

$$\psi_{e_g} = \begin{vmatrix} \beta d_{zz} - (\beta'/\sqrt{2})(\rho_z^{(1)} - \rho_z^{(3)}) \\ \beta d_{yz} - (\beta'/\sqrt{2})(\rho_z^{(2)} - \rho_z^{(4)}) \end{vmatrix}$$

where

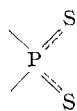
$$\sigma^{(i)} = n p^{(i)} + (1 - n^2)^{1/2} S^{(i)}$$

$$\alpha^2 - 2\alpha\alpha'S + \alpha'^2 = 1$$

We do not take into account the molecular orbital including the d_{z^2} atomic orbital of the copper(II) ion as it is influenced only by the solvent.

The metal-ligand bond parameters are calculated according to Kivelson and Neiman's⁸ method with the use of the parameters in eq 2 and the optical spectral data. The coefficients of the molecular orbitals are $\alpha^2 = 0.56$, $\beta_1^2 = 0.53$, and $\beta^2 = 0.70$; *i.e.*, the σ and π metal-ligand bonds in the xy plane, characterized with α^2 and β_1^2 , respectively, are strongly covalent, while the π bonds in the xy and yz plane (β^2) have less covalent character.

It follows from our studies that both in solution and in a vitreous state the alkyl radical does not exert appreciable influence on the spin-Hamiltonian parameters. The strongly covalent character of both the σ and π metal-ligand bonds is determined exclusively from the fragment



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Negative Ion-Molecule Reactions and the Determination of the Heats of Formation of Inorganic Anions

BY J. C. J. THYNNE AND K. A. G. MACNEIL

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Lattice energies of compounds may be used as criteria of bond types, for the determination of electron affinities, and in discussions of the stabilities of hypothetical compounds.¹ The usual methods of evaluating the lattice energies of inorganic compounds involve Born-Haber cycles, the Born-Landé or Born-Mayer equations,² or extended classical calculations³ involving the use of several experimental parameters.

The simplest method is that involving thermochemical cycles but, because of the limited number of gaseous anions for which heat of formation data are available, few Born-Haber cycles may be used to evaluate cycle lattice energies and consequently few diatomic or polyatomic ionic salts may be studied.

(1) D. A. Johnson, "Some Thermodynamic Aspects of Inorganic Chemistry," Cambridge University Press, Cambridge, England, 1968.

(2) D. F. C. Morris, *J. Inorg. Nucl. Chem.*, **4**, 8 (1957).

(3) T. E. Brakett and E. B. Brakett, *J. Phys. Chem.*, **69**, 3611 (1965).

Ion-molecule reactions occurring in the gas phase have received considerable attention.^{4,5} The requirement that, for such a reaction to occur, the reaction must be thermoneutral or exothermic has enabled an upper limit to be deduced for many bond energies. In addition, the heats of formation of several organic and inorganic positive ions have been determined in this manner.

This situation suggests that a study of the negative ion-molecule reactions which occur with inorganic compounds may offer a relatively simple route to obtaining heat of formation data for some gaseous anions. Clark and Dixon⁶ have recently reported stabilization of the SiF_5^- ion by the formation of tetraphenylarsonium pentafluorosilicate. We decided to examine negative ion formation in silicon tetrafluoride in order to see if thermochemical data could be determined for the SiF_5^- ion.

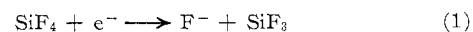
Experimental Section

The experiments were carried out using a Bendix time-of-flight mass spectrometer, Model 3015. The pressure of silicon tetrafluoride in the ion source was varied from <1 to 10^{-6} to $\sim 8 \times 10^{-6}$ Torr. The electron energy was read on a digital voltmeter and the electron current was kept constant over the energy range by automatic regulation.

Use of two channels of the mass spectrometer analog output scanners enabled two mass peaks (*e.g.*, SiF_3^- and SiF_5^-) to be monitored simultaneously so that no switching between peaks was necessary.

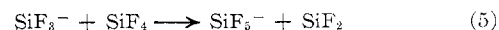
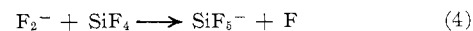
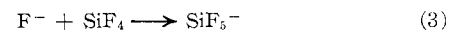
Discussion

Our experiments showed that, at low ion source pressures ($<10^{-6}$ Torr), the primary ions F^- , F_2^- , and SiF_3^- were formed by dissociative attachment processes, *e.g.*



When the pressure of silicon tetrafluoride in the ion source was raised to $>10^{-5}$ Torr, formation of the ion SiF_5^- was observed as a result of an ion-molecule reaction.

Possible ion-molecule reactions leading to SiF_5^- ion formation were



The identity of the reactant ion was established by comparing the dependence of the primary ion current upon electron energy with that obtained for SiF_3^- . It is apparent from Figure 1 that the normalized electron energy profiles for SiF_3^- and SiF_5^- are identical, hence the ion-molecule reaction responsible for SiF_5^- formation is reaction 5.

Recently, Page and Goode,⁷ using the magnetron technique, have measured the electron affinity of SiF_3^-

(4) F. W. Lampe, F. H. Field, and J. L. Franklin, *Progr. React. Kinet.*, **1**, 67 (1961).

(5) P. Ausloos, Ed., *Advan. Chem. Ser.*, **No. 58** (1966).

(6) H. C. Clark and K. R. Dixon, *Chem. Commun.*, 717 (1967).

(7) F. M. Page and G. C. Goode, "Negative Ions and the Magnetron," Wiley, New York, N. Y., 1969.

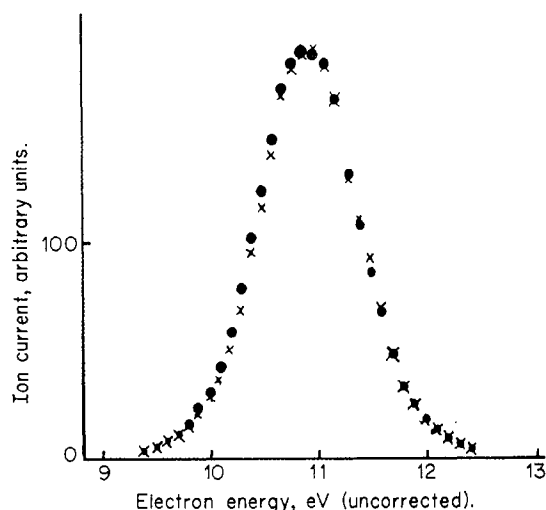


Figure 1.—Normalized ionization efficiency curves for SiF_3^- (crosses) and SiF_5^- (full circles).

to be 77 kcal mol^{-1} ; this result, in conjunction with the value of $-251 \text{ kcal mol}^{-1}$ reported⁸ for ΔH_f° (SiF_8), leads to ΔH_f° (SiF_5^-) = $-328 \text{ kcal mol}^{-1}$.

Since $\Delta H_5 \leq 0$ for the reaction to be observed then, since ΔH_f° (SiF_4) = -373^9 and ΔH_f° (SiF_2) = $-118 \text{ kcal mol}^{-1}$ ⁹ we deduce that ΔH_f° (SiF_5^-) $\leq -583 \text{ kcal mol}^{-1}$.

It is therefore apparent that this approach does yield information regarding the heats of formation of inorganic ions and other systems such as germanium tetrafluoride and phosphorus pentafluoride are being investigated.

Acknowledgment.—We thank the Science Research Council for a grant in support of this work.

(8) V. I. Vedenyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionisation Potentials and Electron Affinities," Arnold, London, 1966, p 135.

(9) "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich.

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An Improved Synthesis of 1,6-Dicarba-*closo*-decaborane(10)

BY PHILIP M. GARRETT, GARY S. DITTA,
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The reported^{1,2} syntheses of 1,6-dicarba-*closo*-decaborane(10), $1,6\text{-B}_8\text{C}_2\text{H}_{10}$, and its C-substituted derivatives were accomplished by the pyrolyses of 1,3-dicarba-*nido*-nonaborane(13), $1,3\text{-B}_7\text{C}_2\text{H}_{13}$, and its C-substituted derivatives in the presence of diborane.

(1) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 869 (1968).

(2) P. M. Garrett, J. C. Smart, G. S. Ditta, and M. F. Hawthorne, *Inorg. Chem.*, **8**, 1907 (1969).

The yields were generally less than 40% and the C-phenyl derivative could not be obtained by this route (Table I). Moreover, the isolation of the pure product

TABLE I
YIELD DATA FOR $1,6\text{-B}_8\text{C}_2\text{H}_{10}$ AND ITS C-MONOMETHYL,
C,C'-DIMETHYL, AND C-MONOPHENYL DERIVATIVES

Compound	Yield, ^a %	Yield, ^b %
$1,6\text{-B}_8\text{C}_2\text{H}_{10}$	29	74 ^c
$1,6\text{-B}_8\text{C}_2\text{H}_9(\text{CH}_3)$	33	86
$1,6\text{-B}_8\text{C}_2\text{H}_8(\text{CH}_3)_2$	41	85
$1,6\text{-B}_8\text{C}_2\text{H}_9(\text{C}_6\text{H}_5)$	Trace	81

^a Prepared by pyrolysis of $\text{B}_7\text{C}_2\text{H}_{13}$ and its C-substituted derivatives in the presence of diborane.^{1,2} ^b Prepared by hydroboration of $\text{NaB}_7\text{C}_2\text{H}_{12}\text{-B}_7\text{C}_2\text{H}_{13}$ and their C-substituted derivatives. ^c The yield was 82% when unreacted $\text{B}_7\text{C}_2\text{H}_{13}$ was recovered.

was quite laborious due to the presence of small amounts of by-product carboranes. We have recently reported representative derivative chemistry of the 1,6- and 1,10- $\text{B}_8\text{C}_2\text{H}_{10}$ carboranes³ and we now wish to report a new and better route to the $1,6\text{-B}_8\text{C}_2\text{H}_{10}$ carborane and its C-substituted derivatives.

Treatment of a diethyl ether solution containing 1 mol each of $\text{NaB}_7\text{C}_2\text{H}_{12}$ and $\text{B}_7\text{C}_2\text{H}_{13}$ with 2 mol of diborane dissolved in tetrahydrofuran (THF) followed by addition of 2 mol of $\text{B}_7\text{C}_2\text{H}_{13}$ dissolved in diethyl ether and an additional 2 mol of diborane dissolved in THF gave $1,6\text{-B}_8\text{C}_2\text{H}_{10}$ in 74% yield. Its C-substituted derivatives could likewise be obtained in somewhat higher yields (Table I). In addition to $1,6\text{-B}_8\text{C}_2\text{H}_{10}$, the only other major product was sodium borohydride and consequently purification procedures were considerably easier than in the previous method. The crude C-monomethyl derivative was found to be an inseparable mixture of the 1-methyl and 6-methyl isomers of $1,6\text{-B}_8\text{C}_2\text{H}_{10}$ in a 2:1 abundance, respectively, which is the same ratio obtained by other routes.² The products were identified by their characteristic infrared and nuclear magnetic resonance spectra.^{1,2} From preliminary results, not discussed here, the reaction path appears to be quite complex and its elucidation is currently underway.

Experimental Section

1,3-Dicarba-*nido*-nonaborane(13) and its C-substituted derivatives were prepared by literature methods.^{1,4} Cylinder diborane was purchased from K & K Laboratories, Plainview, N. Y. The THF was distilled from lithium aluminum hydride prior to use. All other reagents were reagent grade and were used without further purification. All reactions were carried out under a nitrogen atmosphere.

Preparation of Diborane-THF Solution.—Diborane dissolves⁵ in THF with formation of a weak Lewis acid-base complex which could be conveniently syringed in air. The apparatus, listed in its connected order, consisted of the cylinder of diborane, a nitrogen inlet with a T joint near the cylinder, an empty trap, a fritted-disk bubbler which was immersed in the THF, another empty trap, and finally two acetone traps in which undissolved diborane is destroyed. With the exception of the diborane

(3) P. M. Garrett, J. C. Smart, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 4707 (1969).

(4) P. M. Garrett, T. A. George, and M. F. Hawthorne, *Inorg. Chem.*, **8**, 2008 (1969).

(5) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 199.