help of Mr. Lary L. White who wrote the computer program, and helpful discussions with Dr. Thomas A. Milne. We appreciate the willingness of Prof. John L. Margrave of the University of Wisconsin to allow the use of samples that were prepared by F. T. G. while a graduate student under his direction.

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EVIDENCE FOR DUAL AND DISTINCT MECHANISMS IN THE SOLVOLYSIS OF 2-OCTYL BROSYLATE IN AQUEOUS DIOXANE

Sir:

Solvolysis of optically active 2-octyl brosylate in 75 volume per cent. aqueous dioxane at 65° furnished, in addition to small amounts of olefins, the expected inverted alcohol of 77% optical purity.[1,2] However, when solvolysis was conducted in the presence of 0.0307 *M* sodium azide the resulting inverted 2-octanol, formed now in competition with 2-octyl azide, proved to be *100% optically pure.* Thus *sodium azide is influencing the stereochemical course of the solvolysis reaction.* These and other pertinent data are summarized in the table.

TABLE I

SOLVOLYSES OF 2-OCTYL BROSYLATE[a] IN 75 VOLUME PER CENT. AQUEOUS DIOXANE AT 65°

$[NaN_3]$ × 10^2	$[\alpha]_{ROH}$[b,c]	$[\alpha]_{RN_3}$[c]	Azide,[d] %	k,[e] sec.$^{-1}$ × 10^5
...	16.9	...	..	23.8 ± 0.2
0.633	14.5	52.0	8.8	23.3 ± 1.0
1.27	16.7[f] 16.3[f]	84.3	26.4	33–26
1.26	16.8	89.9	..	...
3.07	23.5	120	64.9	...
3.07	22.9	130	..	...
6.18	22.0	125	77.6	109 ± 5

[a] [ROBs] = 0.0176–0.0180 *M*. [b] Authentic, optically pure 2-octanol was found to have $[\alpha]^{365}_{25}$ 21.9 ± 0.1. [c] Products were inverted in all cases. Specific rotations measured at 365 mμ, 25°, in 75 volume per cent. aqueous dioxane on a Rudolph, modified Model 200, Photoelectric Polarimeter. [d] Percentage of alkyl azide formed; determined from titration data. [e] Rates (integrated) of acid production determined by titration. The run at 0.0127 *M* NaN_3 displayed a downward-drifting rate constant reflecting a competing SN2 displacement by azide ion. [f] Duplicate determinations.

We interpret these data to mean that *two distinct paths* are followed in the solvolysis of 2-octyl brosylate in the absence of salt: a nucleophilic SN2 displacement by water to furnish inverted alcohol[3]; and a second mode for reaction involving the formation of an intermediate which subsequently reacts to furnish racemic or retained alcohol. The function of the azide, presumably, is to react preferentially with this intermediate to form alkyl azide, thus preventing its conversion to alcohol. The nature of the intermediate has not as yet been positively identified although it is probably either a solvated carbonium ion or an oxonium ion formed in a nucleophilic SN2 displacement by dioxane.[4] Experiments are in progress to choose between these alternatives. In either event these results would seem to have far-reaching implications concerning the long-standing question of the merging of SN1 and SN2 processes.[5] We hope to report on this question and on other aspects of this work in the near future.

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(1) The product alcohol has been shown to be optically stable under the reaction conditions.

(2) Alcohol was isolated from the reaction mixture by extraction into pentane, concentration, and purification by gas chromatographic separation.

(3) Inversion of configuration in such solvent-substrate reactions appears to be quite general; see, *e.g.*, A. Streitwieser, Jr., and A. C. Waiss, Jr., *J. Org. Chem.*, **27**, 290 (1962).

(4) Evidence already has been deduced for the intermediacy of oxonium ions in the solvolysis of primary alkyl sulfonates; see A. Streitwieser, Jr., and S. Andreades, *J. Am. Chem. Soc.*, **80**, 6553 (1958).

(5) See, for example, M. L. Bird, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 634 (1954); S. Winstein, E. Grunwald and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951); V. Gold, *J. Chem. Soc.*, 4633 (1956).

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SILICON–SILICON BOND DISSOCIATION ENERGIES IN DISILANE AND HEXACHLORODISILANE[1]

Sir:

Bonds formed by silicon to other elements are generally stronger than those formed by carbon. Moreover, chemical evidence exists suggesting that silicon–silicon bonds are in some cases more stable thermally than corresponding carbon–carbon bonds.[2] Limited thermochemical data for the silicon–silicon bond, on the other hand, have given the impression that this bond is considerably weaker than a carbon–carbon bond. Thus, a thermochemical bond energy $E(\text{Si–Si}) = 46.4$ kcal. mole^{-1} has been calculated for disilane,[3] and the activation energy for pyrolysis of disilane has been taken to imply a value for $D(H_3Si\text{–}SiH_3)$ of $\sim$50 kcal. mole^{-1}.[4,5] For ethane $D(H_3C\text{–}CH_3) = 83$ kcal. mole^{-1}.[4] We have now measured the dissociation energies of the silicon–silicon bonds in disilane and hexachlorodisilane by electron impact, and have found that they are comparable in strength to carbon–carbon bonds.

A commercial sample of hexachlorodisilane was purified for use by high vacuum distillation and a sample of disilane was kindly provided by Professor M. Kent Wilson. The appearance potentials were

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(1) This study was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

(2) A. G. MacDiarmid, "Advances in Inorganic Chemistry and Radiochemistry," Eds., H. J. Emeléus and A. G. Sharpe, **3**, 207 (1961).

(3) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961).

(4) See T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths, London, 1958, and references cited therein.

(5) It has been pointed out (reference 4) that the mechanism for pyrolysis of disilane has not been elucidated and may not proceed *via* formation of silyl radicals. Moreover, even if the initial reaction step is $Si_2H_6 \rightarrow SiH_3 + SiH_3$, the activation energy of the recombination reaction may not be zero. Only if this is true will the activation energy of pyrolysis be equal to the bond dissociation energy.

TABLE I

Compound	Ion	A_p, e.v.	$D(X_3Si{-}SiX_3)$, kcal. mole^{-1}
Si_2H_6	SiH_3^+	11.85 ± 0.05	81.3 ± 4
	SiH_2^+	11.94 ± 0.04	......
Si_2Cl_6	$SiCl_3^+$	11.55 ± 0.1	$\leqslant 85 \pm 6$

measured using a Consolidated Electrodynamics Corporation Model 21-103C mass spectrometer modified to allow magnetic scanning. The method used to evaluate the appearance potential data has been described previously.[6]

The silicon–silicon bond dissociation energy in disilane can be calculated from the appearance potentials of the SiH_3^+ ion from silane (12.40 e.v.)[6] and disilane (Table I) and the heats of formation[3] of the two compounds. Thus, if

$$SiH_4 + e^- \longrightarrow SiH_3^+ + H + 2e^- \qquad (1)$$

and

$$Si_2H_6 + e^- \longrightarrow SiH_3^+ + SiH_3 + 2e^- \qquad (2)$$

then

$$\Delta H_f(SiH_3) = A_p(2) - A_p(1) + \Delta H_f(Si_2H_6) - \Delta H_f(SiH_4) + \Delta H_f(H)$$

assuming the SiH_3^+ ions are energetically identical in both reactions. The resulting value of $\Delta H_f(SiH_3) = 49.2$ kcal. mole^{-1} is in excellent agreement with the previous value of 49.5 kcal. mole^{-1} determined by consideration of hydrocarbon ions from several alkylsilanes.[6] This value for the heat of formation of the silyl radical, taken with the heat of formation of disilane,[3] leads to a value of $D(H_3Si{-}SiH_3) = 81.3$ kcal. mole^{-1}. The appearance potential of the SiH_2^+ ion from disilane also has been measured. Assuming formation by the process

$$Si_2H_6 + e^- \longrightarrow SiH_2^+ + SiH_4 + 2e^- \qquad (3)$$

the heat of formation of SiH_2^+ is calculated to be 285 kcal. mole^{-1}, in good agreement with the value of 282 kcal. mole^{-1} derived from silane.[6]

Since the heat of formation of hexachlorodisilane is not known, the above procedure cannot be applied to this compound. However, the Si–Si bond dissociation energy can be calculated from the $SiCl_3^+$ appearance potential (Table I) and the ionization potential of the trichlorosilyl radical (7.88 e.v.).[6] The resulting value is $D(Cl_3Si{-}SiCl_3) = 85$ kcal. mole^{-1}. The near equality of the silicon–silicon bond strengths in Si_2H_6 and Si_2Cl_6 is interesting, being consistent with the observation that Si–Si bond lengths in the two compounds are very similar,[7] as are the silicon–hydrogen bond dissociation energies in silane and trichlorosilane.[6]

The higher values for D(Si–Si) reported here permit a better understanding of recent observations of the properties of several substances with silicon-silicon bonds[2,8] than do the earlier results.

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(6) W. C. Steele, L. D. Nichols and F. G. A. Stone, *J. Am. Chem. Soc.*, in press.

(7) L. O. Brockway and J. Y. Beach, *ibid.*, **60**, 1836 (1938).

(8) F. G. A. Stone, "Hydrogen Compounds of Group IV Elements," Prentice-Hall, Englewood Cliffs, N. J., 1962.

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FERROSILOXANES AND FERROSILICONATE ANIONS[1]

Sir:

Monomeric alkylsiloxanes of definite composition, in which the silicon-atoms are partly replaced by transition metals of the VIII group are practically unknown.[2] We now have succeeded in sythesizing a representative of the series of ferrosiloxanes and wish to describe its preparation, properties and derivatives, while further work on this class of compounds is in progress.

Three moles of an alkali trimethylsilanolate react in ethereal solution with one mole of anhydrous ferric chloride to give a brownish precipitate of alkali chloride (containing ferric oxides) and a brown solution of tris-trimethylsiloxy-iron, according to the equation[3]

$$3(Me_3SiO)Na + FeCl_3 \longrightarrow 3NaCl + (Me_3SiO)_3Fe$$

Evaporation of the solvent and sublimation of the residue *in vacuo* affords a 45% yield of the new compound with the analytical composition $Me_9Si_3O_3Fe$ (Fe calcd. 17.27; found, 17.73).

The ferrosiloxane forms yellow-green waxy crystals with m.p. 179–181° and subl. temp. 130°/1 mm. It shows extremely high solubility in common organic solvents, but is quite sensitive even against traces of moisture and is quickly hydrolyzed, trimethylsilanole and ferric hydroxide being formed. The pure compound, however, is thermally stable up to its melting point, after which its color slowly turns to red-brown with decomposition. According to cryoscopic molecular weight determinations in benzene as a solvent the compound is strictly dimeric (calcd., 646.6; found, 636), a result which was to be expected from our earlier investigations of analogous alumino- and gallo-siloxanes.[1] We therefore propose the structure I, which is supported by the infrared spectrum (in Nujol mull), with strong bands at 7.95, 8.02, 10.00 and 10.57 (ν Si–O–Fe), 11.80, 13.17 and 13.38 μ. The typical infrared lines of the bridging siloxy groups appear at 12.32 and 13.20 μ and are in good agreement with the corresponding lines in the spectra of the Al- and Ga-compounds. The structure of the latter has in turn been confirmed by n.m.r. spectra.[1] N.m.r. investigations in CCl_4 solutions of I and TMS as an internal standard, however, resulted only in quite broadened and unsharp proton signals with very high chemical shifts up to higher fields and proved the paramagnetic character of I.

Among the chemical properties of the new ferrosiloxane the reactions with alkalitrimethylsilanolates are most remarkable. Equimolar solutions of I and a sodium or potassium trimethylsilanolate in CCl_4 undergo an exothermic reaction at room temperature and quantitative yields of the alkali salts of the new tetrakis-trimethylsiloxy-iron-III-

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(1) Heterosiloxanes, IX; Part VIII: H. Schmidbaur and M. Schmidt, *Angew. Chem.*, **74**, 328 (1962).

(2) K. A. Andrianov and A. A. Zhdanov, *Izvest. Akad. Nauk SSR, Otdel. Khim. Nauk*, 1590 (1959); *C. A.*, **54**, 8687 (1960).

(3) It is important that the ferric chloride solution is added to the silanolate solutions (and not *vice versa*), otherwise, only poor yields if any, are obtained. With the potassium trimethylsilanolate and homologous alkylsilanolates the reaction proceeds in the same manner,