flask, equipped with a magnetic spin bar and a dropping funnel with a $CaCl_2$ drying tube, was charged with a solution of 2.46 g (17.4 mmol) of chlorosulfonyl isocyanate in 20 mL of anhydrous Et_2O. While the mixture was stirred vigorously and cooled to 0 °C by means of an ice bath, a solution of 2.29 g (17.4 mmol) of dioxetane 1 in 20 mL of anhydrous Et_2O was added dropwise within 30 min. A 10% aliquot of the reaction mixture was removed and rotary evaporated, affording 475 mg (100%) of a viscous, yellow oil, which exhibited no significant impurities by means of ^1H NMR. Recrystallization twice from 1:1 Et_2O/petroleum ether (bp 30–50 °C) led to 361 mg (76%) of yellow powder: mp 90–91 °C; TLC (silica gel) [CH_2Cl_2] R_f 0.50 (with strong tailing); IR (CCl_4) 3360, 3000, 2980, 1780, 1620, 1435, 1383, 1290, 1193, 1175, 1155 cm^{-1}; ^1H NMR ($CDCl_3$/acetone-d_6, 90 MHz) δ 1.44 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3), 1.63 (s, 3 H, CH_3), 4.76 (s, 2 H, CH_2O), 10.00–10.50 (s, 1 H, NH); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 17.58 (q, CH_3), 21.92 (q, CH_3), 23.83 (q, CH_3), 69.02 (t, CH_2O), 89.06 (s, COO), 89.82 (s, COO), 149.06 (s, C=O); MS (70 eV), m/e 215 (0.03%, M - acetone), 202 (0.06%), 149 (0.2%), 74 (2%), 64 (6%), 58 (28%), 43 (100%). Anal. Calcd for $C_7H_{12}NO_6SCl$ (273.7): C, 30.72; H, 4.42; N, 5.12. Found: C, 30.80; H, 4.41; N, 4.98.

3-(Ethoxymethyl)-3,4,4-trimethyl-1,2-dioxetane (5a). A 100-mL, round-bottomed flask, equipped with a magnetic spin bar and a dropping funnel protected with a $CaCl_2$ drying tube, was charged with a solution of 823 mg (6.24 mmol) of dioxetane 1 in 30 mL of anhydrous CH_2Cl_2 and ca. 4.5 g of anhydrous Na_2CO_3. While the mixture was stirred and the reaction temperature maintained at 0 °C by means of cooling with an external ice bath, a solution of 1.51 g (7.95 mmol) of triethyloxonium tetrafluoroborate in 10 mL of anhydrous CH_2Cl_2 was added within 5 min. After the addition, the ice bath was removed and the reaction mixture allowed to stir at ca. 20 °C for 4 h. Again the reaction mixture was cooled to ca. 0 °C by means of an ice bath and the organic phase separated and washed with concentrated aqueous NH_3 (5 mL), followed by a washing with H_2O (20 mL) and drying. The yellow solution was concentrated to one-third its volume by means of rotary evaporation and flash chromatographed on silica gel (20:1 adsorbent/substrate ratio, CH_2Cl_2, -20 °C). The peroxidic eluates (spotted by means of KI–HOAc) were combined and rotary evaporated (-10 °C at 17 Torr), leading to 183 mg (18%) of a yellow, pungent-smelling oil; peroxide content > 97% by means of iodometry: TLC (silica gel) [CH_2Cl_2] R_f 0.67; IR (CCl_4) 2980, 2935, 2900, 2870, 1470, 1455, 1440, 1410, 1380, 1370, 1260, 1230, 1150, 1113, 1022, 880 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.20 (t, J = 2.3 Hz, 3 H, CH_3CH_2), 1.43 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.59 (s, 3 H, CH_3), 3.55 (q, J = 2.3 Hz, 2 H, CH_2CH_3) [AB system, δ_A 4.62, δ_B 3.66 (J_{AB} = 9.3 Hz, 2 H, CH_2O); ^{13}C NMR ($CDCl_3$, 100.6 Hz) δ 14.97 (q, CH_3CH_2), 18.46 (q, CH_3), 22.28 (q, CH_3), 23.95 (q, CH_3), 66.96 (t, CH_2OEt), 72.88 (t, OCH_2CH_3), 89.05 (s, COO), 89.47 (s, COO); MS (70 eV), m/e 161 (0.07%, M + 1), 159 (0.06%, M - 1), 131 (0.1%, M - C_2H_5), 129 (0.2%, M - O_2), 103 (0.3%, M + 1 - acetone), 102 (0.1%, M - acetone), 87 (2%), 59 (25%), 58 (32%), 57 (7%), 43 (100%).

3-[((Trimethylsilyl)oxy)methyl]-3,4,4-trimethyl-1,2-dioxetane (5b). A 100-mL, round-bottomed flask, equipped with a magnetic spin bar and a 25-mL dropping funnel protected with a $CaCl_2$ drying tube, was charged with 1.09 g (10.1 mmol) of trimethylsilyl chloride in 20 mL of anhydrous CH_2Cl_2. While the mixture was stirred and cooled to 0 °C by means of an ice bath, 797 mg (10.1 mmol) of pyridine was first added and then dropwise within 10 min a solution of 666 mg (5.04 mmol) of dioxetane 1 in 20 mL of anhydrous CH_2Cl_2. After a 40-min reaction time under these conditions, the clear yellow solution was concentrated to a 5-mL volume by means of rotary evaporation and flash chromatographed over alumina (69:1 adsorbent substrate ratio, 1:1 CH_2Cl_2/petroleum ether (bp 30–50 °C), -30 °C), affording 525 mg (51%) of a yellow, pleasant-smelling oil; peroxide content > 97% by means of iodometry: TLC (silica gel) [CH_2Cl_2] R_f 0.77; IR (CCl_4) 3000, 2955, 2920, 2870, 1470, 1375, 1252, 1152, 1095, 980, 877, 842 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.16 (s, 9 H, $SiMe_3$), 1.45 (s, 6 H, CH_3), 1.64 (s, 3 H, CH_3) [AB system, δ_A 4.18, δ_B 3.81 (J_{AB} = 10.2 Hz, 2 H, CH_2O)]; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ -0.72 (q, $SiMe_3$), 18.00 (q, CH_3), 22.19 (q, CH_3), 24.16 (q, CH_3), 65.05 (t, CH_2O), 89.13 (s, COO), 89.98 (s, COO); MS (70 eV), m/e 147 (0.6%, M - acetone), 131 (25%, M - $SiMe_3$), 115 (2%, M - $OSiMe_3$), 73 (42%, $SiMe_3$), 58 (18%), 43 (100%).

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Registry No. 1, 84114-76-1; 2, 92507-36-3; 3a, 108560-91-4; 3b, 108536-11-4; 4, 108536-12-5; 5a, 108536-13-6; 5b, 108536-14-7; 2,3-dimethyl-1,2-epoxy-3-hydroperoxybutane, 108536-15-8; p-nitrobenzoic acid, 62-23-7; 4-(dimethylamino)pyridine, 1122-58-3; methyl chloroformate, 79-22-1; cholesteryl chloroformate, 7144-08-3; chlorosulfonyl isocyanate, 1189-71-5.

Stabilization Energies and Structures of Substituted Methyl Radicals

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The energies and structures of a large number of substituted methyl radicals and methanes have been calculated at the fully geometry optimized UHF and ROHF 4-31G levels. The radical stabilization energies (RSE's) of the various substituents have been calculated according to the isodesmic reaction $X_n\dot{C}H_{3-n} + CH_4 \rightarrow X_nCH_{4-n} + \dot{C}H_3$. These RSE's are compared with other radical stabilization scales and with various types of experimental data derived from radical reactions and provide a scale for evaluating the extent of substituent stabilization in radical-forming reactions.

Over the past decade considerable attention has been devoted to attempts to determine the relative extents of stabilization, or destabilization, of a radical center by an attached substituent and the nature of the orbital interactions between the orbitals of the substituent and the singly occupied molecular orbital (SOMO) of the radical center. The vast majority of these efforts have involved kinetic studies including the following: (1) hydrogen atom

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abstraction involving substituted toluenes,[1,2] (2) the thermolysis of aryl-substituted benzyl azo compounds,[3,4] (3) the thermolysis of 2-substituted azopropanes,[4,5] (4) the thermal rearrangement of aryl-substituted 3-aryl-2,2-dimethylmethylenecyclopropanes,[6] (5) the pyrolytic C–C bond homolysis of substituted alkanes,[7] and (6) the cyclodimerization of substituted trifluorostyrenes.[8] The interpretation of the kinetic data derived from the hydrogen atom abstraction reactions is made difficult by the contribution of polar effects in the transition states that may overwhelm the radical stabilizing effects.[1,2] The isolation of steric effects from electronic effects has been the impetus for the study of the category 4 and 5 reactions. An attempt has been made to develop a σ scale from the relative rate data for the cyclodimerization reactions of the substituted trifluorostyrenes.[8] All of the kinetic procedures suffer from their inability to provide a quantitative determination of the full thermodynamic stabilizing effect of a substituent in the completely formed free radical, the kinetic data providing information only on the extent of the interactions in the transition states for the individual reactions. Ideally, what is required is data derived on the fully formed free radicals that can be directly related to the radical stabilization energies (RSE's) of the substituents.

ESR hyperfine coupling constants have been measured in substituted benzyl radicals and have been related to the relative extents of spin delocalization and, thus in turn, to the stabilization afforded the radical centers by the substituents.[9] Attempts have been made to use heats of formation (ΔH_f's) and bond dissociation energies (BDE's); however, uncertainties in the values of the ΔH_f's and BDE's do not allow for the development of a highly precise correlation of RSE's.[10,11] Stabilization energies (SE's) have been calculated for a large number of substituted radicals, the SE's being defined by eq 1 in which $\Delta H_a°$ is the heat

$$\mathrm{SE} = \Delta H_a° - \sum_l \epsilon_l° \qquad (1)$$

of atomization of the species and the $\epsilon_l°$'s are standard bond energy terms derived from the heats of atomization of reference compounds.[12,13] The only truly accurate thermodynamic RSE determined for any radical thus far would appear to be that of the allyl radical.[14] Isodesmic RSE's have been calculated at the ab initio 3-21G level for a few substituents attached to cyclopropyl and isopropyl radical centers.[15] Finally, and most recently, electrochemical oxidation potentials have been measured for substituted fluorenyl and phenylacetonitrile anions in Me_2SO solution which has allowed for the estimation of relative homolytic bond dissociation energies, which in turn are related to the relative radical stabilities termed acidity oxidation potentials (ΔAOP's).[16]

Our interst in RSE's of substituents has arisen in conjunction with our studies on the effects of substituents on the relative rates of formation, cleavage, and ring closure reactions of the substituted diradical intermediates formed in the (2 + 2) cycloaddition reactions of substituted allenes.[17] In these cycloaddition reactions we have observed that all functional groups, both electron donating and withdrawing, accelerate the rate of formation of the diradical intermediates (relative to hydrogen), suggesting that these reactions proceed via late transition states. It was therefore of interest to try to see if there is a correlation between our relative reactivities and the RSE's of substituents attached to a radical center. A review of the literature revealed that RSE's of various functional groups are not accurately known (suggested values of RSE's for the various functional groups will be cited in the following sections). We have therefore calculated RSE's for a number of substituents attached to the methyl radical center

$$X_n\dot{C}H_{3-n} + CH_4 \rightarrow X_n{-}CH_{4-n} + \dot{C}H_3 \qquad (2)$$

according to the isodesmic reaction suggested as the definition of the stabilization energy of a substituent attached to a radical center.[18] Calculations on the various species have been carried out at the fully geometry optimized UHF or ROHF 4-31G levels for first-row atom substituents and at the 4-31G + d's level for the second-row atom substituents by using the GAUSSIAN80 and -82 and GAMESS packages of programs. A number of systems included in this study have been the subject of prior theoretical investigations which will be cited and compared with the present results in the following individual sections.

The calculated geometrical parameters are provided in the supplementary material or may be obtained directly from the primary author of this paper. The total energies of all species calculated appear in Table I, along with SOMO energies. The calculated RSE's are summarized in Table II.

Discussion

Fluoromethyl Systems. The effect of fluorine substitution on the stability, structure, and electronic structure of radicals has been extensively investigated, both experimentally and theoretically. The 4-F substituent is reported to *increase* the rate of pyrolysis of substituted azocumenes relative to the unsubstituted system.[19] A case for the stabilization of a radical center by a fluorine atom has been made on the basis of perturbation molecular orbital (PMO) theory.[20] Ab initio calculations (3-21G level) on substituted cyclopropyl and isopropyl radicals indicate that fluorine is slightly stabilizing (2.7 kcal/mol) but that the stabilization decreases on inclusion of polarization functions.[15] Other data, however, suggest that fluorine is destabilizing relative to hydrogen. 4-F substitution results in slight *decreases* in the rates of pyrolysis

(1) Kim, S. S.; Choi, S. Y.; Kang, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 4234.
(2) (a) Fisher, T. H.; Meierhoefer, A. W. *J. Org. Chem.* **1978**, *43*, 220; (b) **1978**, *43*, 224.
(3) Shelton, J. R.; Liang, C. K. *J. Org. Chem.* **1973**, *38*, 2301.
(4) Bandlish, B. K.; Garner, A. W.; Hodges, M. L.; Timberlake, J. W. *J. Am. Chem. Soc.* **1975**, *97*, 5856.
(5) Timberlake, J. W.; Garner, A. W.; Hodges, M. L. *Tetrahedron Lett.* **1973**, 309.
(6) (a) Creary, X.; Benage, B.; Mehrsheikh-Mohammadi, M. E.; Bays, J. P. *Tetrahedron Lett.* **1985**, *26*, 238. (b) Creary, X. *J. Org. Chem.* **1980**, *45*, 280. Creary, X. *J. Org. Chem.* **1986**, *51*, 1110.
(7) Rüchardt, C.; Beckhaus, H.-D. *Top. Curr. Chem.* **1985**, *130*, 1.
(8) Jiang, X.-K.; Ji, G.-Z.; Yu, C.-X. *Huaxue Xuebao* **1984**, 82.
(9) (a) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1221. (b) Wagner, D. D.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1164.
(10) Colussi, A. J.; Benson, S. W. *Int. J. Chem. Kinet.* **1977**, *9*, 307.
(11) Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* **1981**, *103*, 1586.
(12) Leroy, G.; Peeters, D.; Wilante, C. *THEOCHEM* **1982**, *86*, 217.
(13) Leroy, G. *Int. J. Quantum Chem.* **1983**, *23*, 271.
(14) Rossi, M.; King, K. D.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1223.
(15) Lien, M. H.; Hopkinson, A. C. *J. Comput. Chem.* **1985**, *6*, 274.
(16) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979.
(17) Pasto, D. J.; Warren, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3670. Pasto, D. J.; Heid, P. J.; Warren, S. E. *Ibid.* **1982**, *104*, 3676. Pasto, D. J.; Yang, S.-H. *Ibid.* **1984**, *106*, 152. Pasto, D. J.; Yang, S.-H. *J. Org. Chem.* **1986**, *51*, 1676. Pasto, D. J.; Yang, S.-H. *Ibid.* **1986**, *51*, 3611.
(18) Dewar, M. J. S.; Fox, M. A.; Nelson, D. J. *J. Organomet. Chem.* **1980**, *185*, 157.
(19) Kovacic, P.; Flynn, R. R.; Gormish, J. F.; Kappelman, A. H.; Shelton, J. R. *J. Org. Chem.* **1969**, *34*, 3312.
(20) Bernardi, F.; Epiotis, N. D.; Cherry, W.; Schlegel, H. B.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1976**, *98*, 469.

Table I. Total and SOMO Energies of the Substituted Methyl Radicals and Methanes

structure	E_{TOT} (au)	E_{SOMO} (eV)	structure	E_{TOT} (au)	E_{SOMO} (eV)
CH_2F (planar)	−138.22562[a]	−10.645	**10c**	−226.80733	−10.942
(nonplanar)	−138.22642[a]	−10.994	**10d**	−226.79993	−11.185
CH_3F	−138.85861		**11a**	−227.44327	
CHF_2 (planar)	−236.94841[a]	−10.845	**11b**	−227.43137	
(nonplanar)	−236.95931[a]	−12.088	**12a** (nonplanar)	−94.45321	−7.599
CH_2F_2	−237.59322		**12b** (planar)	−94.45232	−7.210
CF_3 (planar)	−335.65452[a]	−11.100	CH_3NH_2	−95.07166	
(nonplanar)	−335.69454[a]	−19.550	**13a** (nonplanar)	−133.42083	−7.380
CHF_3	−336.33605		**13b** (planar)	−133.41973	−7.009
1a	−177.21255	−10.953	CH_3NHCH_3	−134.04019	
1b	−177.21240	−10.358	**14a** (nonplanar)	−94.79947	−17.410
CH_3CH_2F	−177.84503		**14b** (planar)	−94.79930	−17.328
2a	−275.95183	−11.621	$CH_3NH_3^+$	−95.44076	
2b	−275.95157	−11.390	**15**	−64.73111	−10.952
CH_3CHF_2	−276.58789		CH_3BH_2	−65.34844	
3b	−374.69626	−12.371	**16** (no d AO's)	−436.55281	−8.724
CH_3CF_3	−375.33319		**16** (with d AO's)	−436.59200	−8.337
CH_2Cl (planar, 4-31G)	−497.90705		CH_3SH (no d AO's)	−437.18375	
(planar, 4-31G + d's)	−497.92886	−9.900	CH_3SH (with d AO's)	−437.21778	
(nonplanar, 4-31G)	−497.90720		**17**	−436.88647	−17.120
(nonplanar, 4-31G + d's)	−497.92892	−9.982	$CH_3S^+H_2$	−437.52633	
CH_3Cl (4-31G)	−498.54278		**18**	−511.26691	−10.033
(4-31G + d's)	−498.55962		CH_3SOH	−511.89993	
$CHCl_2$ (planar, 4-31G)	−956.30027		**19**	−585.97953	−12.524
(planar, 4-31G + d's)	−956.34803	−9.751	CH_3SO_2H	−586.61563	
(nonplanar, 4-31G)	−956.30187		**20a** (nonplanar)	−380.43305	−8.719
(nonplanar, 4-31G + d's)	−956.34939	−10.124	**20b** (planar)	−380.43273	−8.748
CH_2Cl_2 (4-31G)	−956.93619		CH_3PH_2	−381.06098	
(4-31G + d's)	−956.97306		**21**	−380.76567	−12.462
CCl_3 (planar, 4-31G)	−1414.68759		$CH_3PH_3^+$	−381.40114	
(planar, 4-31G + d's)	−1414.76147	−9.671	$CH_2CH{=}CH_2$	−116.27954	−7.768
(nonplanar, 4-31G)	−1414.69076		$CH_3CH{=}CH_2$	−116.90510	
(nonplanar, 4-31G + d's)	−1414.76502	−10.226	**22**	−115.07610	−9.738
$CHCl_3$ (4-31G)	−1415.32182		$HC{\equiv}CCH_3$	−115.70133	
(4-31G + d's)	−1415.38445		**23**	−152.06075	−11.079
4a (nonplanar)	−114.29586	−9.399	CH_3CHO	−152.68653	
4b (planar)	−114.24496	−9.033	**24**	−226.84148	−11.455
CH_3OH	−114.87152		CH_3CO_2H	−227.47034	
6a	−189.00060	−9.168	**25**	−207.04292	−11.091
6b	−188.99171	−9.255	CH_3CONH_2	−207.67217	
$CH_2(OH)_2$ (**7**)	−189.62791		$CH_2C{\equiv}N$	−131.09880	−11.320
8a	−153.21199	−9.087	$CH_3C{\equiv}N$	−131.72827	
8b	−153.20736	−9.748	CH_2NO_2	−242.63928	−12.638
CH_3OCH_3	−153.83835		CH_3NO_2	−243.27450	
10a	−226.81227	−10.205			
10b	−226.80743	−11.016			

[a] Prior literatures values at the 4-31G, non-fully geometry optimized level are CH_2F −138.22558 (planar) and −138.22639 (nonplanar); CHF_2 −236.94839 (planar) and −236.95924 (nonplanar); and CF_3 −335.65451 (planar) and −335.69452 (nonplanar) (see ref 27).

of phenylazoethane[21] and the thermal rearrangement of 2-aryl-3,3-dimethylmethylenecyclopropane.[6b] Fluorine destabilization is also implied from the hyperfine coupling constant data derived from substituted benzyl radicals.[9a] Increasing fluorine substitution has been proposed to result in progressive destabilization, with eventual destabilization in the case of CF_3.[20] Experimental support for this proposal is evident in the radical fragmentation of trifluoromethyl *tert*-butoxy radical in which the methyl radical is formed ten times faster than the trifluoromethyl radical.[22]

Numerous theoretical calculations have been carried out on the fluoromethyl radicals. Calculations on CH_2F and CHF_2 have been carried out at the CNDO,[23] MNDO,[24] STO-3G,[25] and 4-31G[26,27] levels, while calculations on CF_3 have been carried out at the CNDO,[23] MNDO,[24] STO-3G.[25,28] 4-31G,[26] (5212) Gaussian basis set,[29] and (9s5p14s2p) double ζ[30] basis set levels. Calculations have also been carried out on the fluoromethanes at the semiempirical and 4-31G levels.[26] The calculations on CH_2F and CHF_2 at the 4-31G were carried out with only apparent partial geometry optimization.[26]

In the present study calculations have been carried out at the UHF 4-31G level on the mono-, di-, and trifluoromethyl radicals with full geometry optimization and on the restricted planar structures.[31] Calculations were also

(21) Shelton, J. R.; Liang, C. K. *J. Org. Chem.* **1973**, *38*, 2301.
(22) Jiang, X.-K.; Li, X.-Y.; Wang, K. Y. *J. Chem. Soc., Chem. Commun.* **1986**, 745.
(23) Beveridge, D. L.; Dobash, P. A.; Pople, J. A. *J. Chem. Phys.* **1968**, *48*, 4802.
(24) Molina, L. M.; Poblet, J. M.; Canadell, E. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1217.
(25) Leroy, G.; Peeters, D.; Wilante, C.; Khalil, M. *Nouv. J. Chim.* **1980**, *4*, 403.
(26) Baird, N. C. *Can. J. Chem.* **1983**, *61*, 1567.
(27) Bernardi, F.; Cherry, W.; Shaik, S.; Eipotis, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 1352. Leroy, G.; Peeters, D. *J. Mol. Struct. (THEOCHEM)* **1981**, *85*, 133.
(28) So, S. P. *Chem. Phys. Lett.* **1979**, *67*, 516.
(29) Morokuma, K.; Pederson, L.; Karplus, M. *J. Chem. Phys.* **1968**, *48*, 4801.
(30) Benzel, M. A.; Maurice, A. M.; Belford, R. L.; Dykstra, C. E. *J. Am. Chem. Soc.* **1983**, *105*, 3802.
(31) Calculations were also carried out at the ROHF 4-31G level on CH_2F and CH_3 in order to determine the effect of the slight higher multiplicity spin-state contamination in the UHF calculations CH_2F and CH_3. The ROHF energies were −138.22354 and −39.50179 au, respectively. These values give a value of the RSE for CH_2F only slightly smaller than that from the UHF calculations.

Table II. Calculated RSEs for Substituents Attached to the Methyl Radical

substituent(s) X[a]	RSE (kcal mol^{-1})[b]	substituent(s) X[a]	RSE (kcal mol^{-1})[b]
CH_3[c,d]	+3.27	HS	+5.66 (+2.39)[h]
CH_3CH_2[e]	+2.84	H_2S^+	−3.17
$(CH_3)_2$[f]	+5.81	HSO	+1.12
$(CH_3)_3$[g]	+7.98	HSO_2	−0.82
F	+1.64	H_2N	+10.26
F_2	+0.56	H_3N^+	−4.07
F_3	−4.21	CH_3NH	+9.69
FCH_2	+1.46	H_2P	+4.31
F_2CH	+0.16	H_3P^+	−0.42
F_3C	−1.34	H_2B	+11.00
Cl	+2.57 (−0.49)[h]	$H_2C{=}CH$	+7.80
Cl_2	+6.98 (+0.30)[h]	$HC{\equiv}C$	+8.00
Cl_3	+9.64 (+2.53)[h]	HCO	+7.66
HO	+5.73	HO_2C	+5.72
$(HO)_2$	+4.70	H_2NCO	+5.48
HCOO	+2.38	$N{\equiv}C$	+5.34
CH_3O	+5.30	O_2N	+1.73

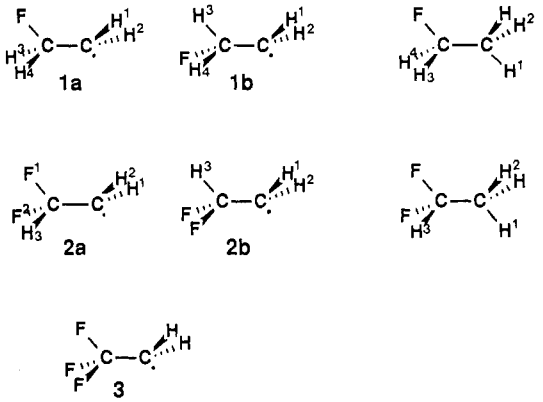
[a] See equation 2. [b] A positive sign indicates stabilization of the radical center. [c] The 4-31G energies for the methyl radical and methane have been taken from ref 34. [d] The energy of the ethyl radical was calculated from the optimized geometry reported in ref 74 and that of ethane from ref 34. [e] The energies for the propyl radical and propane have been taken from ref 75. [f] The energy of the isopropyl radical has been taken from ref 76. [g] The energy of the *tert*-butyl radical has been taken from ref 77, and the energy of isobutane was calculated from the optimized structure reported in ref 77. [h] Calculated with the 4-31G basis set without the inclusion of d AO's on chlorine or sulfur.

carried out at the RHF 4-31G level on the mono-, di- and trifluoromethanes. The total and SOMO energies of the species are given in Table I. The nonplanar radical structures are all lower in energy than the planar structures, the nonplanarity increasing with fluorine substitution. This is consistent with the results of earlier ESR[32] and theoretical studies. The nonplanarity of the radical center, as indicated by the angle of the bisector, is 28.8° in CH_2F, 42.4° in CHF_2, and 49.1° in CF_3 with calculated inversion barriers of 0.5, 6.8, and 25.1 kcal/mol, respectively.

The calculated RSE's are +1.64 for CH_2F, +0.56 for CHF_2, and −4.21 kcal/mol for CF_3. A single fluorine is slightly radical stabilizing (relative to hydrogen), but less so than the methyl group (+3.17 kcal/mol). Increased fluorine substitution results in a decrease in the stabilization of the radical center, with three fluorines having a substantial destabilizing effect. This would appear to be a destabilizing effect due to the highly electronegative nature of the fluorine atoms (see later discussion on the effects of other highly electron-withdrawing groups).

2-Fluoroethyl Systems. There appears to be relatively little information on the effect of β-fluorine substitution on the stability or structure of a radical. The ESR hyperfine coupling constant of the 4-(trifluoromethyl)benzyl radical suggests essentially no delocalization of spin density from the radical center,[9a] while the trifluoromethyl group accelerates slightly the rate of the 2-aryl-3,3-dimethylmethylenecyclopropane thermal rearrangement.[6b] This effect has been discussed in terms of β-C–F bond hyperconjugation.[6b] The results of ESR studies indicate that the β-fluoroethyl radical prefers to exist in a conformation in which the β-C–F bond and the SOMO are eclipsed.[33] Theoretical calculations have been carried out on the β-fluoroethyl radical at the 3-21G and 6-31G basis set levels.[34]

The present calculations have been carried out on the 2-mono-, 2,2-di-, and 2,2,2-trifluoroethyl radicals **1–3**. Full



geometry optimization UHF 4-31G calculations have been carried out on the C–F (**1a** and **2a**) and C–H (**1b** and **2b**) antiperiplanar conformations of **1** and **2**. The total and SOMO energies of **1–3** and of the corresponding fluoroethanes are given in Table I, and the calculated structural parameters are given in Table 4 of the supplementary material. In both **1** and **2** there is a very slight preference (0.09 and 0.16 kcal/mol, respectively) for the conformations having the C–F bond antiperiplanar to the radical center, with the radial centers being slightly pyramidalized as in the ethyl radical.[35]

The calculated RSE's for the mono-, di-, and trifluoromethyl substituents are +1.46, +0.16, and −1.34 kcal/mol. The monofluoromethyl group as a whole is radical stabilizing relative to the hydrogen atom, but it is less radical stabilizing than the methyl group (+3.17 kcal/mol). Again, increasing fluorine substitution at the β-position results in decreasing stabilization, with the trifluoromethyl group being predicted to be destabilizing. This would appear to be due primarily to a destabilizing inductive effect, which will also be evident with several other functional groups.

Chloromethyl Systems. Chlorine substitution accelerates the thermal decomposition of 4-substituted arylazo compounds[4,21] and the thermal rearrangement of the 4-substituted 2-aryl-3,3-dimethylmethylenecyclopropane.[6b] The accelerating effects of chlorine are greater than those observed for the methyl group. The ESR hyperfine coupling constant data also suggest that chlorine is more stabilizing than a methyl group.[9a] There appears to be no experimental data concerning the relative stabilities of the di- and trichloromethyl radicals. MNDO calculations have been carried out on CH_2Cl, $CHCl_2$, and CCl_3, which predict all to be planar species.[24] An INDO calculation on $CHCl_2$ also predicts a nearly planar structure.[36] Calculations on CH_2Cl, $CHCl_2$, and CCl_3 and the corresponding chloromethanes have been carried out at a variety of ab initio and semiempirical levels with the primary focus on structural features, differences in heats of formation, and relative bond dissociation energies.[26] Calculations on CH_2Cl at the 4-31G level with partial geometry optimization predicts a nonplanar structure.[20]

Initial calculations in our laboratories were carried out on the monochloromethyl–chloromethane system to assess the relative importance of the inclusion of d AO's on chlorine in the 4-31G basis set. It had been previously concluded that there is negligible participation of d-type

(32) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1965**, *43*, 2704.
(33) Chen, K. S.; Krusic, P. J.; Meakin, P.; Kochi, J. K. *J. Phys. Chem.* **1974**, *78*, 2014. Edge, D. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 6485. Kawamura, T.; Edge, D. J.; Kochi, J. K. *Ibid.* **1972**, *94*, 1752. Bowles, A. J.; Hudson, A.; Jackson, R. A. *Chem. Phys. Lett.* **1970**, *5*, 552.
(34) Schlegel, H. B. *J. Phys. Chem.* **1982**, *86*, 4878.
(35) Lathan, W. A.; Hehre, W. J.; People, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 808.
(36) Biddles, I.; Hudson, A. *Mol. Phys.* **1973**, *25*, 707.

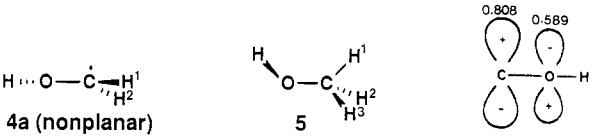
functions on sulfur with the radical center in CH_2SH.[37] Calculations at the 4-31G level gave a value of −0.49 for the RSE of the chlorine atom, suggesting that the chlorine is radical destabilizing. This result was obviously not consistent with experimental data. The inclusion of d AO's on chlorine gives a RSE of +2.57. Although calculations have been carried out at both the 4-31G and 4-31G + d's levels for comparison purposes, the results obtained with the 4-31G + d's basis set are considered to be more consistent with the available experimental data. Calculations have been carried out on CH_2Cl, $CHCl_2$, and CCl_3 and the corresponding methanes at the fully geometry optimized 4-31G and 4-31G + d's level, and also on the enforced planar radical species. The calculated total and SOMO energies for the chloro-substituted radicals and methanes are given in Table I. The calculated geometrical parameters are given in Table 5 of the supplementary material.

The nonplanar structures of the radical species are predicted to be lower in energy, with the extent of nonplanarity increasing with increasing chlorine substitution (the angles of the bisectors being 15.83°, 29.10°, and 31.00°, respectively). The extent of nonplanarity is less than that calculated for the fluoromethyl radicals. The barriers for inversion are also much smaller, being 0.04, 0.85, 2.27 kcal/mol, respectively.

In contrast to the fluoromethyl system, increasing chlorine substitution results in increasing stabilization, the RSE being +2.67 kcal/mol for $CHCl_2$, +6.98 for $CHCl_2$, and +9.64 for CCl_3.

Hydroxy-, Dihydroxy-, Methoxy-, and (Formyloxy)methyl Systems. The presence of a 4-methoxy substituent significantly increases the rates of pyrolysis of arylazoalkanes[4,21] and the thermal rearrangement of the 2-aryl-3,3-dimethylmethylenecyclopropane.[6b] ESR data indicate that the methoxy group is considerably more radical stabilizing than the methyl group.[9a] Stabilization energies of 8 and 11 kcal/mol for the hydroxymethyl[38] and methoxymethyl radicals[39] have been estimated on the basis of measurements of the bond dissociation energies in methanol and dimethyl ether. The rate increase in the pyrolysis of (arylazo)alkanes induced by an acetoxyl group is less than that induced by the methoxyl group.[4] Stabilization energies have been calculated for the hydroxy substituent in cyclopropyl and isopropyl radicals, the values being roughly double those calculated for the methyl group.[15] STO-3G[25] and 4-31G[20,25] calculations have been carried out with partial geometry optimization, and ab initio and semiempirical calculations have been carried out on methanol and dihydroxymethane.[26] Calculations on the dihydroxy-, methoxy-, and (formyloxy)methyl (as a model for the acetoxymethyl radical) systems have not been reported.

The fully geometry optimized structural parameters for the hydroxymethyl radical **4** and methanol are given in Table 6 of the supplementary material.[40] The total and SOMO energies are given in Table I. In **4** the radical center is highly pyramidalized, with the singly occupied orbital on carbon being roughly alligned with the predominantly 2p nonbonded AO on oxygen. This conformation has been inferred to be the most stable on the basis of the relative rates of hydrogen atom abstraction reactions with cyclic ethers.[41] The optimized planar structure lies 25.7 kcal/mol higher in energy. The SOMO wave function is shown below and has its major contribution from the carbon AO. The RSE of the hydroxyl group is calculated



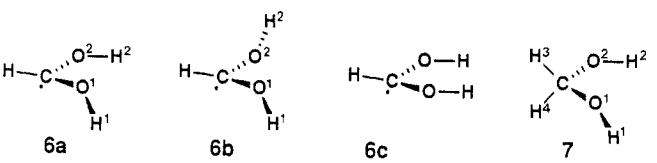
4a (nonplanar)
4b (planar)

5

to be +5.73 kcal/mol, considerably larger than that of the methyl group of +3.17 kcal/mol but much smaller than the value deduced from bond dissociation data.[38]

Calculations have also been carried out on the dihydroxymethyl radical system. It was of interest to see if increased oxygen substitution decreases the RSE of the system as was observed with fluorine substitution or if it increases the RSE as observed for chlorine substitution. The results of a study of the stereoelectronic effects on the rates of hydrogen atom abstraction from conformationally constrained cyclic ethers, acetals, ketals, and ortho esters have shown that the rates of abstraction are greatest when the C–H bonds adjacent to an oxygen atom have a small dihedral angle (ca. 30°) with respect to the p-type nonbonded pair orbital on oxygen.[24b] When two oxygen atoms are appropriately positioned the rate of hydrogen atom abstraction is 5–20 times that observed when only one oxygen atom is present.[41] However, when the dihedral angle is ca. 90°, the presence of two oxygen atoms result in reduced reactivity.

There are three conformations of the dihydroxymethyl radical that allow for excellent overlap of the p-type nonbonded pairs on oxygen with the singly occupied MO on the carbon atom. These are shown in structures **6a–c**.



6a 6b 6c 7

Of these structures **6a** and **6b** represent energy minima. (Total and SOMO energies are given in Table I, and the calculated structural parameters are given in Table 7 of the supplementary material). **6c** does not represent a minimum energy structure, apparently due to repulsion between the two O–H bonds. **6a** is calculated to be the lowest energy conformation. In **6b** the conformation about the $C–O^1$ bond allows for excellent overlap of the p-type nonbonded orbital with the radical center. The nonbonded pair orbital on O^2, however, is not well aligned for overlap with the radical center. The HCO^2H^2 dihedral angle is forced to be too large for excellent overlap in order to relieve the C–H—O–H bond eclipsing interaction.

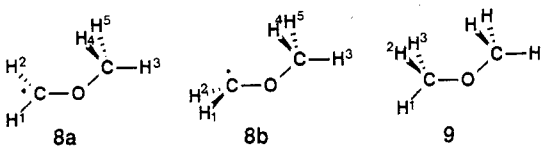
Several conformations were explored for dihydroxymethane. The lowest energy conformation detected is that shown in **7**, which resembles the lowest energy conformation of the dihydroxymethyl radical **6a**. Again, the conformation of **7** resembling that shown in **6c** appeared to be highest in energy.

The RSE for **6a**, relative to the conformation of dihydroxymethane shown in **7**, is calculated to be +4.70 kcal/mol, *less* than that of +5.73 calculated for the hydroxymethyl radical. These results are basically consistent with experimental observations. The conformation of dihydroxymethane and the radical required for enhanced

(37) Bernardi, F.; Csizmadia, I. G.; Schlegel, H. B.; Tieco, M.; Whangbo, M.-H.; Wolfe, S. *Gazz. Chim. Ital.* **1974**, *104*, 1101.
(38) Cruickshank, F. R.; Benson, S. W. *J. Phys. Chem.* **1969**, *73*, 733.
(39) Cruickshank, F. R.; Benson, S. W. *Int. J. Chem. Kinet.* **1969**, *1*, 381.
(40) The calculated structural parameters for **4** differ somewhat from those published earlier (ref 20).
(41) (a) Malatesta, V.; Scaiano, J. C. *J. Org. Chem.* **1982**, *47*, 1455. (b) Maletesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 609.

stabilization by two oxygen atoms is that shown in **6c**, the "enhanced stabilization" in the radical arising from a higher ground-state energy of the dihydroxymethane due to electron repulsion and eclipsing between the O–H bonds (or the O–C bonds in a constrained cyclic system).[41b]

The report that the stabilization energy of the methoxymethyl radical is larger than that of the hydroxymethyl radical[39] led us to carry out calculations on the methoxymethyl radical system. The lowest energy conformations of 8 and dimethyl ether (**9**) are shown below. The total

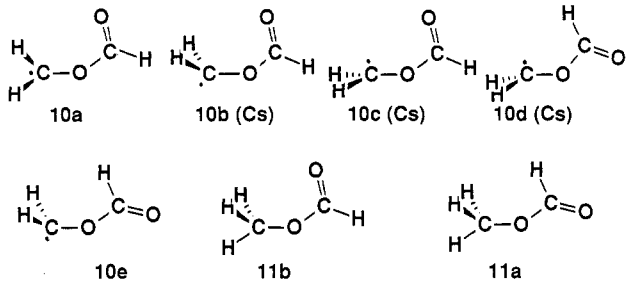


8a **8b** **9**

and SOMO energies are given in Table I, and the calculated structural parameters are given in Table 8 of the supplementary material. Of the two conformations of 8, **8a** is lower in energy than **8b** by 2.84 kcal/mol. In **8a** the singly occupied orbital mixes with a lower lying nonbonded pair hybrid orbital on oxygen (−17.98 eV in **8a**), while in **8b** the singly occupied orbital mixes with a higher lying nonbonded pair ($p_y + p_z$) hybrid orbital (−16.89 eV in **8b**), resulting in a significantly higher lying SOMO (see Table I). The radical center in **8a** is significantly more pyramidalized (α = 28.05°) than in **8b** (α = 21.65°).

The value of the RSE based on **8a** is +5.39 kcal/mol, which is smaller than that calculated for the hydroxymethyl radical. Substitution of the hydrogen by methyl reduces the value of the RSE. This would suggest that the hydrogen atom abstraction reactions do not involve the lowest energy conformations of both the hydrocarbon and radical.

The acetoxy group appears to be slightly less radical stabilizing than is the methoxy group.[4,9a] As a model for the acetoxymethyl radical, calculations have been carried out on the (formyloxy)methyl radical (**10**) and methyl formate (**11**). An extensive search of the potential energy surface of **10** indicated the presence of, at least, four minimum energy structures **10a–d**. Conformation **10e**



10a **10b (Cs)** **10c (Cs)** **10d (Cs)**

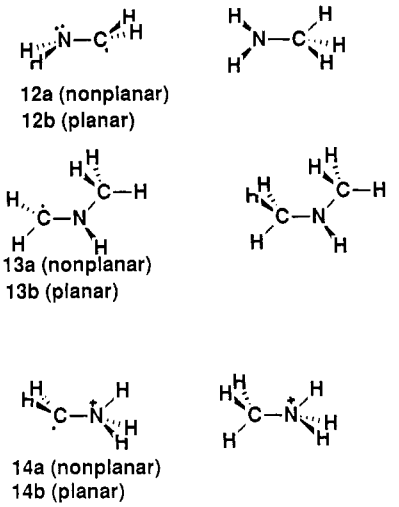
10e **11b** **11a**

does not appear to represent a minimum energy structure. Of the minimum energy structures **10a** is lowest in energy folllowed by **10b**, **10c**, and **10d**. Of the two possible conformations of methyl formate, **11a** is calculated to be significantly lower in energy than **11b** (7.47 kcal/mol). The total and SOMO energies are given in Table I, and the calculated geometrical parameters are given in Table 9 of the supplementary material.

The RSE based on the energy of **10a** is +2.38 kcal/mol, less than that of the methoxy group and consistent with the experimental data. Again, a substantial conformational effect on the value of the RSE is noted.

Amino-, (Methylamino)-, and Ammoniomethyl System. Hydrogen atom abstraction reactions are greatly accelerated when the C–H bond is α to an amino group, particularly when the C–H bond is eclipsed with the nonbonded pair of electrons on the nitrogen atom.[42] Several attempts have been made to estimate RSE's for the amino-, (methylamino)-, and (dimethylamino)methyl radicals using kinetic and thermochemical data. RSE's of 9[10] and 10[11] kcal/mol have been derived from the aminomethyl radical. Methyl substitution on nitrogen is reported to substantially increase the RSE's, the RSE of the (methylamino)methyl radical being reported as 17 kcal/mol[11] and that for the (dimethylamino)methyl radical 19[43] and 20[11] kcal/mol. Theoretical calculations on the aminomethyl radical have been carried out at the 4-31G level with full geometry optimization.[44] These calculations indicated a value for the RSE of the amino group of 10.2 kcal/mol.[44] Theoretical calculations on amino-substituted isopropyl and cyclopropyl radical systems give RSE's of 9.3 and 6.7, respectively.[15]

In the present study calculations have been carried out on the nonplanar and planar aminomethyl (**12**), (methylamino)methyl (**13**), and ammoniomethyl (**14**) radicals and the corresponding substituted methanes. The total and SOMO energies are given in Table I, and the calculated structural parameters are given in Tables 10–12 of the supplementary material. In **12** and **13** the singly occupied orbital on carbon prefers to be antiperiplanar to the nonbonded pair of electrons on nitrogen. The lowest energy structures have nonplanar radical centers; however, the barriers to inversion via the planar forms are very low, being 0.56 kcal/mol for **12**, 0.69 for **13**, and 0.10 for **14**. The RSE calculated for the aminomethyl radical **12** is +10.3 kcal/mol, in good correspondence with the previously calculated value of 10.2[44] and the experimentally derived values of 9 and 10 kcal/mol.[10,11] The replacement of a hydrogen on nitrogen by a methyl group results in a decrease in the RSE to a value of +9.69 kcal/mol. This result is similar with that observed with the hydroxy- and methoxymethyl radicals in that replacement of hydrogen on nitrogen by methyl results in a decrease in the RSE.



12a (nonplanar) **12b (planar)**

13a (nonplanar) **13b (planar)**

14a (nonplanar) **14b (planar)**

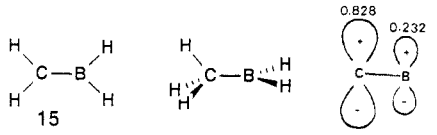
Protonation of the amino group to form **14** results in a large decrease in the value of the RSE to −4.07 (destabilizing) kcal/mol. The ammonio group, as a model for a trialkylamino function, is the most radical-destabilizing function encountered in this study. This must be due to the very powerful electron-withdrawing (electronegative) effect of the protonated nitrogen. Protonation of the ni-

(42) Griller, D.; Howard, J. A.; Marriott, P. R.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 619.
(43) Richey, H. G., Jr.; Shull, D. W. *Tetrahedron Lett.* **1976**, 575.
(44) Crans, D.; Clark, T. and Schleyer, P. v. R. *Tetrahedron Lett.* **1980**, *21*, 3681. Structural parameters were not reported.

trogen nonbonded pair of electrons also results in a substantial lowering in the energy of the SOMO.

Borylmethyl System. Alkylboranes,[45] borinates[46] and boronates[47] undergo facile free radical bromination reactions α to the boron atom, indicating that boron-containing functions stabilize radical centers. In contrast to the other radical species discussed in this paper that involve "three-electron" stabilization of a radical center by interaction of the radical center with a nonbonding or bonding pair of electrons, the stabilization by a boron function involves a "one-electron" stabilization arising from the interaction of the singly occupied orbital with the vacant 2p AO on the boron atom. The reative reactivities toward free radical bromination decrease in the order boranes > borinates > boronates.[45-47] This is as might be expected in that increasing donation of a nonbonded pair of electrons on oxygen to the vacant orbital on boron will decrease its ability to interact with a neighboring radical center. In addition, the introduction of oxygen atoms on the boron will increase the electronegativity of the group, which also results in decreased radical stabilization (vide infra). Theoretical calculations have been carried out at the 4-31G level on the borylmethyl radical, resulting in a calculated value for the RSE of 10.9 kcal/mol.[44]

In the present study calculations have been repeated on the borylmethyl radical (**15**) and methylborane as models



15

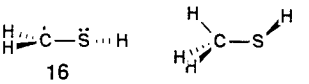
for the more highly substituted systems. The total and SOMO energies are given in Table I, and the calculated structural parameters are given in Table 13 of the supplementary material.

The borylmethyl radical is predicted to be a completely coplanar species. The SOMO of **15** is a π-bonding type of MO with the greatest contribution being from the carbon 2p AO. The RSE calculated for the borylmethyl radical is +11.0 kcal/mol, the largest calculated in this study.

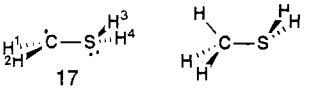
Mercapto-, S-Protonated Mercapto-, Sulfinyl-, and Sulfonylmethyl Systems. The methylthio (CH_3S) group greatly accelerates the rate of pyrolysis of 2-substituted azopropanes (factor of $\sim 2 \times 10^3$ relative to the methoxy group).[47] The methylthio group also accelerates the rate of the thermal rearrangement of the 2-aryl-3,3-dimethylmethylenecyclopropane system.[6b] ESR hyperfine coupling constant data also indicate that the methylthio group is more radical stabilizing than is the methoxy group.[9b]

Two theoretical studies have been carried out on the thiomethyl radical (**16**). The initial calculations were carried out by using a double ζ quality basis set which included two linearly independent d functions on sulfur.[37] Complete geometry optimization was not carried out. The results of the calculations indicated that the radical center was planar and implied that 3 d orbital conjugative effects were not significant. Subsequent calculations on CH_2SH carried out at the 4-31G level without inclusion of d AO's on sulfur, with limited geometry optimization, indicated the radical center to be nonplanar, but with an inversion barrier of only 0.08 kcal/mol.[20] The apparent greater radical stabilizing effect of sulfur vs. oxygen was attributed to a smaller energy gap between the sulfur nonbonded orbital and the singly occupied orbital on carbon than between oxygen and carbon.[20] In this analysis the energy level of the sulfur nonbonded pair level was considered to reside *below* the energy level of the SOMO of the radical center. In such a situation the dominant contribution to the SOMO would be the carbon 2p AO, i.e., the highest spin density would be on carbon. In the course of this study it became apparent that these arguments were quantitatively incorrect. The sulfur nonbonded pair level resides *above* the SOMO level of the methyl radical and, thus, the SOMO of the mercaptomethyl radical is dominated by the contribution of the 3p AO on sulfur, i.e., most of the spin denstiy resides on the sulfur atom.[48] The implications of this have been pointed out in a recent communication from our laboratories.[48]

In the present study we have carried out full geometry optimization calculations at the 4-31G and 4-31G + d's on sulfur level for the mercaptomethyl radical **16** and methanethiol. The total and SOMO energies are given in Table



16



17

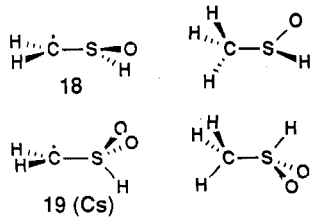
I, and the calculated structural parameters are given in Table 15 of the supplementary material. Calculations were also carried out on the planar radical species; however, the differences in the energies between the nonplanar and planar radical species **16** were less than a few tens of calories per mole, and further calculations on the planar species were not carried out in this series.

The isodesmic RSE calculated for **16** at the 4-31G level is +2.39 kcal/mol. This value is far too small, indicating that, as in the case of the chlorine, the inclusion of d AO's in the basis set is necessary to provide a reasonable correspondence with experimental observations. The RSE calculated at the 4-31G + d's level is 5.66 kcal/mol, a value comparable with that for the methoxyl group.

Calculations have been carried out at the 4-31G + d's on sulfur level on the S-protonated mercaptomethyl radical (**17**) system as a model for an alkylsulfonium-substituted radical. The total and SOMO energies are given in Table I, and the calculated structural parameters are given in Table 15 of the supplementary material. The RSE calculated for the sulfonio group is -3.17 kcal/mol, strongly destabilizing. This destabilization is despite the fact that the singly occupied MO on carbon and the 3p-type nonbonded pair orbital on sulfur are perfectly alligned for overlap and interaction of the orbitals. This destabilization must be due to an electronegative inductive effect due to the formal positive charge on sulfur similar to that observed with the ammoniomethyl radical, and the poor overlap between the 3p AO on sulfur and the 2p AO on carbon.

ESR hyperfine coupling data indicate that the ability to stabilize a radical center by a sulfur substituent decreases on oxidation to the sulfinyl and sulfonyl states.[9b] Calculations have been carried out at the 4-31G + d's on sulfur level on the sulfinyl (**18**) and sulfonyl (**19**) methyl radicals and the corresponding sulfoxide and sulfone, giving local minima for the conformations shown. Attempts were made to locate other possible local minima

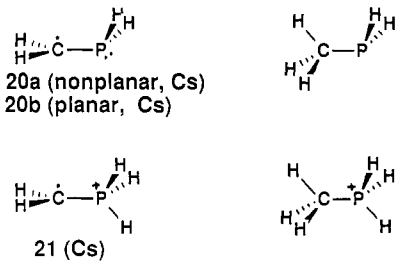
(45) Lane, C. F.; Brown, H. C. *J. Am. Chem. Soc.* **1970**, *92*, 7212.
(46) Pasto, D. J.; McReynolds, K. *Tetrahedron Lett.* **1971**, 801.
(47) Timberlake, J. W.; Garner, A. W.; Hodges, M. L. *Tetrahedron Lett.* **1973**, 309.
(48) Pasto, D. J. *Tetrahedron Lett.* **1986**, *27*, 2941.



for **18** and **19**, but none were found. The total and SOMO energies are given in Table I, and the calculated structural parameters are given in Tables 16 and 17 of the supplementary material. The radical centers in **18** and **19** are nearly planar, the angles of the bisectors being 2.90 and 5.61°, respectively. The energies of the planar radical structures are virtually the same as for the nonplanar structures. The singly occupied orbital on the carbon atom in **18** is perfectly alligned for interaction with the S–O π system, the SOMO being an allyl antibonding type MO. In **19** the singly occupied orbital on carbon bisects the SO_2 group.

The RSE's for **18** and **19** are +1.12 and –0.82 kcal/mol; the sulfinyl group is slightly stabilizing, while the sulfonyl group is slightly destabilizing.

Phosphino- and Phosphoniomethyl Systems. Calculations have been carried out at the 4-31G + d's on phosphorus level on the fully optimized (nonplanar) and planar phosphino- (**20**) and phosphonio- (**21**) methyl rad-



icals and the corresponding methanes. The total and SOMO energies are given in Table I, and the calculated structural parameters are given in Tables 18 and 19 of the supplementary material. The radical center in **20** is distinctly pyramidalized (angle of the HHCP bisector of 12.11°), with the singly occupied orbital on carbon oriented antiperiplanar to the phosphorus nonbonded pair similar to that observed with the aminomethyl radical. The nonplanar and planar forms of **20** differ slightly in energy (0.20 kcal/mol). The radical center in **21** is nearly planar (α of 2.31°), and there is essentially no difference in energy between the nonplanar and planar forms.

The RSE calculated for the phosphinomethyl radical is +4.31/kcal/mol. This is an unexpectedly small value. In the first-row atoms the RSE's increase significantly on going from fluoro- to the hydroxy- to the aminomethyl radical. There is also an increase in the RSE's on going from the chloro- to the mercaptomethyl radical. The RSE of **24**, however, is significantly less than that of the mercaptomethyl radical of +5.66 kcal/mol, indicating that the phosphino group is less capable of stabilizing a radical center than is the mercapto group. This would appear to be due to the geometry about the phosphorus atom which produces a hybrid nonbonded orbital on phosphorus which contains extensive 3s character, and hence much lower in energy. The CPH and HPH bond angles and the angles of the HHPC bisector are very similar in **20** and methylphosphine.

The phosphoniomethyl radical **21**, a model for an alkylphosphonium system, is calculated to have an RSE of –0.42 kcal/mol, slightly destabilizing.

π-Group Stabilized Radicals

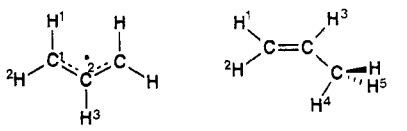
Allyl System. Several experimental and theoretical studies have been carried out on the allyl radical in an attempt to determine its resonance energy. Values of 10.2 ± 1.4 and 11.4 ± 1.5 kcal/mol have been estimated from gas-phase kinetic data on the reactions of propene with iodine[49] and hydrogen iodide.[50] A value of 14.0–14.5 kcal/mol has been estimated from kinetic data on the isomerization of the 1-deuterioallyl radical.[51] A thermodynamic value of 9.6 ± 2–3 kcal/mol was originally estimated from gas-phase equilibrium data for the dissociation–recombination reaction between 1,5-hexadiene and the allyl radical.[52] The value of 9.6 kcal/mol was later reevaluated upward to a value of 11.7 ± 2.0 kcal/mol based on a C–H bond dissociation energy of a methyl C–H bond in propane of 98.0 kcal/mol.[14] The results of several theoretical studies on the allyl radical have appeared, the most extensive being carried out with the GVB method with full CI giving a value for the resonance energy of 11.4 kcal/mol.[53]

In the present study calculations carried out at UHF 4-31G level gave a value of +22.14 for the RSE of the allyl radical, a value that appeared to be unrealistically high. The "extra stability" of the allyl radical arises from extensive contributions of higher multiplicity wave functions to the UHF wave function as indicatd by the value of $\langle S \rangle^2$ of 1.107 (for a pure doublet state $\langle S \rangle^2$ is 0.75). Contamination by higher spin states artifically lowers the energy of the ground doublet state and, thus, increases its apparent RSE. In order to avoid this complication, calculations on the π-group containing radicals have been carried out with complete geometry optimization at the ROHF 4-31G level which produces pure doublet-state wave functions. The total and SOMO energies are given in Table I, and the calculated structural parameters are given in Table 20 of the supplementary material.

The value of the RSE for the vinyl group based on ROHF energies for the allyl and methyl[54] radicals is +7.80 kcal/mol. It is interesting to note that the RSE for the vinyl group based on the isodesmic reaction

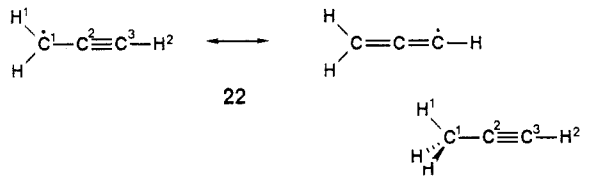
$$H_2C{=}CHCH_2\cdot + CH_3CH_2CH_3 \rightarrow H_2C{=}CHCH_3 + CH_3CH_2CH_2\cdot$$

is +3.01 kcal/mol. This difference reflects the effects on the energies of the C–H bond in propane and the radical center in the *n*-propyl radical arising from delocalizing orbital interactions present in propane and the propyl radical which are not present in methane and the methyl radical.



Propargyl System. The results of gas-phase kinetic studies have resulted in estimates for the resonance energy of the propargyl radical (**22**) of 4.1[55] and 9.6[56] kcal/mol.

(49) Golden, D. M.; Rodgers, A. S.; Benson, S. W. *J. Am. Chem. Soc.* **1966**, *88*, 3196.
(50) Rossi, M.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1230.
(51) Korth, H.-G.; Trill, H.; Sustmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4483.
(52) Golden, D. M.; Gac, N. A.; Benson, S. W. *J. Am. Chem. Soc.* **1969**, *91*, 2136.
(53) Levin, G.; Goddard, W. A., III, *J. Am. Chem. Soc.* **1975**, *97*, 1649.
(54) ROHF 4-31G geometry optimization calculations were also carried out on the methyl radical (planar), giving a total energy of –39.50179 au [the UHF 4-31G energy is –39.50497 au with a C–H bond length of 1.0691 Å (see ref 34)].



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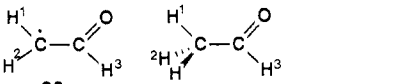
The present calculations on the proprargyl radical have been carried out at the ROHF 4-31G fully geometry optimized level. The total and SOMO energies are given in Table I, and the calculated structural parameters are given in Table 21 of the supplementary material. These calculations give a value of +8.00 kcal/mol for the RSE of the propargyl radical. This value is very close to that for the allyl radical. The SOMO wave function (c_1 = −0.890, c_2 = 0.067, c_3 = 0.343) indicates that the proprgyl structure is the most important resonance contributing structure, consistent with its radical chemistry.[57]

Carbonyl-Containing Systems. An analysis of the kinetic data for the hydrogen atom abstraction from acetone by a bromine atom suggests that the resonance stabilization energy of the acetylmethyl radical is ~0 kcal/mol.[58] Data derived from the pyrolytic C–C bond homolysis of substituted alkanes indicated resonance stabilization energies of 6.5 and 3.5 kcal/mol for the ketone and carbomethoxy groups.[59] ESR hyperfine coupling constant and electrochemical data suggest that the acetyl,[9a] carbomethoxy[8,16] and carboxamido[16] groups substantially stabilize a radical center.

Calculations have been carried out on **23–25** at the ROHF 4-31G level and the substituted methanes with full geometry optimization. Total and orbital energies are given in Table I, and the calculated structural parameters are given in Table 22 of the supplementary material. The calculations on the formyl (**23**), carboxy (**24**), and carboxamido (**25**) substituted methyl radicals result in RSE's of −7.66, −5.72, and −5.48 kcal/mol, respectively. The radical centers in **23–25** are all planar; however, there are



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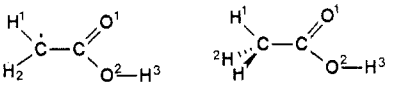

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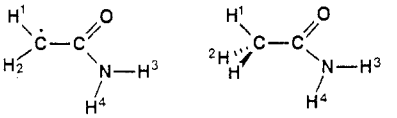

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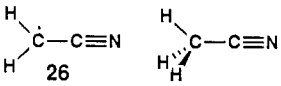
only relatively small changes in the C—C and C=O bond lengths between the radical species and the parent substituted methanes. In all three radicals the SOMO's are dominated by contributions of the 2p AO on carbon,[60] indicating that these are highly carbon-centered radicals.[61]

Cyanomethyl System. Several kinetic studies have provided estimates of the radical stabilization energy of the cyano group, including the thermal rearrangements of cyanocyclopropane (5.0 kcal/mol),[63] cyanocyclobutane (5.1),[64] 1,4-dicyanobicyclo[2.2.0]hexane (7.3),[65] 1,2-dicyanocyclobutane (8[66] and ~5[67]), and 1,2-dicyano-1-methylcyclopropane,[66] and the thermal fragmentation of methyl substituted acetonitriles (5.1–5.5).[68]

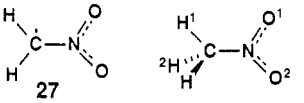
Calculations have been previously carried out on the cyanomethyl radical at the UHF 4-31G level with full geometry optimization giving a total energy of −131.11346 hartree, and a value for the RSE of the cyanomethyl radical of +12.5 kcal/mol.[44] Similar calculations in our laboratories at the UHF 4-31G level gave an identical energy; however, the wave function is highly contaminated by higher spin-state wave functions as indicated by the value of $\langle S \rangle^2$ of 1.036. Full geometry optimization calculations at the ROHF 4-31G level give a total energy of −131.09880 hartree, substantially less than that obtained by the UHF method, which, in turn, results in a value of +5.34 kcal/mol for the RSE. The radical center of **26** is



26

planar, and most of the SOMO is localized on the carbon atom.[69] The total and SOMO energies are given in Table I, and the calculated structural parameters are given in Table 23 of the supplementary material.

Nitromethyl System. There appears to be no reasonable estimate of the radical stabilizing ability of the nitro group. The nitro group stabilizes the 1-nitro-1-cyclopropylethyl radical toward ring opening,[70] and the 4-nitro group greatly accelerates the thermal rearrangement of the 2-aryl-3,3-dimethylmethylenecyclopropane.[71] A variety of ab initio calculations have been carried out on the nitromethyl radical and nitromethane, but not at the 4-31G level.[72] Our calculations indicate a value of +1.73 kcal/mol for the RSE of the nitro group, suggesting that the nitro group is less radical stabilizing than a methyl group. The radical center in **27** is planar, and the SOMO



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wave function indicates that most of the spin density is on the carbon atom.[73] The total and SOMO energies are given in Table I, and the calculated structural parameters

(55) Walsh, R. *Trans. Faraday Soc.* **1971**, *67*, 2085.
(56) Tsang, W. *Int. J. Chem. Kinet.* **1970**, *2*, 23.
(57) Fantazier, R. M.; Poutsma, M. L. *J. Am. Chem. Soc.* **1968**, *90*, 5490.
(58) King, K. D.; Golden, D. M.; Benson, S. W. *J. Am. Chem. Soc.* **1970**, *92*, 5541.
(59) Unpublished data cited in ref 7.
(60) The SOMO wave functions are for **23**, c_{c1} = 0.863, c_{c2} = 0.086, c_0 = −0.345; for **24**, c_{c1} = 0.879, c_{c2} = 0.093, c_0 = −0.275; and for **25**, c_{c1} = 0.893, c_{c2} = 0.065, c_0 = −0.244.
(61) An analysis of the extent of spin delocalization in 2-alkanoyl radicals by EPR has led to the conclusion that only ~15% of the spin density resides on oxygen (ref 61).
(62) Camaioni, D. M.; Walter, H. F.; Jordan, J. E.; Pratt, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 7978.
(63) Luckraft, D. A.; Robinson, P. J. *Int. J. Chem. Kinet.* **1973**, *5*, 137.
(64) Sarner, S. F.; Gale, D. M.; Hall, H. K., Jr.; Richmond, A. B. *J. Phys. Chem.* **1972**, *76*, 2817. King, K. D.; Goddard, R. D. *Int. J. Chem. Kinet.* **1973**, *7*, 109.
(65) Bellus, D.; Rist, G. *Helv. Chim. Acta* **1974**, *57*, 194.
(66) Doering, W. v. E.; Horowitz, G.; Sachdev, K. *Tetrahedron* **1977**, *33*, 273.
(67) King, K. D.; Goddard, R. D. *Int. J. Chem. Kinet.* **1978**, *10*, 453.
(68) King, K. D.; Goddard, R. D. *Int. J. Chem. Kinet.* **1975**, *7*, 837; *J. Am. Chem. Soc.* **1975**, *97*, 4504; *J. Phys. Chem.* **1976**, *80*, 546.
(69) The SOMO wave function of **26** has the coefficients c_{c1} = 0.894, c_{c2} = −0.041, and c_n = −0.182.
(70) Russell, G. A.; Dedolph, D. F. *J. Org. Chem.* **1985**, *50*, 2498.
(71) Private communication from Prof. X. Creary, Dept of Chemistry, University of Notre Dame.
(72) McKee, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1900.
(73) The SOMO wave function of **27** has the following coefficients: c_c = 0.891, c_n = −0.040, and c_0 = −0.229.
(74) Pecansky, J.; Dupuis, M. *J. Am. Chem. Soc.* **1982**, *104*, 415.
(75) Pecansky, J.; Dupuis, M. *J. Chem. Phys.* **1979**, *71*, 2095.
(76) Pecansky, J.; Dupuis, M. *J. Chem. Phys.* **1980**, *73*, 1867.
(77) Yoshimine, M.; Pacansky, J. *J. Chem. Phys.* **1981**, *74*, 5168.
(78) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

are given in Table 24 of the supplementary material.

Summary

In the present study gas-phase, thermodynamic radical stabilization energies (RSE's) have been calculated according to the isodesmic reaction shown in eq 2 in which the substituted methyl radical and methane exist in their lowest energy conformation. Several points must be stressed concerning these calculated RSE's.

(1) The calculated RSE's are not true resonance stabilization energies as defined by resonance theory; however, they should be qualitatively similar. The RSE's are differences between the abilities of the attached groups to stabilize, or destabilize, a radical center relative to the hydrogen atom as a substituent (which cannot stabilize, or destabilize, the radical center by delocalization).

(2) Quantitatively, the calculated RSE's will vary depending on the structure of the organic framework to which it is attached due to the C–H bond (in the alkane) and SOMO (in the radical) delocalization effects in the more complex molecules (as exemplified with the allyl radical–methane system vs. the allyl radical–propane system). Qualitatively, however, the calculated RSE's will reflect the relative abilities of the substituents to stabilize, or destabilize, a radical center in any system and, therefore, should be useful for radical reactivity correlation purposes.

(3) The results of the calculations indicate that there is not only a delocalization (stabilizing) effect but that there is also an electronegative inductive (destabilizing) effect on the RSE. Thus, as a highly electronegative substituent is removed from the radical center in a conjugated π system, the inductive destabilizing effect is expected to dramatically decrease, and the stabilizing delocalization effect, if any, will become more apparent.

(4) The calculations on systems that may exist in more than a single conformtation indicate that the RSE is highly conformationally dependent, not only in the radical but also in the saturated system. This will have significant effects on the relative reactivities in radical forming reactions when the relative energies of the conformations of the reactant do not parallel the relative energies of the conformations of the product radical.

The gas-phase, thermodynamic RSE's calculated for the various functional groups as defined in the isodesmic relationship in eq 2 are summarized in Table II. The RSE's of various alkyl-substituted methyl radicals have been calculated based on the 4-31G total energies of the substituted methyl radicals and methanes reported previously in the literature. Several important trends are to be noted.

(1) The RSE's increase significantly on going from F to O to N atom substituents. This is due to the fact that the energy levels of the nonbonded pair electrons on F, O, and N decrease in the sequence reducing the energy gap between the nonbonded pair MO's and that of the SOMO of the methyl radical, thus increasing the interaction energy and the stabilization of the system. A similar trend is observed on going from Cl to S, but P deviates from this trend.

(2) Multiple functionalization with F and O atom substituents does not result in additional stabilization, but in destabilization. This appears to be due to the required occupancy of the antibonding π-allyl-type MO and increased π-electron repulsion. This will be discussed in greater detail in a future article from the author's laboratories on the RSE's of disubstituted radical systems.

(3) Cation ($^+NR_3$, $^+SR_2$, and $^+RP_3$) and highly electronegative groups (CF_3, SOR, SO_2R) are radical destabilizing.

Plots of the calculated RSE's vs. previous radical stabilization scales and selected experimental data are shown in Figures 1–7. Figure 1 shows the plot of the log of the relative rates for the thermolysis of 2-substituted azopropanes in hydrocarbon solvents.[4] The correlation is very good (slope is 1.22, $r = 0.916$) over a very large rate range. Figure 2 shows the plot of the log of the relative rates of the thermal rearrangements of 2-aryl-3,3-dimethylmethylenecyclopropanes[6] vs. the RSE values. There is considerable scatter (slope is 4.43×10^{-2}, $r = 0.664$), but the rate range is quite limited. The point for the nitro group lies well above the correlation line, indicating a much greater stabilization by the nitro group than expected from its RSE value. This would appear to be due to reduced electronegative destabilization by the nitro group when in the 4-position of the aromtic ring compared to when it is directly attached to the radical center. The plot of the ESR-derived α_a's[9a] vs. the RSE's is shown in Figure 3 (slope is 7.5×10^{-3}, $r = 0.860$). Although there is some scattering of the points, there is a general correspondence between the two sets of data.

Figures 4–6 show plots of the electrochemically derived ΔAOP values[16] for 3-substituted fluorenide, 4-substituted phenylacetonitrile, and 9-substituted fluorenide systems. Excellent correlations are evident for the first two systems (slope is –0.251, $r = 0.994$; slope is –0.469, $r = 0.986$). For the 9-substituted fluorenide system the correlation is very poor (the slope of the line which is shown is 0.744, $r = 0.658$). The reason for the lack of a reasonable correlation may be steric in nature which prevents the 9-substituent from becoming coplanar with the radical center and thus reducing delocalization of the radical.

Finally, Figure 7 shows the plot of SE's calculated according to eq 1[13] vs. RSE values. There is little correlation between the two sets of calculated stabilization energies.

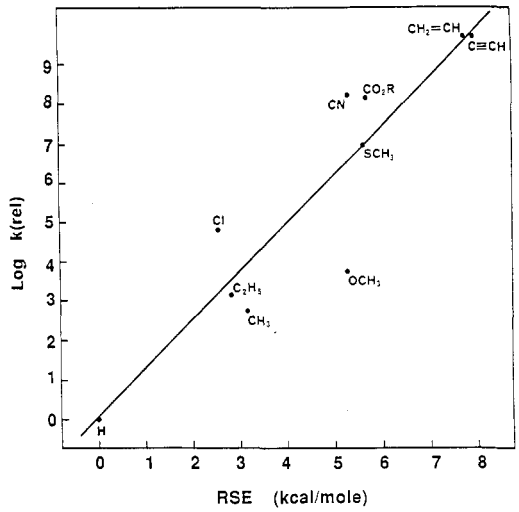

Figure 1. Plot of log of the relative rate constants for the thermolysis of 2-substituted azopropanes (ref 4) vs. RSE values.

Note Added in Proof. Concern has been expressed over the potential need to have included electron correlation corrections in the calculations on the species shown in eq 2. It was originally suggested that in isodesmic reactions involving bond separations (homolytic reactions) electron correlation would not be important due to the fact that there are no changes in the number and types of bonds between reactants and products.[78] Test calculations have been carried out at the MP2/4-31G level on the one-electron system **15**, the three-electron system **12**, and the allyl radical. The resulting RSE's for **15** and **12** are 11.54 and 12.56 kcal/mol, respectively, both slightly larger than the RSE given in Table II (5.2% and 22.4%, respectively). In both of these cases there are relatively small differences in bond lengths in the substituted radical and

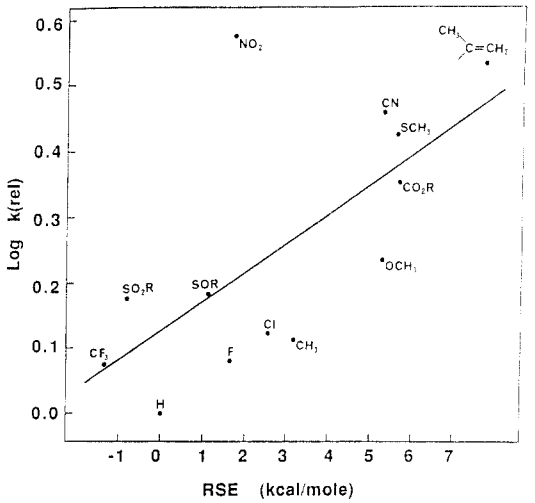

Figure 2. Plot of the log of the relative rate constants for the thermal rearrangement of 3-aryl-2,2-dimethylmethylenecyclopropanes (ref 6) vs. RSE values.

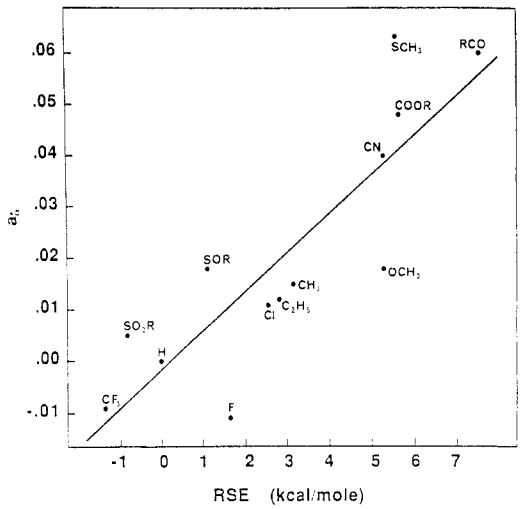

Figure 3. Plot of the ESR α_a values for 4-substituted benzyl radicals (ref 9) vs. RSE values.

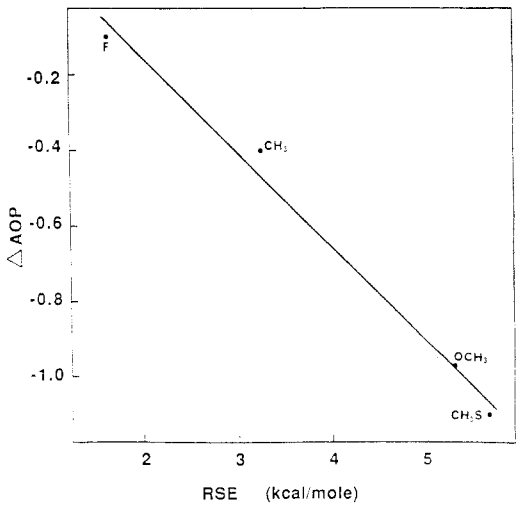

Figure 4. Plot of ΔAOP values derived from the 3-substituted fluorenide system (ref 16) vs. RSE values.

methane. This is the case with all of the substituted radicals except with the allyl radical in which there are substantial changes in the C–C bond distances. The RSE calculated for the allyl radical at the MP2/4-31G level is 11.60 kcal/mol. It thus appears that the calculational approach used to calculate the RSE's described in this article is reasonable as long as no large changes in geometry occur.

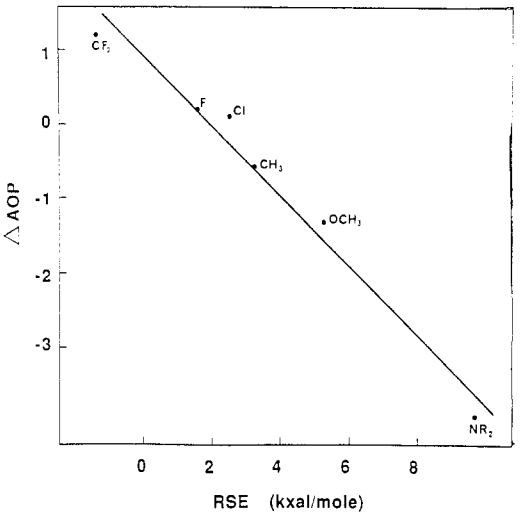

Figure 5. Plot of ΔAOP values derived from the 4-substituted phenylacetonitrile system (ref 16) vs. RSE values.

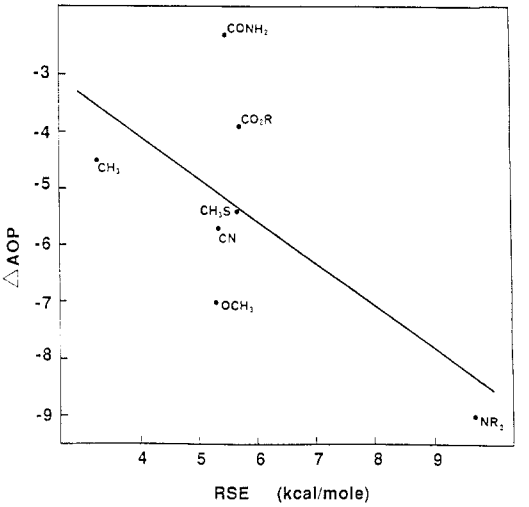

Figure 6. Plot of ΔAOP values derived from the 9-substituted fluorenide system (ref 16) vs. RSE values.

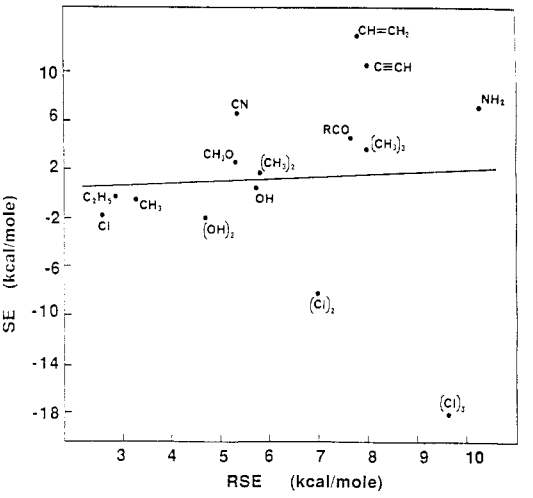

Figure 7. Plot of SE values (ref 13) vs. RSE values.

Supplementary Material Available: Tables of the calculated geometrical parameters for all substituted methyl radicals and methanes (28 pages). Ordering information is given on any current masthead page.