phenyl)-2-phenylethanone,[8] 1,4-diphenyl-3-buten-2-one,[9] 1-phenyl-2-dodecanone,[10] 1-phenyl-2-heptanone,[11] 2-methyl-1-phenyl-3-buten-1-one,[12] 1-(4-chlorophenyl)-2-methyl-3-buten-1-one,[12] 2-methyl-1-(4-nitrophenyl)-2-buten-1-one,[2] 3-methyl-1-undecen-4-one,[12] 1-phenyl-3-buten-1-one,[12] 1-(4-chlorophenyl)-3-buten-1-one,[12] valerophenone,[13] 2-phenyl-4-penten-2-ol,[14] 1-allylcyclohexanol,[15] 1-allylcyclopentanol,[15] 3-ethyl-5-hexen-3-ol,[16] 1-(1-methyl-2-propenyl)cyclohexanol,[17] 3-ethyl-4-methyl-5-hexen-3-ol.[18]

Acknowledgment. Thanks are due to the National Natural Science Foundation of China and Academia Sinica for financial support.

Registry No. 1, 128160-29-2; **2**, 131973-46-1; **3a**, 451-40-1; **3b**, 2001-28-7; **3c**, 1889-71-0; **3d**, 2001-29-8; **3e**, 5409-59-6; **3f**, 51439-03-3; **3g**, 6683-94-9; **4**, 137626-43-8; **5h**, 50599-02-5; **5i**, 95827-01-3; **5j**, 137626-44-9; **5k**, 87305-73-5; **5l**, 135987-22-3; **5m**, 95827-02-4; **7**, 137626-45-0; **8n**, 6249-80-5; **8o**, 95827-00-2; **9a**, 51439-94-2; **9b**, 137647-69-9; **9c**, 51439-91-9; **9d**, 137626-46-1; **9e**, 137626-47-2; **9f**, 137626-48-3; **9g**, 137626-49-4; **10a**, 1009-14-9; **10b**, 119-61-9; **10c**, 98-86-2; **10e**, 93-55-0; **11a**, 4743-74-2; **11b**, 1123-34-8; **11c**, 36399-21-0; **11d**, 1907-46-6; **12e**, 36971-11-6; **12f**, 25201-42-7; C_6H_5COCl, 98-88-4; p-$CH_3C_6H_4COCl$, 874-60-2; p-ClC_6H_4COCl, 122-01-0; p-BrC_6H_4COCl, 586-75-4; $C_6H_5CH{=}CHCOCl$, 102-92-1; $CH_3(CH_2)_4COCl$, 142-61-0; $CH_3(CH_2)_9COCl$, 17746-05-3; p-$NO_2C_6H_4COCl$, 122-04-3; $C_6H_5CH_2COCl$, 103-80-0; $CH_3(CH_2)_6COCl$, 111-64-8; $PhCH_2Br$, 100-39-0; Bu_3Sb, 2155-73-9; BuMgBr, 693-03-8; crotyltributylstibonium bromide, 133896-80-7; crotyl bromide, 4784-77-4; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; 3-pentanone, 96-22-0.

Supplementary Material Available: Experimental data for compounds **3a–g**, **5h,i,k,m**, **8n,o**, **10a**, **11a–d**, and **12e,f** (3 pages). Ordering information is available on any current masthead page.

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(8) Speer, J. H.; Hill, A. J. *J. Org. Chem.* **1937**, *2*, 139.

(9) Fleming, L.; Pearce, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2485.

(10) Decock, P.; Vidal, B.; Goudmand, P. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1973**, *277*, 407.

(11) Sund, E. H.; Henze, H. R. *J. Chem. Eng. Data* **1970**, *15*, 200.

(12) Reetz, M. T.; Wenderoth, B.; Urz, R. *Chem. Ber.* **1985**, *118*, 348.

(13) Shriner, R. L.; Turner, T. A. *J. Am. Chem. Soc.* **1930**, *52*, 1267.

(14) Jaworsky, W. *Chem. Ber.* **1909**, *42*, 435.

(15) Marcou, A.; Normant, H. *Bull. Soc. Chim. Fr.* **1965**, 3491.

(16) Schirokoff, A.; Saytzeff, A. *Ann. Chem.* **1879**, *196*, 113.

(17) Blais, J.; L'Honore, A.; Soulie, J.; Cadiot, P. *J. Organomet. Chem.* **1974**, *78*(3), 323.

(18) Benkeser, R. A.; Siklosi, M. P.; Mozdzen, E. C. *J. Am. Chem. Soc.* **1978**, *100*, 2134.

Alkyl Radical Displacement Reactions at Sulfur: On the Question of Intermediacy in Alkylsulfuranyl Radicals[1]

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Received July 5, 1991

Introduction

Radical displacement reactions at sulfur centers are of particular interest since the reaction may proceed through a relative energy minimum corresponding to a tricoordinate, hypervalent sulfuranyl radical intermediate.[2] Sulfuranyl radicals have been reported with σ-, σ^*-, and π-type ground-state electronic structures.[3,4] By analogy with closed shell 9-S-4 (9 formal electrons about 4-coordinate sulfur) sulfuranes, one or more electronegative ligands are probably required to achieve stable 9-S-3 sulfuranyl radicals.[5] Previous electronic structure calculations on SF_3 have indicated that the species is a stable intermediate, while SH_3 is probably a transition state.[2] Neither prediction was experimentally verifiable due to limitations in methodology and experiment. While our earlier kinetic studies[6] have revealed that the rate-determining step of alkyl radical displacement at sulfur centers is sensitive to the stability of the displaced radical, the intermediacy of a 9-S-3 alkyl species could not be rigorously excluded. Thus, ab initio molecular orbital calculations were performed on a series of sulfuranyl species ($(H_3C)_3S^\bullet$, $(H_3C)_2HS^\bullet$, and $H_3S^\bullet$) with weakly electron-donating ligands to resolve the question of intermediacy of alkylsulfuranyl radicals and to determine the applicability of many-body perturbation methods[7] for achieving accurate thermochemical estimates of second-row free-radical reaction energetics.

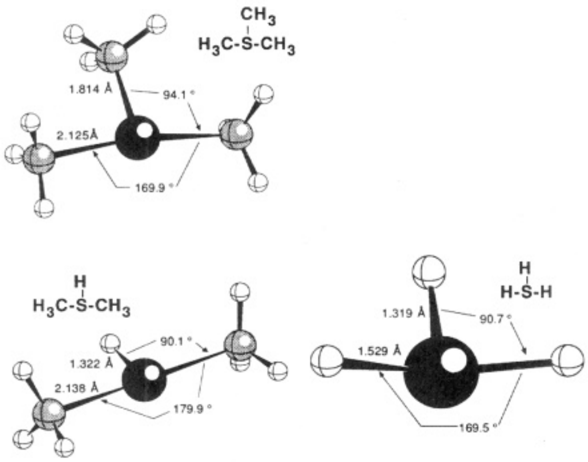

Figure 1. Molecular structure of (a) trimethylsulfuranyl, (b) dimethylsulfuranyl, and (c) sulfuranyl radicals.

Computational Methods

Electronic structure calculations were performed with the ACES[8] and GAUSSIAN-86[9] systems of programs. The geometries for reactants and transition states were optimized at the SCF level with the 4-31G*[10] split valence basis set. Electron correlation

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(1) This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC06-76RLO 1830.

(2) Volatron, F.; Demolliens, A.; Lefour, J.-M.; Eisenstein, O. *Chem. Phys. Lett.* **1986**, 419. Volatron, F. THEOCHEM **1989**, 186, 167.

(3) Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, 102, 7753 and references cited therein.

(4) Perkins, C. W.; Clarkson, R. B.; Martin, J. C. *J. Am. Chem. Soc.* **1986**, 108, 3206. Perkins, C. W.; Martin, J. C. *J. Am. Chem. Soc.* **1986**, 3211.

(5) Martin, J. C.; Perozzi, E. F. *Science* **1976**, 191, 154. Martin, J. C. *Science* **1983**, 221, 509.

(6) Franz, J. A.; Roberts, D. H.; Ferris, K. F. *J. Org. Chem.* **1987**, 52, 2256.

(7) Bartlett, R. J. Many-Body Perturbation Theory and Coupled Cluster Theory for Electron Correlation in Molecules. *Ann. Rev. Phys. Chem.* **1981**, 32, 359. Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, 76, 1910. Urban, M.; Noga, J.; Cole, S. J.; Bartlett, R. J. *J. Chem. Phys.* **1985**, 83, 4041.

(8) ACES (Advanced Concepts in Electronic Structure), an ab initio program system authored by Bartlett, R. J.; Purvis, G. D., III; Fitzgerald, G. B.; Harrison, R. J.; Lee, Y. S.; Laidig, W. D.; Cole, S. J.; Magers, D. H.; Salter, E. A.; Trucks, G. W.; Sosa, C.; Rittby, M.; Pal, S. Quantum Theory Project, University of Florida, Gainesville, FL, 1987.

(9) GAUSSIAN 86: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A., Carnegie-Mellon Chemistry Publishing Unit, Pittsburgh, 1984.

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Table I. Activation Energies (ΔE^{*}, kcal/mol) for $H_3CSCH_3 + CH_3 \rightarrow [(H_3C)_3S]^{*} \rightarrow CH_3 + H_3CSCH_3$

level	ΔE^{a}	ΔE(spin)^{b}	ΔE^{*c}
SCF	26.54	19.46	19.19
MBPT(2)	19.23	13.48	13.21
MBPT(3)	20.06	16.15	15.88
DQ-MBPT(4)	20.25		
SDTQ-MBPT(4)	17.32	13.41	13.14

[a] Interaction energies calculated as $\Delta E = E(AB) - (E(A) + E(B))$. [b] Using spin-projected molecular energies[11] after annihilation of unwanted spin states. Fourth-order spin annihilation correction was estimated as $E_{PMBPT4} - E_{MBPT4} \approx E_{PMBPT3} - E_{MBPT3}$. [c] Thermodynamic corrections (zero point and thermal energies) were estimated by standard statistical mechanical techniques using unscaled frequencies.

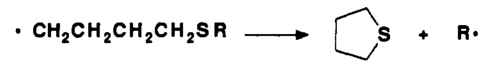

Figure 2. Intramolecular displacement reaction of 4-(alkylthio)butyl radicals.[6]

corrections were estimated by open-shell many-body perturbation theory (MBPT) through fourth order at the SCF determined geometries. Spin-corrected total energies had their unwanted spin contaminants removed using the Löwdin spin annihilator operator,[11,12] with the spin correction to the fourth-order perturbation energy estimated from the third-order method.[13] Vibrational frequencies were evaluated using analytical second derivatives at the SCF level and thermodynamic quantities estimated by standard statistical mechanical techniques.[14]

Results and Discussion

The optimized geometries of the trial sulfuranyl species, $(H_3C)_3S^{\bullet}$, $(H_3C)_2HS^{\bullet}$, and $H_3S^{\bullet}$, are summarized in Figure 1. Relative energetics for the symmetric displacement reaction of methyl radical and dimethyl sulfide are collected in Table I. Extensive geometry searches failed to reveal a stable 9-S-3 structure but did locate transition-state structures for the displacement reactions. The molecular structures resemble those of phosphoranyl radicals,[15] exhibiting a T-shaped molecular structure (⟨eq-S-axial ~90°, ⟨axial-S-axial ~175°), with both the sulfur lone pair and the singly occupied orbital assuming pseudoequatorial positions.[3] For the three structures, the vibrational frequency analysis has revealed one eigenvalue of 690i, 677i, and 1454i cm^{-1} for $(H_3C)_3S^{\bullet}$, $(H_3C)_2HS^{\bullet}$, and $H_3S^{\bullet}$, respectively. The eigenfunctions of these frequencies exhibit axial compression and displacements modes, consistent with a displacement-type reaction. In previous work, we have shown that the singly occupied molecular orbital (SOMO) of the trimethyl- and propyl-1,4-butylidenesulfuranyl radicals show antibonding interactions between the axial groups consistent with axial-axial displacements.[6] Thus, we conclude that alkyl radical displacement at dialkyl and alkyl sulfides procedes through an axial–axial transition state rather than a 9-S-3 intermediate, consistent with our kinetic studies[6] and other lines of experimentation.[15]

Although the activation energy for the trimethylsulfuranyl radical has not been experimentally determined, activation barriers for the closely analogous reactions of 4-(*n*-propylthio)butyl ($\Delta H^{\circ} = 2.1$ kcal/mol, $\Delta E^{*} = 12.2$ kcal/mol) and 4-(*tert*-butylthio)butyl radical ($\Delta H^{\circ} = -2.2$ kcal/mol, $\Delta E^{*} = 11.4 \pm 0.4$ kcal/mol) lead us to estimate a barrier of 12 ± 2 kcal/mol for the displacement reaction of methyl radical and dimethyl sulfide. For the theoretical treatment of the open-shell transition state, past experience for first-row reactions suggests that spin contamination will be a complicating effect. Our results (Table I) indicate that the barrier heights calculated at the UHF and MBPT levels without spin annihilation are also too high, but can offer good agreement after elimination of unwanted spin components. Both correlation energy corrections ($\Delta E \approx 6.3$–9.2 kcal/mol) and spin annihilation ($\Delta E \approx 3.9$–7.1 kcal/mol) in the unpaired electron species result in significant corrections to the activation energy. Consistent with previous studies on the $C_2H_2 + H^{\bullet}$ reaction, higher orders of perturbation theory recovers greater degrees of correlation energy, but only marginally improve the spin contamination problems.[13] Upon removal of the first spin contaminant, the S^2 value for the trimethyl sulfuranyl radical changes from 0.877 to 0.754. Thermochemical corrections for zero point energy and internal energy were calculated at the SCF level and result in a −0.27 kcal/mol difference. The resulting theoretical values at the MBPT(2) and MBPT(4) levels are in good agreement with the predicted experimental value (12 ± 2 kcal/mol).

In summary, we conclude that radical displacement at sulfur lacking electronegative ligands proceed through 9-S-3 transition states, rather than hypervalent reaction intermediates. The application of many-body perturbation methods allows one to approach thermochemical quality in second-row free-radical systems, with MBPT(2) capturing the majority of the correlation energy. Spin contamination of the wavefunction presents a major problem for accurately predicting the relative energetics for these species.

Registry No. H_3CSCH_3, 75-18-3; CH_3, 2229-07-4.

Supplementary Material Available: Molecular structures of $H_3S^{\bullet}$, $(H_3C)_2HS^{\bullet}$, and $(H_3C)_3S^{\bullet}$ (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(10) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, 72, 650. Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, 80, 3265.

(11) Löwdin, P.-O. *Phys. Rev.* **1955**, 97, 1509.

(12) Schlegel, H. B. *J. Chem. Phys.* **1986**, 84, 4530.

(13) Sosa, C.; Schegel, H. B. *Int. J. Quant. Chem.* **1986**, 29, 1001. Sosa, C.; Schegel, H. B. *Int. J. Quant. Chem.* **1986**, 30, 155. Sosa, C.; Schlegel, H. B. *Int. J. Quant. Chem.* **1987**, S21, 267.

(14) Davidson, N. *Statistical Mechanics*; New York: McGraw-Hill, 1962.

(15) Beak, P.; Sullivan, T. A. *J. Am. Chem. Soc.* **1982**, 104, 4450.

Formation of Sterically Hindered Primary Vicinal Diamines from Vicinal and Geminal Dinitro Compounds

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Received February 5, 1991 (Revised Manuscript Received October 3, 1991)

Vicinal diamines find wide application in synthesis as both synthons and catalysts.[1,2] While tertiary diamines such as *N,N,N′,N′*-tetramethylethylenediamine are common in catalysis,[3,4] the secondary and primary diamines

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(1) (a) Fieser, L.; Fieser, M. *Reagents for Organic Synthesis*; Vol. 1, p 372; Vol. 2, p 403; Vol. 3, p 284; Vol. 4, pp 231, 485, 614; Vol. 5, p 652; Vol. 6, p 576; Vol. 7, p 358; Vol. 12, 477. (b) Agami, C. *Bull. Chim. Soc. Fr.* **1970**, *4*, 1619. (c) Lindnoy, L. F. In *Synthesis of Macrocycles*; Izatt, R. M., Christensen, J. J., Eds.; Wiley: New York, 1987.

(2) *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Wiley: New York, 1979.

0022-3263/92/1957-0778$03.00/0 © 1992 American Chemical Society