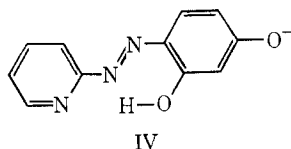
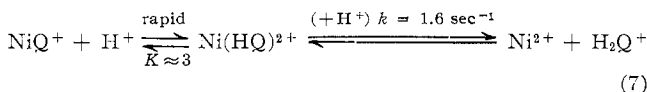


Recently Funahashi and Tanaka¹² have measured the rate constant for reaction of nickel(II) with a ligand showing similar features to the oxines, namely, 4-(2-pyridylazo)resorcinol (IV). The value, $1.7 \times 10^3 M^{-1} \text{sec}^{-1}$ at 25°, is interestingly close to that of II.



Complex Dissociation.—A few experiments on the dissociation of the mono nickel chelate with 8-hydroxyquinoline gave interesting results. The first-order constant for dissociation (Table I) increased from pH 5 to 3 and was then independent of pH 3–1. More significantly, however, the reaction in the lower pH range was attended by a *small increase* in optical density at 360 m μ , whereas the spectra of NiQ⁺ ($\epsilon 2.2 \times 10^3$) and H₂Q⁺ ($\epsilon 1.6 \times 10^3$) would indicate that a *large decrease* should be observed. This indicated that NiQ⁺ generated in neutral solution (pH 5–6) was rapidly (within milliseconds) converted into another species at pH 3 and lower and that the dissociation of this new species was pH invariant (7). We speculate that this



species is Ni(HQ)²⁺ in which a proton is attached to the oxygen, either maintaining a chelate structure or rupturing the nickel–oxygen bond to leave a unidentate ligand. The latter viewpoint tends to be supported by the relatively large value for the rate constant (1.6 sec⁻¹ at 25°), which can be associated with the breakage of a unidentate rather than a bidentate ligand.¹ We attempted to obtain the spectra of the protonated species by lowering the pH and raising the nickel concentration of a solution containing 8-hydroxyquinoline. The absorption of the broad peak was markedly reduced as the pH of a solution containing 0.1 M Ni²⁺–10⁻⁴ M (Q)_{total} was lowered from 5.0 to 3.0, at which pH $\epsilon_{360 \text{ m}\mu}$ was $\approx 1.3 \times 10^3$ and below which substantial dissociation of the whole ligand occurred. Plunging the solution at pH 3 into a buffer at pH 6 on the flow machine gave little indication of a complex formation reaction. This confirms that the solutions at pH 3 have the oxine coordinated (as HQ) and that only a very rapid unobservable loss of a proton from Ni(HQ)²⁺ occurs in changing the pH from 3 to 6.

Acknowledgment.—This work was supported by National Science Foundation Grant GP-8099. Dr. Johnson (Whitworth College, Spokane, Wash.) received a grant from the National Science Foundation Research Participation for College Teachers Program. We are grateful for these aids.

(12) S. Funahashi and M. Tanaka, *Inorg. Chem.*, **8**, 2159 (1969).

CONTRIBUTION FROM THE INSTITUTE OF PHYSICAL CHEMISTRY,
UNIVERSITY OF PERUGIA, PERUGIA 06100, ITALY

Photoionization Study of Tetramethylsilicon

By G. DISTEFANO

Received January 20, 1970

Several mass spectrometric studies by electron impact^{1–11} have been reported on tetramethylsilicon and/or related compounds. The agreement among the electron impact mass spectra^{1–4} is satisfactory. However, discrepancies exist for the threshold^{2,3,5,7} of the (CH₃)₃Si⁺ ion and especially among the results regarding the bond dissociation energy $D_1[(\text{CH}_3)_3\text{Si}-\text{CH}_3]$ (ranging between 59⁵ and 85⁸ kcal mol⁻¹) and the ionization potential of the (CH₃)₃Si radical (ranging between 6.94³ and 7.97⁵ eV). To our knowledge there are no published photoionization data for this molecule. For these reasons new data have been obtained by photon impact mass spectrometry on tetramethylsilicon.

The relative intensities of the positive ions in the photoionization mass spectrum at 21.22 eV (584 Å) are as follows: (CH₃)₄Si⁺, 2.9; (CH₃)₃Si⁺, 100.0; HSi(CH₃)₂⁺, 1.6; H₂SiCH₃⁺, 13.4; (CH₃)₂Si⁺, CH₂SiCH₃⁺, HSiCH₃⁺, CH₃Si⁺, H₃Si⁺, HSi⁺, Si⁺, 0.4–0.7. They are in qualitative agreement with those of the electron impact mass spectra previously reported^{1–4} considering the different nature and energy of the ionizing beam. A maximum number of three atoms and/or methyl groups attached to the silicon is (as by electron impact) the general rule: they account for 96% of the ion current in the present experimental conditions.

Photoionization efficiency curves from onset to 600 Å have been obtained for the three most abundant ions in the spectrum ((CH₃)₄Si⁺, (CH₃)₃Si⁺, and H₂SiCH₃⁺). These curves are shown in Figure 1. All the three curves show a low-intensity tail near the threshold. As an example of this behavior, the threshold region of the ion-yield curve for H₂SiCH₃⁺ is reported at high sensitivity in Figure 2. These tails begin at 0.17, 0.19, and 0.21 eV for (CH₃)₄Si⁺, (CH₃)₃Si⁺, and H₂SiCH₃⁺, respectively, before the ion-yield curves start to rise quickly. The tail is probably due to hot bands, that is to the formation of ions from thermally excited mole-

- (1) V. H. Dibeler, *J. Res. Nat. Bur. Stand.*, **49**, 235 (1952).
- (2) B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **65**, 2186 (1961).
- (3) G. G. Hess, F. W. Lampe, and L. H. Sommer, *J. Amer. Chem. Soc.*, **87**, 5327 (1965).
- (4) G. P. van der Kelen, O. Volders, H. van Onckelen, and Z. Eeckhaut, *Z. Anorg. Allg. Chem.*, **338**, 106 (1965).
- (5) J. A. Connor, G. Finney, F. J. Leigh, R. N. Haszeldine, P. J. Robinson, R. D. Sedwick, and R. F. Simmons, *Chem. Commun.*, 178 (1966).
- (6) I. M. T. Davidson and I. L. Stephenson, *ibid.*, 746 (1966).
- (7) S. J. Band, I. M. T. Davidson, C. A. Lambert, and I. L. Stephenson, *ibid.*, 723 (1967).
- (8) I. M. T. Davidson and I. L. Stephenson, *J. Chem. Soc. A*, 282 (1968).
- (9) S. J. Band, I. M. T. Davidson, and C. A. Lambert, *ibid.*, A, 2068 (1968).
- (10) M. F. Lappert, J. Simpson, and T. R. Spalding, *J. Organometal. Chem.*, **17**, 1 (1969).
- (11) W. C. Steele, L. D. Nichols, and G. A. Stone, *J. Amer. Chem. Soc.*, **84**, 4441 (1962).

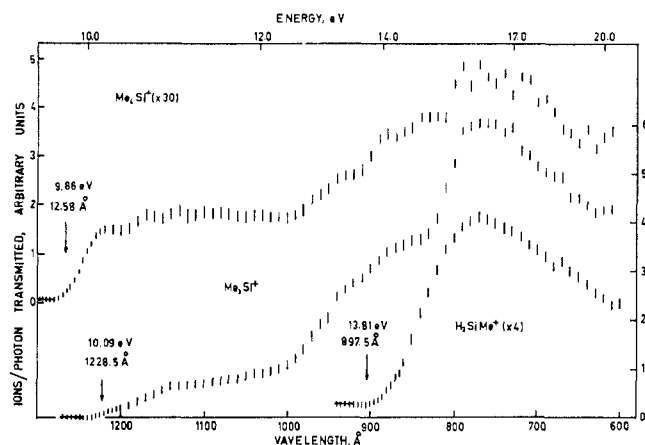


Figure 1.—Photoionization yield curves from onset to 600 Å for the $(\text{CH}_3)_4\text{Si}^+$ (left scale) and $(\text{CH}_3)_3\text{Si}^+$ and $\text{H}_2\text{Si}(\text{CH}_3)^+$ ions (right scale) of tetramethylsilicon.

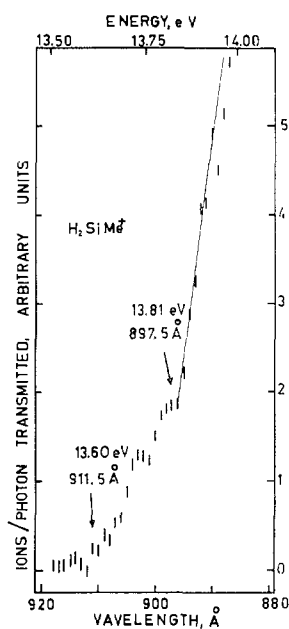


Figure 2.—Photoionization yield curve from onset to 880 Å for the $\text{H}_2\text{SiCH}_3^+$ ion of tetramethylsilicon.

cles, and the beginning of the sharp rise is an upper limit for the adiabatic threshold value.

After the tail, the molecular ion-yield curve shows a slowly rising region (see Figure 1) and becomes constant at an energy corresponding to the onset of the first fragment ion, as expected.¹² The curve remains nearly constant to about 1000 Å and then slowly rises to a broad maximum between 800 and 700 Å. The last structure may be assigned to unresolved autoionization or to new electronically excited states.

The shape of the $(\text{CH}_3)_3\text{Si}^+$ ion-yield curve is very similar to that of the molecular ion along all the wavelength range. This suggests that the same Rydberg levels may produce autoionization or predissociation excited fragment and molecular ions.

In Table I the threshold values and the heats of formation of the most abundant ions from tetramethyl-

(12) See for example W. A. Chupka, *J. Chem. Phys.*, **48**, 2337 (1968).

TABLE I

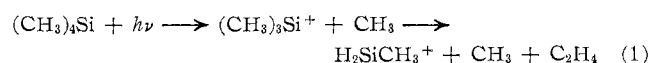
THRESHOLD VALUES AND HEATS OF FORMATION OF THE MOST ABUNDANT IONS FROM $(\text{CH}_3)_4\text{Si}$ BY PHOTON IMPACT

	Threshold value, eV		Ionic ΔH_f°	
	This work	Lit.	eV	kcal mol ⁻¹
$(\text{CH}_3)_4\text{Si}^+$	9.69 ± 0.02^a	9.8 ± 0.15^2	7.38 ± 0.02	170.2 ± 0.5
	9.86 ± 0.02^b	9.85 ± 0.16^{10}		
$(\text{CH}_3)_3\text{Si}^+$	9.90 ± 0.02^a	10.4 ± 0.17	6.17 ± 0.02	142.3 ± 0.5
	10.09 ± 0.02^b	10.53 ± 0.1^6		
$\text{H}_2\text{SiCH}_3^+$	13.60 ± 0.02^a		9.35 ± 0.02	215.6 ± 0.5
	13.81 ± 0.02^b			

^a Onset of the ion-yield curve. ^b Beginning of the sharp rise in the ion-yield curve.

silicon are reported. The estimated upper limit for the adiabatic onset of the molecular ion, that is the energy corresponding to the beginning of the sharp rise in the ion-yield curve, is at 1258 Å (9.86 ± 0.02 eV). From this value $\Delta H_f^\circ((\text{CH}_3)_4\text{Si}^+) = 7.38 \pm 0.02$ eV (170.2 ± 0.5 kcal mol⁻¹) is obtained.^{13,14} The adiabatic threshold for the $(\text{CH}_3)_3\text{Si}^+$ ion (estimated to be at 1228.5 Å, 10.09 ± 0.02 eV) is at least 0.3 eV lower than all previously reported values (see Table I). $\Delta H_f^\circ((\text{CH}_3)_3\text{Si}^+) = 6.17 \pm 0.02$ eV (142.3 ± 0.5 kcal mol⁻¹) is obtained from the present threshold value. As previously discussed, a quite large range of data has been reported for the bond dissociation energy D_1 . The only one directly measured, as activation energy for the thermal decomposition of the tetramethylsilane,¹⁵ is 78.8 kcal mol⁻¹. In connection with the present onset value for the $(\text{CH}_3)_3\text{Si}^+$ ion, it gives 6.67 eV¹⁶ as the ionization threshold of the $(\text{CH}_3)_3\text{Si}$ radical. Again this value is lower than all the previous data. This new value is supported by the following consideration. From the thermochemical value of the bond dissociation energy in the hexamethyldisilane⁸ $D((\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_3) = 67.3 \pm 2$ kcal mol⁻¹ and from the lowest electron impact threshold value for the $(\text{CH}_3)_3\text{Si}^+$ ion from $((\text{CH}_3)_3\text{Si})_2$ (10.0 ± 0.1 eV),^{5,7} Davidson *et al.*,⁸ obtained 7.08 eV for $\text{IP}((\text{CH}_3)_3\text{Si})_{\text{rad}}$ and about 69 kcal mol⁻¹ for $D((\text{CH}_3)_3\text{Si}-\text{CH}_3)$. However, the electron impact onset for the trimethyl ion from hexamethyldisilane likely is too high by 0.3–0.4 eV (as the electron impact onset of $(\text{CH}_3)_3\text{Si}^+$ ion from $(\text{CH}_3)_4\text{Si}$ is). If this is true, $\text{IP}((\text{CH}_3)_3\text{Si})_{\text{rad}}$ becomes 6.68–6.78 eV (and $D_1 = 76$ –79 kcal mol⁻¹) in agreement with the photon impact value.

The adiabatic onset for the $\text{H}_2\text{SiCH}_3^+$ ion is estimated to be at 897.5 Å (13.81 ± 0.02 eV). The relatively low value for the onset of this rearrangement ion and its high abundance agree with the formation process



(13) The following heats of formation at 298°K (in kcal mol⁻¹) have been used throughout this paper:¹⁴ $\Delta H_f^\circ((\text{CH}_3)_4\text{Si}(\text{g})) = -57.149$, $\Delta H_f^\circ(\text{CH}_4) = 33.2$, $\Delta H_f^\circ(\text{C}_2\text{H}_4) = 12.49$, $\Delta H_f^\circ(\text{Si}(\text{g})) = 108.9$, $\Delta H_f^\circ(\text{Si}^+) = 298.35$.

(14) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Technical Note 270-3, U. S. Government Printing Office, Washington, D. C., 1968.

(15) D. F. Helm and E. Mack, *J. Amer. Chem. Soc.*, **59**, 60 (1937).

(16) In this figure the accuracy depends on that of the thermochemical datum.

(confirmed by metastable transition⁴) in which a stable molecule is formed. From reaction 1, $\Delta H_f^\circ(\text{H}_2\text{SiCH}_3^+) = 9.35 \pm 0.02 \text{ eV}$ ($215.6 \pm 0.5 \text{ kcal mol}^{-1}$) is obtained.

From heats of formation,^{13,14} the Si^+ ion threshold value is 21.17 eV. This onset is too high to be obtained by direct measurements with the present apparatus. Using the calculated value in connection with heats of formation and the molecular ionization threshold, the following total bond energies (in kcal mol^{-1}) are obtained: $D((\text{CH}_3)_4\text{-Si}) = 298.85$ and $D((\text{CH}_3)_4\text{-Si}^+) = 260.82$. These results suggest that ionization occurs by the loss of one of the bonding electrons between the central atom and the methyl groups.

The measurements have been performed by using the apparatus described by Dibeler, *et al.*,^{17,18} with an optical resolution of about 1 Å and an ionization efficiency uncertainty of the order of 3%.

Acknowledgments.—The author gratefully acknowledges helpful discussions with Dr. H. M. Rosenstock and Dr. V. H. Dibeler and the use of the facilities of the Mass Spectrometry Section of the National Bureau of Standards, Washington, D. C.

(17) V. H. Dibeler and R. M. Reese, *J. Res. Nat. Bur. Stand., Sect. A*, **68**, 409 (1964).

(18) V. H. Dibeler and J. A. Walker, *J. Opt. Soc. Amer.*, **57**, 1007 (1967).

CONTRIBUTION FROM THE RESEARCH SCHOOL OF CHEMISTRY, AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA 2600, AUSTRALIA, AND THE SCHOOL OF CHEMISTRY, UNIVERSITY OF SYDNEY 2006, SYDNEY, AUSTRALIA

The Chelate Ring Conformations of the β -Triethylenetetramine Configuration in Cobalt(III) Complexes

BY D. A. BUCKINGHAM,^{1a} I. E. MAXWELL,^{1a} A. M. SARGESON,^{1a} AND H. C. FREEMAN^{1b}

Received January 22, 1970

Recently X-ray crystal structure analyses have been carried out on a number of cobalt(III) complexes containing trien coordinated in the β configuration (Figure 1), namely, $[\text{Co}(\text{trien})\text{Cl}(\text{OH}_2)](\text{ClO}_4)_2$,^{2a} $\Delta\text{-}\beta_2\text{-}(\text{RRS})\text{-}[\text{Co}(\text{trien})((\text{S})\text{-Pro})]_2 \cdot 2\text{H}_2\text{O}$,^{2b} and $\Lambda\text{-}\beta_2\text{-}(\text{SSS})\text{-}[\text{Co}(\text{trien})((\text{S})\text{-Pro})]\text{ZnCl}_4$ ^{2b} (trien = triethylenetetramine). In addition, in the complex *sym*- $[\text{Co}(\text{trenen})\text{N}_3]\text{-}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ³ (trenen = 4-(2-aminoethyl)-1,4,7,10-tetraazadecane) trenen can be considered as β -trien substituted at the "angular" nitrogen atom by an aminoethyl group. These four structures provide independent determinations of the geometry of the β -trien configuration in different crystal lattices. Prior to these structural analyses only the gross features of the geometry of the β -trien configuration could be in-

ferred from Dreiding stereomodels. However, the models did indicate which were likely to be the more important conformational features. In particular, it was decided that conformational inversion was possible for the apical chelate ring, but at the time it was difficult to decide which was the preferred conformation. Angular strain was also evident, particularly at the "planar" secondary nitrogen atom, but it was difficult to determine how this strain was distributed. With these problems in mind the conformations of the chelate rings in coordinated trien are now compared using three different criteria. In this way any correlations are not biased to one particular set of results. Also the comparison is made between molecular conformations which are found in different crystal lattices where the molecules are subject to different types of intermolecular forces (*e.g.*, H-bonding, electrostatic, and nonbonded forces). Such a comparison should give some indication of the relative importance of intermolecular and intramolecular forces in determining conformation; for example, large conformational differences have been observed for the $\text{Cr}(\text{en})_3^{3+}$ ion in different lattices.⁴

Comparison of β -trien Geometries

Bond Angles and Bond Lengths.—A comparison of the Co-N bond distances involving trien for the β -Co-(trien)Cl(OH₂)²⁺,^{2a} $\Delta\text{-}\beta_2\text{-}(\text{RRS})\text{-Co}(\text{trien})((\text{S})\text{-Pro})^{2+}$,^{2b} and $\Lambda\text{-}\beta_2\text{-}(\text{SSS})\text{-Co}(\text{trien})((\text{S})\text{-Pro})^{2+}$ ^{2b} structures showed that in each case the bond to the "planar" nitrogen was the shortest. The Co-N(2) bond lengths averaged to 1.921 (7) Å, whereas the mean value for the other Co-N distances was 1.953 (4) Å (the standard deviations of the means, σ_{av} , were calculated using the relationship $\sigma_{\text{av}}^2 = 1/\sum 1/\sigma_i^2$). Another geometrical feature of the "planar" secondary N atom common to all three structures was the expansion of the C(2)-N(2)-C(3) bond angle (mean 114.0 (7)°). The Co-N(2) bond length is reduced relative to the other Co-N bond distances in order to reduce angular strain at this center. By comparison there is no significant distortion in the C(4)-N(3)-C(5) bond angle (110.7 (7)°) or any other angle about the "angular" secondary N atom. Likewise there are no other significant intraligand angular distortions in the polyamine skeleton.

The angles subtended by the chelate rings at the metal ion are similar. For the three complexes the mean N-Co-N angle is 85.8 (2)°. This angle compares with an N-Co-N angle of 86° found in cobalt(III)-ethylenediamine complexes^{5,6} where the chelate rings are not fused. Mean C-C and C-N bond lengths for the trien ligand are 1.509 (8) and 1.499 (3) Å, respectively. For the present structures these bond lengths were sensitive to the inclusion of hydrogen atoms at calculated positions during least-squares refinement. When hydrogen atom contributions were not included,

(1) (a) Australian National University. (b) University of Sydney.

(2) (a) H. C. Freeman and I. E. Maxwell, *Inorg. Chem.*, **8**, 1293 (1969);

(b) D. A. Buckingham, L. G. Marzilli, I. E. Maxwell, A. M. Sargeson, and H. C. Freeman, *Chem. Commun.*, 583 (1969).

(3) D. A. Buckingham, P. A. Marzilli, I. E. Maxwell, A. M. Sargeson, and H. C. Freeman, *ibid.*, 473 (1969).

(4) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842 (1968).

(5) O. Foss and K. Maroy, *Acta Chem. Scand.*, **19**, 2219 (1965).

(6) J. H. Dunlop, R. D. Gillard, N. C. Payne, and G. B. Robertson, *Chem. Commun.*, 874 (1966).