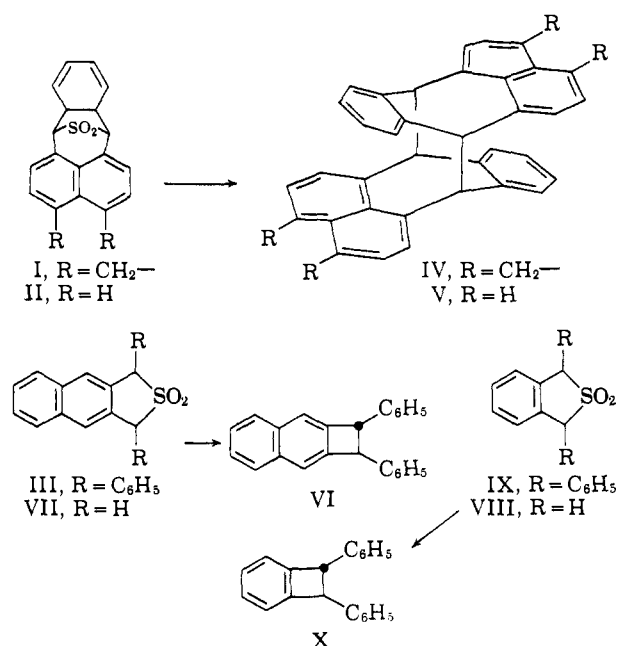


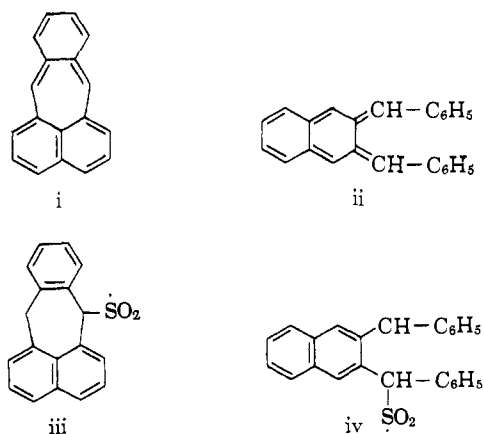
stable of the group discussed here, correspond to the least stabilized *o*-quinodimethanes of the series.¹²

From the synthetic point of view, the sulfone photolysis reaction has practical utility. Thus, the conversion of the diphenyl sulfones III and IX to the corresponding condensed cyclobutenes VI and X can be accomplished only photochemically. The effective pyrolysis temperatures of sulfones III and IX are higher than the temperature at which the cyclobutenoid hydrocarbons VI and X rearrange to secondary pyrolysis products.^{8,13}



Acknowledgment.—We are grateful for support of this work by the U. S. Army Research Office (Durham) and the National Science Foundation.

(12) The possibility that sulfones I, II, III, and IX all decompose initially by homolytic fission to diradicals appears unlikely on the basis of the marked difference in the photolytic stabilities of II and III. Whereas the *o*-quinoid hydrocarbons generated from II and III (i and ii) by concerted loss of sulfur dioxide are structures of very different energy content, the diradicals (iii and iv) formed from II and III by rupture of a carbon-sulfur bond are structures which should have very similar energy.



(13) Sulfone III is stable at 150°, at which temperature hydrocarbon VI rearranges to a phenylidihydronaphthalene.^{5b}

EVANS CHEMICAL LABORATORY
THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

M. P. CAVA
R. H. SCHLESSINGER
J. P. VAN METER

RECEIVED MARCH 26, 1964

Bond Dissociation Energies and Ion Energetics in Organosilicon Compounds by Electron Impact

Sir:

Recent reports^{1,2} of electron impact studies of silane, disilane, and alkyl-substituted silanes have indicated that silicon-silicon and silicon-hydrogen bonds are considerably stronger than thermochemical data would suggest, and that silicon-carbon bonds are of comparable strength to the analogous carbon-carbon bonds. In electron impact studies of the formation of the trimethylsilanium ion from substituted trimethylsilanes we have obtained results of a similar nature. The compounds studied were synthesized in this laboratory by standard methods³ from trimethylchlorosilane and hexachlorodisilane. Appearance potentials of the (CH₃)₃Si⁺ ion were determined by the retarding-potential-difference method⁴ on a modified Bendix Model 14-101 time-of-flight mass spectrometer. The energy spread of the electrons was approximately 0.1 e.v.; xenon was used to calibrate the electron energy scale. Results are shown in Table I, where the indicated errors are average deviations of replicate measurements.

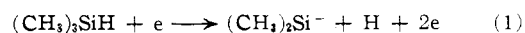
TABLE I

(CH₃)₃Si⁺ APPEARANCE POTENTIALS AND BOND DISSOCIATION ENERGIES IN SUBSTITUTED TRIMETHYLSILANES

Bond	$A[(CH_3)_3Si^+]$, e.v.	ΔH_f° [(CH ₃) ₃ Si ⁺], kcal. mole ⁻¹	ΔH_f° [Si-X], kcal. mole ⁻¹	D [Si-X], kcal. mole ⁻¹
(CH ₃) ₃ Si-H	10.78 ± 0.07	137	-60 ^a	83
(CH ₃) ₃ Si-CH ₃	10.63 ± 0.13	143	-69 ^a	79
(CH ₃) ₃ Si-C ₂ H ₅	10.53 ± 0.09	...	-77	77
(CH ₃) ₃ Si-CH(CH ₃) ₂	10.56 ± 0.16	...	-91	77
(CH ₃) ₃ Si-C(CH ₃) ₃	10.53 ± 0.09	...	-98	77
(CH ₃) ₂ Si-Cl	12.42 ± 0.03	...	-118	120
(CH ₃) ₂ Si-Si(CH ₃) ₃	10.69 ± 0.04	...	-129 ^b	81

^a Reference 7. ^b Estimated by group equivalent method of Franklin.¹⁰

Our appearance potential of (CH₃)₃Si⁺ from trimethylsilane agrees well with that of Hobrock and Kiser.⁵ On the other hand, the value of $A[(CH_3)_3Si^+]$ from tetramethylsilane is in serious disagreement with that determined by Hobrock and Kiser,⁶ ours being lower by nearly 0.7 e.v. We believe our value is to be preferred, because taking simple dissociation processes, *viz.*



assuming no excess energy involved, and combining with thermochemical data^{7,8} leads to consistent values for $\Delta H_f^\circ[(CH_3)_3Si^+]$ (column 3, Table I). Assuming that (CH₃)₃Si⁺ is formed from all compounds by simple

- (1) W. C. Steele and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 3599 (1962).
- (2) W. C. Steele, L. D. Nichols, and F. G. A. Stone, *ibid.*, **84**, 4441 (1962).
- (3) C. Eaborn, "Organosilicon Compounds," Academic Press, New York, N. Y., 1960.
- (4) R. E. Fox, W. M. Hickam, and T. Kjeldaa, *Rev. Sci. Instr.*, **26**, 1101 (1955).
- (5) B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **66**, 155 (1962).
- (6) B. G. Hobrock and R. W. Kiser, *ibid.*, **65**, 2186 (1961).
- (7) S. Tannenbaum, *J. Am. Chem. Soc.*, **76**, 1027 (1954).
- (8) B. E. Knox and H. B. Palmer, *Chem. Rev.*, **61**, 247 (1961).

processes analogous to eq. 1 and 2 and combining the appearance potentials with the implied value of 140 ± 3 kcal. mole⁻¹ for $\Delta H_f^\circ[(\text{CH}_3)_3\text{Si}^+]$ and with thermochemical values for the radical heats of formation^{8,9} leads to molecular heats of formation for $(\text{CH}_3)_3\text{SiC}_2\text{H}_5$, $(\text{CH}_3)_3\text{SiCH}(\text{CH}_3)_2$, $(\text{CH}_3)_3\text{SiC}(\text{CH}_3)_3$, and $(\text{CH}_3)_3\text{SiCl}$ (column 4, Table I). To our knowledge there are no reported values for $\Delta H_f^\circ[(\text{CH}_3)_6\text{Si}_2]$ and, of course, it cannot be obtained from the electron impact data since $\Delta H_f^\circ[(\text{CH}_3)_3\text{Si}]$ is unknown.

We have estimated $\Delta H_f^\circ[(\text{CH}_3)_6\text{Si}_2]$ as -129 kcal. mole⁻¹ by means of the group equivalent method of Franklin¹⁰ using the heats of formation shown in column 4, Table I. We may use the same heats of formation to deduce the bond energy parameters required by Allen's calculational method.^{11,12} These parameters, which are consistent with those for other substituted paraffins,¹² yield a value for $\Delta H_f^\circ[(\text{CH}_3)_6\text{Si}_2]$ that is within a few kilocalories per mole of that obtained by Franklin's method. Combination of our estimate of $\Delta H_f^\circ[(\text{CH}_3)_6\text{Si}_2]$ with the appearance potential of $(\text{CH}_3)_3\text{Si}^+$ from $(\text{CH}_3)_6\text{Si}_2$ and with $\Delta H_f^\circ[(\text{CH}_3)_3\text{Si}^+]$ gives 7.2 e.v. for the ionization potential of the $(\text{CH}_3)_3\text{Si}$ radical or, equivalently, a value of -22 kcal. mole⁻¹ for $\Delta H_f^\circ[(\text{CH}_3)_3\text{Si}]$. This is expressed as bond dissociation energy of $(\text{CH}_3)_3\text{Si-X}$ in column 5 of Table I. The uncertainty in these dissociation energies which is estimated as ± 10 kcal./mole arises principally from the estimate of $\Delta H_f^\circ[(\text{CH}_3)_6\text{Si}_2]$.

Some indirect support for the ionization potential of the $(\text{CH}_3)_3\text{Si}$ radical (and therefore for the bond dissociation energies) may be derived from the following consideration: the appearance potential of $m/e = 57$ from $(\text{CH}_3)_3\text{SiC}(\text{CH}_3)_3$, namely 11.88 e.v., is too high to reflect a simple dissociation process to $(\text{CH}_3)_3\text{C}^+$ and $(\text{CH}_3)_3\text{Si}$. If Stevenson's rule¹³ can be applied to organosilanes as well as to paraffinic hydrocarbons, one derives the following relationship of radical ionization potentials

$$I_z[(\text{CH}_3)_3\text{Si}] < I_z[(\text{CH}_3)_3\text{C}] = 7.42^{14}$$

Hence, lower limits for $D[(\text{CH}_3)_3\text{Si-X}]$ that are only 5 kcal. mole⁻¹ less than those in Table I are quite certain.

As found by previous investigators^{1,2} the Si-H and Si-Si bonds (particularly the latter) are considerably stronger than indicated by the thermochemical bond energies of 77.4 and 47.9 kcal. mole⁻¹, respectively.¹² Also, the dissociation energies of the C-Si bonds are of comparable magnitude to the corresponding C-C bonds although the dependence on alkyl type (R) is much less than for H₃Si-R bonds² or R-R bonds.¹⁵

The data in Table I indicate that in the gas phase the trimethylsilylium ion is sometimes somewhat easier to form from its molecular precursor than is the corresponding *t*-butylcarbonium ion. This is perhaps better seen in Table II in which we compare the difference between the heats of formation of the ions¹⁶ and

the molecular precursors for the corresponding carbon and silicon compounds.

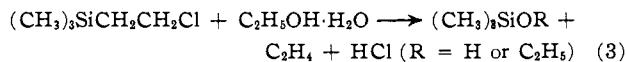
Interestingly enough only in the case of the chloride is there any really significant difference in the ease of formation of the trimethylsilylium and trimethylcarbonium ions, and in this case the large difference reflects the large dissociation energy of the Si-Cl bond.

In connection with possible significance of the data in Table II for reactions in solution, it is interesting to note the previous conclusion, based on various lines of

TABLE II
COMPARISON OF SILICONIUM AND
CARBONIUM IONIC STABILITIES

Compound	ΔH_f° [[$(\text{CH}_3)_3\text{Si}^+$] - $\Delta H_f^\circ[(\text{CH}_3)_3\text{Si-X}]$, kcal. mole ⁻¹	Compound	ΔH_f° [[$(\text{CH}_3)_3\text{C}^+$] - $\Delta H_f^\circ[(\text{CH}_3)_3\text{C-X}]$, kcal. mole ⁻¹
$(\text{CH}_3)_3\text{SiH}$	200	$(\text{CH}_3)_3\text{CH}$	208
$(\text{CH}_3)_3\text{SiCH}_3$	209	$(\text{CH}_3)_3\text{CCH}_3$	217
$(\text{CH}_3)_3\text{SiC}_2\text{H}_5$	217	$(\text{CH}_3)_3\text{CC}_2\text{H}_5$	222
$(\text{CH}_3)_3\text{SiCH}(\text{CH}_3)_2$	231	$(\text{CH}_3)_3\text{CCH}(\text{CH}_3)_2$	226
$(\text{CH}_3)_3\text{SiC}(\text{CH}_3)_3$	238	$(\text{CH}_3)_3\text{CC}(\text{CH}_3)_3$	236
$(\text{CH}_3)_3\text{SiCl}$	258	$(\text{CH}_3)_3\text{CCl}$	209

evidence, that reaction 3 proceeds *via* the silylium ion-pair intermediate¹⁷, and the previously expressed conviction¹⁷ that trialkylsilylium cations, R_3Si^+ , and trialkylcarbon cations, R_3C^+ may, in certain circumstances, be of comparable stability relative to their precursors.



Acknowledgment.—This work was supported in part by the Petroleum Research Fund, Grant No. 833-A1, and in part by a fellowship grant from Dow Corning Corporation. We wish to thank the National Science Foundation for providing funds to aid in the purchase of the mass spectrometer.

(17) L. H. Sommer and G. L. Baughman, *J. Am. Chem. Soc.*, **83**, 3346 (1961).

WHITMORE LABORATORY
DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA

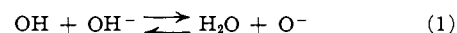
G. G. HESS
F. W. LAMPE
L. H. SOMMER

RECEIVED MAY 16, 1964

Pulse Radiolytic Determination of *pK* for Hydroxyl Ionic Dissociation in Water¹

Sir:

In several papers² the dissociation of OH has been assumed to account for radiation chemical results in alkaline solutions. The reaction most likely is



However, previous data did not permit calculation of the dissociation constant for OH, and values deduced

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) E. J. Hart, S. Gordon, and D. A. Hutchison, *J. Am. Chem. Soc.*, **75**, 6165 (1953); (b) *J. Chim. Phys.*, **52**, 570 (1955); (c) H. L. Friedman and A. H. Zeltmann, *J. Chem. Phys.*, **28**, 878 (1958); (d) G. Hughes and C. Willis, *Discussions Faraday Soc.*, **36**, 223 (1963).

(9) J. L. Franklin and F. W. Lampe, *Trans. Faraday Soc.*, **57**, 1449 (1961).
 (10) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).
 (11) T. L. Allen, *J. Chem. Phys.*, **31**, 1039 (1959).
 (12) H. A. Skinner and G. Pilcher, *Quart. Rev. (London)*, **17**, 264 (1963).
 (13) D. P. Stevenson, *Discussions Faraday Soc.*, **10**, 35 (1951).
 (14) F. P. Lossing, P. Kebarle, and J. B. DeSousa, "Advances in Mass Spectrometry," J. P. Waldron, Ed., Pergamon Press, London, 1959.
 (15) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworth and Co., Ltd., London, 1958.
 (16) F. H. Field, and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.