylide **3**, $\lambda_{max} = 370$ nm. The



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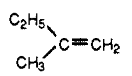

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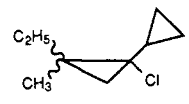

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observed rate constants for ylide growth at 20 °C were linear in pyridine with $k_2 = (3.6 \pm 0.4) \times 10^8$ M^{-1} s^{-1} for the CyCCl + Pyr → **3** reaction. The intercept, at [pyridine] = 0, was $k_0 = (7.7 \pm 1.7) \times 10^5$ s^{-1}, which we take as $k_{1,2}$ for CyCCl → **2**, in good agreement with the $k_{1,2}$ value (8.5×10^5 s^{-1}) obtained above from direct observation of CyCCl. Determinations of $k_{1,2}$ by the ylide method at five temperatures, $309 \geq T \geq 248$ K, followed by an Arrhenius analysis, gave $E_a = 3.1 \pm 0.3$ kcal/mol, log $A = 8.2$ s^{-1}, $r = 0.984$.[14] Rate constants (k_0) determined by the ylide method are less precise than the directly measured ones (due to the extrapolation necessary in the ylide method), but the Arrhenius correlation is good,[14] and the derived activation parameters are experimentally identical with those obtained by method 1.

(3) Competition against an Alkene. CyCCl was generated from **1** by LFP in 0.9–4.6 M solutions of 2-methyl-1-butene (**4**) in isooctane. Intramolecular rearrangement of CyCCl to **2** and intermolecular addition of CyCCl to **4**, affording adducts **5**, occurred competitively. The observed rate constants for CyCCl decay at 255 nm were linear in **4**, giving (e.g., at 16 °C) $k_{add} = (1.00 \pm 0.06) \times 10^6$ M^{-1} s^{-1} for the addition reaction. The intercept at [**4**] = 0 was $k_0 = (8.2 \pm 0.9) \times 10^5$ s^{-1}, which we again equate with $k_{1,2}$ for CyCCl → **2**, also in good agreement with the previous values. Determinations of $k_{1,2}$ at five temperatures, $301 \geq T \geq 251$ K, followed by Arrhenius analysis gave $E_a = 3.8 \pm 0.5$ kcal/mol, log $A = 8.74 \pm 0.05$ s^{-1}, $r = 0.977$.[14] An Arrhenius treatment of the k_{add} data gave $E_a^{add} = 0.74 \pm 0.08$ kcal/mol, log $A = 6.57 \pm 0.01$ M^{-1} s^{-1}. The very low E_a for the addition of CyCCl to **4** is consistent with previous studies of ArCCl–alkene cycloadditions,[2] and the E_a for the CyCCl → **2** rearrangement is similar to the values obtained by methods 1 and 2.

(4) Product Analysis. The product mixtures from reactions of CyCCl with 1.0 M **4** in isooctane[17] at five temperatures, $301 \geq T \geq 251$ K, were analyzed by SE-30 capillary GC. The molar ratios of **5**/**2** were obtained with a calibrated flame-ionization detector, affording $k_{add}/k_{1,2}$ at each temperature (e.g., $k_{add}/k_{1,2} = 1.40$ at 28 °C). An Arrhenius analysis gave $E_a^{1,2} - E_a^{add} = 2.4 \pm 0.3$ kcal/mol and $A_{1,2}/A_{add} = 34.1 \pm 0.9$ M, $r = 0.979$.[14] From these results and the absolute activation parameters for the addition reaction (see above), we find $E_a = 3.1 \pm 0.3$ kcal/mol and log $A = 8.1 \pm 0.2$ s^{-1} for the rearrangement of CyCCl to **2**, in very good agreement with the parameters obtained by the more "direct" methods.

From methods 1–4, the "average" activation parameters for the CyCCl → **2** rearrangement are $E_a = 3.0 \pm 0.4$ kcal/mol and log $A = 8.2 \pm 0.2$ s^{-1}. Conversion to Eyring parameters affords $\Delta G^* \sim 9$ kcal/mol, $\Delta H^* \sim 2$–3 kcal/mol, and $\Delta S^* \sim -20$ to -24 eu. For comparison, Liu and Bonneau report[12] $k_{1,2}$ (23 °C)

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(3) Stevens, I. D. R.; Liu, M. T. H.; Soundararajan, N.; Paike, N. *Tetrahedron Lett.* **1989**, *30*, 481.

(4) Bonneau, R.; Liu, M. T. H.; Suresh, R. V. *J. Phys. Chem.* **1989**, *93*, 4802. Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.*, in press.

(5) Jackson, J. E.; Soundararajan, N.; White, W.; Liu, M. T. H.; Bonneau, R.; Platz, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 6874.

(6) La Villa, J.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 6877.

(7) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1989**, *111*, 6873.

(8) Bonneau, R.; Liu, M. T. H.; Rayez, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 5973.

(9) Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, *110*, 5595. However, this is not a simple methyl migration.

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(11) Moss, R. A.; Fantina, M. E. *J. Am. Chem. Soc.* **1978**, *100*, 6788. Moss, R. A.; Vezza, M.; Guo, W.; Munjal, R. C.; Houk, K. N.; Rondan, N. G. *Ibid.* **1979**, *101*, 5088.

(12) Liu, M. T. H.; Bonneau, R. *J. Phys. Chem.* **1989**, *93*, 7298. We thank Professor Liu for a preprint.

(13) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

(14) Tabulations of the individual rate constants are included in the supplementary material. An error analysis for method 2 is also included.

(15) Detection was by mass spectroscopy; no yield was given.[12]

(16) These product studies also exclude complications due to azine formation. Cyclobutene **2**, however, does absorb near 250 nm, and its "growth" can distort the kinetics of the last 10% of the CyCCl → **2** reaction. Our results by method 1 do not seem to be seriously affected by this problem, because similar values of k and E_a were obtained by method 2 (see below), which does not rely on spectroscopic measurements at 255 nm.

(17) Diazirine **1**, $A_{348} \sim 1.0$, was photolyzed for 2 h with a 200-W Xe UV lamp (Pyrex filter). Adducts **5** were characterized by NMR and GC–mass spectroscopy.

$= 3.8 \times 10^5$ s^{-1}, based on correction of the LFP carbene decay data (method 1) for competing dimerization, and $E_a = 7.4$ kcal/mol, log $A = 11.1$ s^{-1}. This affords $\Delta G^{\ddagger} \sim 9.8$ kcal/mol, $\Delta H^{\ddagger} \sim 6.8$ kcal/mol, and $\Delta S^{\ddagger} \sim -10$ eu. Note that our previously reported parameters, based on ab initio molecular orbital calculations, are $\Delta G^{\ddagger} = 9.0$ kcal/mol, $\Delta H^{\ddagger} = 8.2$ kcal/mol, and $\Delta S^{\ddagger} = -2.7$ eu.[10]

The important difference between our results and those of Liu and Bonneau lies in *the relative roles of enthalpy and entropy*. Both laboratories, using experimental and computational approaches, arrive at very similar $\Delta G^{\ddagger}$ values (9–10 kcal/mol), but the apportionment between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ varies greatly. Whereas we now find $\Delta S^{\ddagger}$ to be principally responsible for the "slow" CyCCl → **2** rearrangement, Liu and Bonneau and our electronic structure calculations implicate a "high" E_a ($\Delta H^{\ddagger}$). However, the present E_a and log A values are confirmed by four independent sets of measurements, and we observe no complications due to dimerization. Accordingly, we suggest that $\Delta H^{\ddagger} \sim 2.5$ kcal/mol and $\Delta S^{\ddagger} \sim -20$ eu represent a more accurate picture of the CyCCl → **2** isomerization process.[18]

Why is the unimolecular rearrangement of CyCCl, driven by ~50 kcal/mol in ΔG_{rx},[10] opposed by such an unfavorable entropy? The experimental determination of activation parameters characterizes a statistical ensemble of carbene molecules in solution, whereas the computed values reflect properties of two stationary points on the potential energy surface of an isolated carbene in the gas phase. The very different values obtained imply that significant differences exist between the energy surfaces. One possibility is that the variational transition state of the reaction (corresponding to the maximum on the $\Delta G^{\ddagger}$ profile) does not coincide with the calculated conventional minimum energy transition state.[19] In a reaction that crosses a relatively flat potential energy surface (low E_a),[2,19] entropic control may become particularly important. Interestingly, a detailed computational analysis of the concerted rearrangement of CyCH to cyclobutene reveals a very intricate, correlated set of atomic motions between the migrating methylene and carbenic carbons.[20] Should analogous behavior occur in the CyCCl → **2** isomerization, it could contribute to the unfavorable $\Delta S^{\ddagger}$. Furthermore, the migrating group is always "anchored" to the other methylene carbon in the ring, and this may also restrict the ease of travel across the barrier. The pass over the energy barrier would be very narrow with steep side walls due to the unusual constraints imposed on the transition state by the required changes in bonding and geometry. Many energetically favorable collisions will not be effective in channelling the energy into motion along the reaction coordinate through the pass, hence a large negative entropy of activation will be measured.[21] This effect must be dynamic in origin because an entropic change of −20 eu in an isolated molecule as small as CyCCl during a 1,2 shift is inconceivable. The large negative entropy of activation indicates that the reaction must have a transmission coefficient that is significantly less than unity. Extensive theoretical explorations of the reaction surfaces will be essential for a clearer understanding of intramolecular carbenic rearrangements.

Acknowledgments. We are grateful to the National Science Foundation (R.A.M.) and to the donors of the Petroleum Research Fund, administered by the American Chemical Society (K.K.-J.), for financial support. We thank Professors R. S. Sheridan and M. A. Cotter for helpful discussions.

Supplementary Material Available: Tables of rate constants and temperatures for the Arrhenius correlations of methods 1–4 (3 pages). Ordering information is given on any current masthead page.

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[18] Indeed, the 1,2 hydride shift of CH_3CCl to vinyl chloride ($k \sim 1.3 \times 10^6$ s^{-1}) appears to be governed by $E_a \sim 4.9$ kcal/mol ($\Delta H^{\ddagger} \sim 4.3$ kcal/mol), log $A = 9.7$ s^{-1} ($\Delta S^{\ddagger} \sim -16$ eu), and hence $\Delta G^{\ddagger} \sim 8.1$ kcal/mol, consistent with "a highly ordered transition state."[6] Molecular orbital calculations on CH_3CCl (analogous to those presented in ref 10 for CyCCl) give $\Delta H^{\ddagger} = 11.4$ kcal/mol, $\Delta S^{\ddagger} = -2.2$ eu, and thus $\Delta G^{\ddagger} = 12.4$ kcal/mol at $T = 300$ K.

[19] Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 1919. See also: Houk, K. N.; Rondan, N. G.; Mareda, J., ref 2.

[20] Wang, R.; Deng, C. *Tetrahedron* **1988**, *44*, 7335. See also: Shevlin, P. B.; McKee, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 519.

[21] This viewpoint is analogous to the introduction of the empirical "steric" factor ($P = A_{obsd}/A_{calcd}$) in simple collision theory to account for the fraction of energetically suitable bimolecular collisions that also have the proper geometric orientation. The ratio of computed to measured $\Delta S^{\ddagger}$ is ~7, corresponding to a correction factor (or a transmission coefficient) of ~10^{-3}.

Transmembrane Electron Transfer Catalyzed by Phospholipid-Linked Manganese Porphyrins

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Synthetic models can be very helpful in studying the effect of distance and orientation in electron transfer reactions in biological membrane processes such as occur in photosynthesis and mitochondoria.[1-3] To provide a model for the electron transfer where porphyrin pigments play the key role, the preparation of porphyrin derivatives that are capable of light-induced intra- or intermolecular electron transfer was reported.[3] However, there has been little study of ground-state electron transfer between porphyrin complexes to provide insight into the effect of distance and orientation in the electron transfer so that a vectorial electron transfer system may be constructed in the biological membrane.[4-8] We now report transmembrane electron transfer catalyzed by manganese complexes of bilayer-active phospholipid-linked porphyrins **1**, PE-C_n-MnTTP (n = 0, 5, 11) (Scheme I), which can be easily immersed into the lipid bilayer. The synthetic procedures leading to compound **1** are described in the following sequence of steps. The porphyrins 5-[4-[[(5-carboxyalkyl)amino]carbonyl]-phenyl]-10,15,20-tri-*p*-tolylporphyrin, TTPCONH$(CH_2)_n$*COOH*, **2** (n = 0, 5, 11), and their manganese complexes, Mn(III)-TTPCONH$(CH_2)_n$*COOH*, **3**, were synthesized as described in an earlier paper.[6] Either **2** or **3** was treated with ethyl chloroformate in chloroform at low temperature and reacted with dipalmitoylphosphatidylethanolamine (DPPE) overnight to give the phospholipid-linked porphyrin PE-C_n-MTTP (yields 60–70%), followed by chromatographic separation (silica gel, 10% acetone–chloroform).[9] The ^{1}H NMR and mass spectra of PE-C_n-TTP support unambiguously the assigned structure. The chemical shifts of NMR spectra for all peaks were as expected.[9] MS spectra of PE-C_n-TTP indicated one porphyrin per phospholipid. The absorption spectra of PE-C_n-MTTP in CH_2Cl_2–10% EtOH and phospholipid vesicles such as egg yolk phosphatidylcholine (egg PC, Nippon Fine Chemical Co.) and dipalmitoylphosphatidylcholine (DPPC, Nippon Fine Chemical Co.) were identical, and all showed the presence of a normal porphyrin chromophore. No change of these absorption spectra of PE-C_n-TTP and PE-C_n-

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