

Methyl and Silyl Halide Radical Anions: An *Ab initio* Study

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**Summary** *Ab initio* molecular orbital calculations suggest that, whereas  $\text{CH}_3\text{F}^{\cdot-}$  and  $\text{CH}_3\text{Cl}^{\cdot-}$  are loose  $C_{3v}$  complexes between the methyl radical and a halide ion,  $\text{SiH}_3\text{F}^{\cdot-}$  and  $\text{SiH}_3\text{Cl}^{\cdot-}$  are T-shaped complexes with one unique hydrogen atom.

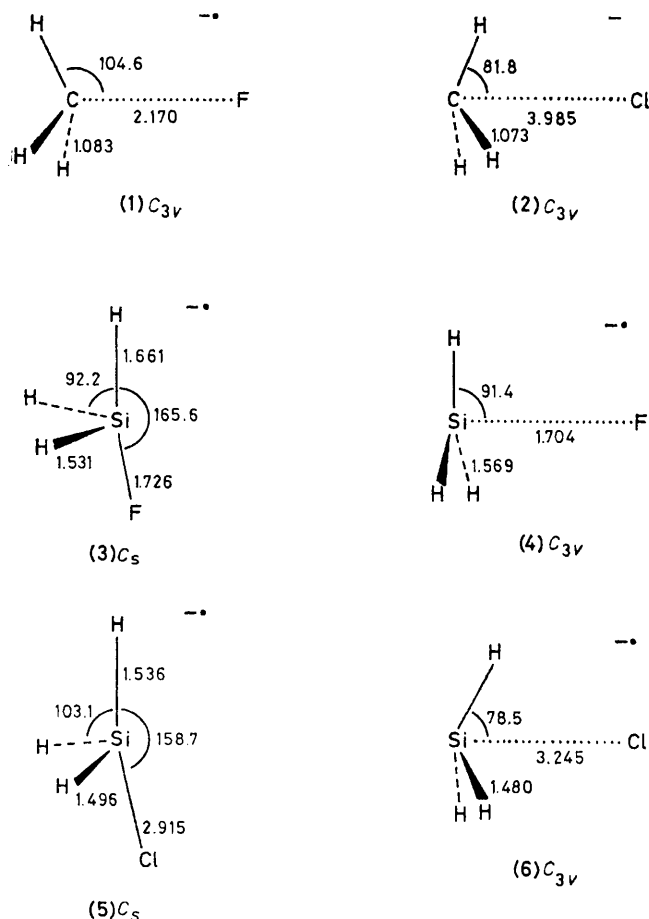
ONE-ELECTRON reduction of alkyl halides is an important means of carbon-halogen bond cleavage<sup>1</sup> and so the alkyl halide radical anions have received considerable experimental<sup>2</sup> attention. Recently, however, e.s.r. studies<sup>3</sup> on silyl halide radical anions have revealed that one hydrogen is unique, indicating a  $C_s$  'T-shaped,' structure. On the other hand, germyl halide radical anions appear to have a  $C_{3v}$  structure<sup>4</sup> as do the methyl halide anions.<sup>2</sup> We have used *ab initio* molecular orbital theory† to investigate the structures and energies of  $\text{CH}_3\text{F}^{\cdot-}$ ,  $\text{CH}_3\text{Cl}^{\cdot-}$ ,  $\text{SiH}_3\text{F}^{\cdot-}$ , and  $\text{SiH}_3\text{Cl}^{\cdot-}$ .

Geometry optimisation at the 3-21G<sup>5</sup> (33-21G for silicon and chlorine)<sup>6</sup> basis set level revealed only one,  $C_{3v}$ , minimum each for  $\text{CH}_3\text{F}^{\cdot-}$  and  $\text{CH}_3\text{Cl}^{\cdot-}$  [(1) and (2), respectively]. At the UHF/3-21G level  $\text{CH}_3\text{F}^{\cdot-}$  is bound by 10.2 kcal mol<sup>-1</sup> relative to  $\text{CH}_3^{\cdot} + \text{F}^-$ , and  $\text{CH}_3\text{Cl}^{\cdot-}$  lies 0.4 kcal mol<sup>-1</sup>‡ higher in energy than separated  $\text{CH}_3^{\cdot}$  and  $\text{Cl}^-$ . These results are in accord with the detailed experimental studies on alkyl halide radical anions.<sup>2</sup>

$\text{SiH}_3\text{F}^{\cdot-}$ , however, gave a  $C_s$  structure, (3), on optimisation. A second structure, (4), obtained by optimisation within  $C_{3v}$  symmetry, is 9.7 kcal mol<sup>-1</sup> less stable than (3) at UHF/3-21G. Similarly,  $C_s$   $\text{SiH}_3\text{Cl}^{\cdot-}$ , (5), is calculated to be 5.7 kcal mol<sup>-1</sup> more stable than the  $C_{3v}$  structure, (6).  $\text{SiH}_3\text{F}^{\cdot-}$  is found to be strongly bound, lying 86.3 kcal mol<sup>-1</sup> lower in energy than  $\text{SiH}_3^{\cdot} + \text{F}^-$ , and 38.1 kcal mol<sup>-1</sup> lower than  $\text{SiH}_3^- + \text{F}^{\cdot}$ . The dissociation of  $\text{SiH}_3\text{Cl}^{\cdot-}$  to  $\text{SiH}_3^{\cdot} + \text{Cl}^-$  is calculated to be endothermic by 11.3 kcal mol<sup>-1</sup>, and the alternative dissociation, to  $\text{SiH}_3^- + \text{Cl}^{\cdot}$ , requires 57.2 kcal mol<sup>-1</sup>. These dissociation energies must be considered approximate as the 3-21G basis set is not large enough to handle anions adequately,<sup>7</sup> and because of the RHF/UHF size consistency problem inherent in calculating association energies between open and closed shell species.

Nevertheless,  $\text{SiH}_3\text{F}^{\cdot-}$  appears to be a strongly bound species, the bond energy being comparable with that in  $\text{R}_2\text{SSR}_2^{\cdot+}$  radical cations,<sup>8</sup> some of which are stable for days in solution.<sup>9</sup>

The preference of  $\text{SiH}_3\text{F}^{\cdot-}$  and  $\text{SiH}_3\text{Cl}^{\cdot-}$  for the  $C_s$  structures, (3) and (5), is an interesting example of radical reactivity in which the SOMO is not involved. Consider



All distances are given in Angstroms, all angles in degrees.

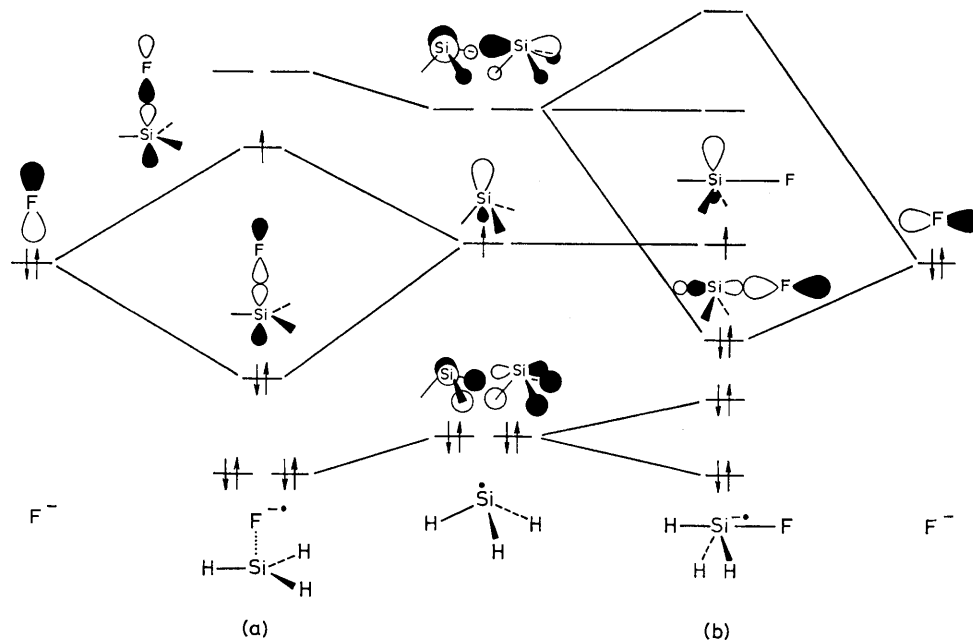
the interaction of  $\text{SiH}_3^{\cdot}$  with  $\text{F}^-$ . There are two possible contending orbitals which can lead to a stabilising interaction with the nucleophile, the radical SOMO and the degenerate  $\sigma_{\text{SiH}}^*$  LUMO's (see the Figure). The three-electron interaction between the nucleophile and the radical SOMO may or may not be stabilising, depending on the relative energy levels and on the overlap.<sup>10</sup> In this case, however, the back-side overlap with a  $\sigma_{\text{SiH}}^*$  orbital is particularly favourable because the unoccupied MO's are polarised strongly towards the electropositive silicon. The result is the formation of an  $S_N2$ -type complex, (3) or (5),

† All calculations employed the Gaussian 76 series of programs. (J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. D. Newton, 'Quantum Chemistry Program Exchange' Program No. 368, Indiana University, 1978). Geometry optimisations used analytically evaluated atomic forces (H. B. Schlegel, S. Wolfe, and F. Bernardi, *J. Chem. Phys.*, 1975, **63**, 3632) in a Davidson-Fletcher-Powell multiparameter search routine (W. C. Davidson, *Comput. J.*, 1968, **10**, 406; R. Fletcher and M. J. D. Powell, *ibid.*, 1963, **6**, 163; D. Poppinger, *Chem. Phys. Lett.*, 1975, **34**, 332). The UHF/3-21G wave functions for (1)–(6) show essentially no spin contamination. Optimised UHF/3-21G total energies (a.u.) are: -138.13093, -496.69590, -387.99024, -387.97482, -746.45219, and -746.44308, for (1) to (6), respectively.

‡ 1 kcal mol<sup>-1</sup> = 4.184 kJ mol<sup>-1</sup>.

rather than a three-electron bonded complex, (2) or (6).  $S_N2$  reactions on silicon have recently been treated theoretically.<sup>11</sup> The Figure (a) shows the orbital interactions leading to a  $C_{3v}$ , three-electron bonded, complex and (b) shows the corresponding diagram for the  $C_s$  species. The UHF/3-21G spin densities show that the spin is concentrated

Sn group alternate,<sup>12</sup> silicon and tin (1.74 and 1.72, respectively) being more electropositive than carbon and germanium (2.50 and 2.02). As the stability of the  $C_s$  structures depends on the back-side overlap, which is strongest for electropositive central atoms, it appears likely that  $SnH_3X^{\cdot-}$  radical anions will resemble their silicon



FIGURE

on silicon, the halogen, and the unique hydrogen in (3) and (5), as observed experimentally.<sup>3</sup> The  $\sigma_{SiH}^*$  orbitals also function as  $\pi$ -acceptors in (3), giving a short SiF bond and long SiH bonds. The SiF bond in (3) is actually shorter than the CF bond in (1). A comparison of the SiH bond lengths in (4) and (6) shows the importance of this type of interaction in  $SiH_3F^{\cdot-}$ .

The simple orbital interaction diagrams shown in the Figure allow a prediction as to the structure of  $SnH_3X^{\cdot-}$  radical anions. The electronegativities of the C, Si, Ge, and

counterparts, rather than the carbon and germanium analogues.

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<sup>5</sup> J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939.

<sup>6</sup> W. J. Hehre, J. S. Binkley, J. A. Pople, and M. S. Gordon, unpublished work.

<sup>7</sup> J. Chandrasekhar, J. G. Andrade, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1981, **103**, in the press.

<sup>8</sup> T. Clark, *J. Comput. Chem.*, 1981, **2**, in the press.

<sup>9</sup> See W. K. Muster, *Acc. Chem. Res.*, 1980, **13**, 200, and references therein.

<sup>10</sup> N. C. Baird, *J. Chem. Ed.*, 1977, **54**, 291.

<sup>11</sup> N. T. Anh and C. Minot, *J. Am. Chem. Soc.*, 1980, **102**, 103.

<sup>12</sup> See: F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd Edition, Wiley-Interscience, New York, 1972, p. 115.