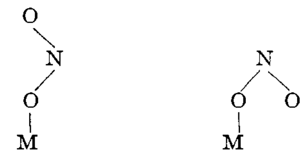
other evidence.) Thus, there is very little uncertainty in the formulation of the new complexes of this paper as *cis*- and *trans*-$Cr(en)_2(ONO)_2^+$ cations in both solution and the solid state.

Alkyl nitrites can exhibit *cis–trans* rotational isomerism, and these rotational isomers are quite different in regard to wavelengths and intensities of the vibrational structure in the 300–400-mμ band.[34] For the inorganic nitrito compounds discussed in this paper, the split peaks around 360 mμ correspond best to those found in *trans* alkyl nitrites; *i.e.*, it seems probable that the metal bonds to an oxygen atom at a position which puts it *trans* to the other oxygen atom, as shown in Figure 5 (a). This result is as expected simply on consideration of steric interaction with ethylenediamine ligands.

In conclusion, a distinguishing criterion based on spectral differences of organic nitro compounds and alkyl nitrites seems valid in relation to inorganic nitro and nitrito complexes. Such differentiation by spectroscopic means is useful in inorganic systems where absorption by the metal group in the region 300–400 mμ is not strong.



(a) *trans* (b) *cis*

Figure 5.—Possible rotational isomers for a group coordinated to the oxygen of nitrite ion.

Acknowledgments.—We thank Drs. G. Winter and G. M. Lukaszewski of the Mineral Chemistry Division, C.S.I.R.O., Melbourne, for the use of a Beckman DK-2A spectrophotometer for the reflectance spectral measurements.

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Substituent Exchange Equilibria between the Dimethyl- and Trimethylsilicon Moieties

BY KURT MOEDRITZER AND JOHN R. VAN WAZER

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Scrambling equilibria resulting from the exchange of pairs of monofunctional substituents between the difunctional dimethylsilicon and the monofunctional trimethylsilicon moieties have been studied by proton nuclear magnetic resonance. The resulting data have been evaluated in terms of two equilibrium constants, one describing the scrambling of the two kinds of substituents on the dimethylsilicon moiety and another one, an intersystem constant, representing the distribution of the two kinds of monofunctional substituents between the dimethyl- and trimethylsilicon moieties. The observed deviations of the latter constant from the value for ideal random sorting have been attributed to π-bonding effects.

In previous papers[1–3] from this laboratory, quantitative data were reported regarding substituent-exchange equilibria in systems in which two different monofunctional substituents were scrambled between two kinds of central moieties, both exhibiting a given functionality of either 2 or 3. The present paper contains examples of exchange in systems of the above kind where the monofunctional substituents exchange between central moieties of different functionalities—in this case $(CH_3)_2Si<$ and $(CH_3)_3Si–$. The studies reported herein are related to two other communications[4,5] dealing with exchange equilibria in systems where the two monofunctional substituents exchange between $CH_3Si\lessdot$ and $(CH_3)_2Si<$ and between $CH_3Si\lessdot$ and $(CH_3)_3Si–$. In all of these investigations, the methylsilicon moieties remain intact and do not exchange methyl groups under the chosen reaction conditions.

Experimental Section

Materials.—Trimethylchlorosilane and dimethyldimethoxysilane were obtained from the Anderson Chemical Co., Weston, Mich., and fractionated before use. Trimethylbromosilane,[5] dimethylbis(methylthio)silane,[6] dimethyldibromosilane,[7] and dimethylbis(dimethylamino)silane[8] were prepared according to procedures of the literature.

Equilibration and Measurements.—Mixtures of the two components, $(CH_3)_2SiZ_2$ and $(CH_3)_3SiT$, in various mole ratios were sealed in 5-mm o.d. precision nuclear magnetic resonance (nmr) tubes and heated at 120°. Equilibrium was assumed to be attained when the nmr pattern of pilot samples did not exhibit further changes upon additional heating. The samples were

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[1] K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **5**, 547 (1966).

[2] J. R. Van Wazer, K. Moedritzer, and L. C. D. Groenweghe, *J. Organometal. Chem.* (Amsterdam), **5**, 420 (1966).

[3] K. Moedritzer and J. R. Van Wazer, *J. Inorg. Nucl. Chem.*, **28**, 957 (1966).

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[5] K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **5**, 1254 (1966).

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quenched to room temperature immediately before equilibrium was measured so that the equilibrium data correspond to 120°. In view of the slow rate of equilibration experienced in the systems described in this paper, this technique is experimentally sound. Equilibrium in the systems was reached in periods less than the ones given below, with the times at which the data were obtained given in parentheses: for Z = Br and T = Cl, 16 hr at 120° (39 hr at 120°); Z = OCH_3 and T = Cl, 17 hr at 120° (49 hr at 120°); Z = SCH_3 and T = Cl, 137 hr at 120° (209 hr at 120°); Z = SCH_3 and T = Br, 45 hr at 120° (162 hr at 120°); Z = $N(CH_3)_2$ and T = Cl, 10 days at room temperature (20 days at room temperature); and Z = $N(CH_3)_2$ and T = Br, 2 hr at room temperature (23 days at room temperature).

Proton nmr spectra were obtained on a Varian A-60 spectrometer, with measurements generally being carried out in the neat liquids at the probe temperature of 33°. Only the systems involving exchange of dimethylamino groups were measured in 1:1 benzene solutions. Proton nmr chemical shifts of the dimethylsilicon and trimethylsilicon moieties in the species present at equilibrium are reported in Table I. Peak areas were determined by electronic integration or—in cases of signal overlap—by cutting out and weighing Xerox copies of the spectra.

TABLE I

PROTON NMR CHEMICAL SHIFTS OF THE DIMETHYL- AND TRIMETHYLSILICON MOIETIES OBSERVED IN EQUILIBRATED MIXTURES OF EQUIMOLAR AMOUNTS OF $(CH_3)_2SiZ_2$ *vs.* $(CH_3)_3SiT$, WHERE Z AND T ARE EXCHANGEABLE MONOFUNCTIONAL SUBSTITUENTS (IN PPM RELATIVE TO TMS AS INTERNAL STANDARD IN THE NEAT LIQUIDS)

Z	T	$(CH_3)_2$-SiT_2	$(CH_3)_2$-SiZT	$(CH_3)_2$-SiZ_2	$(CH_3)_3$-SiT	$(CH_3)_3$-SiZ
Br	Cl	−0.753	−0.900	−1.053	−0.392	−0.545
OCH_3	Cl	...[a]	−0.379[b]	−0.021[c]	−0.379	−0.052[d]
SCH_3	Cl	−0.773	−0.638[e]	−0.462[f]	−0.398	−0.267[g]
SCH_3	Br	−1.083	−0.791[h]	−0.473[i]	−0.550	−0.272[j]
$N(CH_3)_2$	Cl	...[a]	−0.313[k]	−0.027[l]	−0.263	0.000[m]
$N(CH_3)_2$	Br	...[a]	−0.543[n]	0.000[o]	−0.538	+0.075[p]

[a] Not observed. [b] CH_3O, −3.431 ppm. [c] CH_3O, −3.381 ppm. [d] CH_3O, −3.315 ppm. [e] CH_3S, −2.073 ppm. [f] CH_3S, −1.983 ppm. [g] CH_3S, −1.920 ppm. [h] CH_3S, −2.076 ppm. [i] CH_3S, −1.983 ppm. [j] CH_3S, −1.915 ppm. [k] $(CH_3)_2N$, −2.317 ppm. [l] $(CH_3)_2N$, −2.408 ppm. [m] $(CH_3)_2N$, −2.367 ppm. [n] $(CH_3)_2N$, −2.275 ppm. [o] $(CH_3)_2N$, −2.417 ppm. [p] $(CH_3)_2N$, −2.367 ppm.

Data Reduction.—The general principle of the calculation of equilibrium constants in systems involving the exchange of two kinds of monofunctional substituents between two kinds of central moieties has been discussed in detail elsewhere.[2,9] Calculations and statistical data evaluations were done on an IBM 7040 computer.

Results

In studying equilibria involving exchange of pairs of monofunctional substituents between two central moieties, one is generally interested in the distribution of these substituents between the pair of central moieties. Equation 1 describes the equilibrium that represents the above distribution, with the central moieties being the $(CH_3)_2Si<$ and $(CH_3)_3Si–$ groups. An additional equilibrium reaction is required because any scrambling reaction involving the dimethylsilicon moiety must necessarily take into account the presence at equilibrium of the species containing both of the exchangeable substituents, $(CH_3)_2SiZT$. The reaction relating this compound to the other dimethylsilicon species is

$$(CH_3)_2SiZ_2 + 2(CH_3)_3SiT \rightleftarrows (CH_3)_2SiT_2 + 2(CH_3)_3SiZ \quad (1)$$

$$2(CH_3)_2SiZT \rightleftarrows (CH_3)_2SiZ_2 + (CH_3)_2SiT_2 \quad (2)$$

Therefore, in order to describe quantitatively the over-all equilibrium situation involving the five kinds of compounds resulting from permuting Z and T on the dimethylsilicon and trimethylsilicon moieties, at least two independent equilibrium constants have to be determined. A suitable form for these constants is

$$K_I = [(CH_3)_2SiT_2][(CH_3)_3SiZ]^2/[(CH_3)_2SiZ_2][(CH_3)_3SiT]^2 \quad (3)$$

$$K_1 = [(CH_3)_2SiZ_2][(CH_3)_2SiT_2]/[(CH_3)_2SiZT]^2 \quad (4)$$

Values for these constants were computed by quantitatively evaluating proton nmr spectra of equilibrated mixtures in systems $(CH_3)_2SiZ_2$ *vs.* $(CH_3)_3SiT$. These data are presented in Table II. It is seen that the intersystem constants, K_I, in Table II, deviate from the value expected for ideal random sorting of substituents, $(K_I)_{rand}$ = 1.00. The observed deviations indicate that at equilibrium the central moieties exhibit a preference for one of the monofunctional substituents. With the exchangeable substituents being chlorine and bromine, the dimethylsilicon moiety at equilibrium has a slightly greater tendency to associate itself with bromine atoms than with chlorine atoms. A much stronger effect of preferred association at equilibrium is seen for the scrambling of halogens—chlorine as well as bromine—with CH_3S, CH_3O, and $(CH_3)_2N$ groups. The very small value of the constant K_I for these systems suggests a greater affinity at equilibrium of the halogens for the trimethylsilicon moiety than the dimethylsilicon moiety and *vice versa* for the other participating substituents.

TABLE II

EQUILIBRIUM CONSTANTS IN SYSTEMS $(CH_3)_2SiZ_2$ *vs.* $(CH_3)_3SiT$ AT 120°, WHERE Z AND T ARE EXCHANGEABLE MONOFUNCTIONAL SUBSTITUENTS

Z	T	$K_1 = \frac{[(CH_3)_2SiZ_2][(CH_3)_2SiT_2]}{[(CH_3)_2SiZT]^2}$	$K_I = \frac{[(CH_3)_2SiT_2][(CH_3)_3SiZ]^2}{[(CH_3)_2SiZ_2][(CH_3)_3SiT]^2}$
Br	Cl	0.25[a] (0.31)[b,c]	2.5 ± 0.2
OCH_3	Cl	...[g] (1.0×10^{-2})[d]	$5.3 \times 10^{-4} \pm 1.7 \times 10^{-4}$
SCH_3	Cl	0.15 (0.18)[e]	$9.8 \times 10^{-3} \pm 1.8 \times 10^{-3}$
SCH_3	Br	3.3×10^{-2} (4.9×10^{-2})[e]	$3.5 \times 10^{-3} \pm 0.3 \times 10^{-3}$
$N(CH_3)_2$	Cl[f]	...[g] (1.5×10^{-4})[d]	$8.0 \times 10^{-4} \pm 3.3 \times 10^{-4}$
$N(CH_3)_2$	Br[f]	...[g] (1.0×10^{-4})[h]	$4.2 \times 10^{-4} \pm 0.2 \times 10^{-4}$
Ideal randomness		0.250	1.0

[a] Data not in parentheses were obtained in the system $(CH_3)_2SiZ_2$ *vs.* $(CH_3)_3SiT$. [b] Data in parentheses were obtained in the system $(CH_3)_2SiZ_2$ *vs.* $(CH_3)_2SiT_2$. [c] Reference 2. [d] Reference 10. [e] Reference 3. [f] Data correspond to room temperature. [g] Constants could not be determined owing to insufficient number of components present at equilibrium. [h] Unpublished results.

The constant K_1 could be determined in only three of the seven systems investigated. Good agreement

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(9) L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, **36**, 303 (1964).

is observed for the values of this constant as determined from the data in the $(CH_3)_2SiZ_2$ *vs.* $(CH_3)_3SiT$ system and the $(CH_3)_2SiZ_2$ *vs.* $(CH_3)_2SiT_2$ system,[2,3] respectively. The presence at equilibrium of only two components, based on the dimethylsilicon moiety in the other systems, prevented the calculation of K_1. However, the values for these constants have been determined separately[10] from equilibrium data in the systems $(CH_3)_2SiZ_2$ *vs.* $(CH_3)_2SiT_2$.

The constants K_1 and K_I of Table II were used to compute theoretical distributions of substituents for the compositions for which experimental equilibrium data were obtained. A comparison of the experimental and calculated data listed in Table III shows good agreement. In those systems where the constant K_1 could not be determined from the experimental data listed in Table III, the corresponding theoretical data were computed using the values of this constant given in parentheses in Table II.

Discussion

The influence of K_I on the distribution of the constituent molecules in an equilibrated system in which two different monofunctional substituents undergo exchange between two kinds of central moieties is usually represented in the form of graphs. In a previous paper,[2] such graphs describing the equilibrium distribution of molecules in systems in which the two kinds of central moieties are both bifunctional have been shown to change considerably when K_I varied from very small to very large values. Since this is not the case for the studies reported here, it is of interest to show similar diagrams for the equilibrium distribution of molecules in systems where one central moiety, Q, is bifunctional and the other, M, is monofunctional. Letting T and Z each stand for an exchangeable monofunctional substituent, the graphs in Figure 1 were calculated for values of the intersystem constant, $K_I = [QT_2][MZ]^2/[QZ_2][MT]^2$, ranging from 10^{-20} to 10^{+20}, with the constant $K_1 = [QZ_2][MT_2]/[QZT]^2$ having the fixed value of 0.25 (ideal randomness). These graphs, however, will look considerably different when K_1 assumes values which are larger or smaller than the random value.

The results of this study confirm the general trends with regard to the preference of association at equilibrium of a given pair of monofunctional substituents on methylsilicon moieties reported elsewhere.[4,5] In each of the three systems—CH_3SiZ_3 *vs.* $(CH_3)_2SiT_2$, CH_3SiZ_3 *vs.* $(CH_3)_3SiT$, and $(CH_3)_2SiZ_2$ *vs.* $(CH_3)_3SiT$—for one substituent, Z, being Br and the other, T, being Cl, the chlorine atoms always prefer to be associated with the silicon moiety bearing the lesser number of methyl groups. However, when halogens—bromine as well as chlorine—are exchanged with other groups (OCH_3, SCH_3, or $N(CH_3)_2$, respectively) the halogens in these systems at equilibrium always prefer to be bonded to the silicon moiety containing the larger number of

TABLE III

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA (IN MOLE PER CENT) IN THE SYSTEM QZ_2 *vs.* MT WHERE $Q = (CH_3)_2Si$ AND $M = (CH_3)_3Si$

A. System $(CH_3)_2SiBr_2$ vs. $(CH_3)_3SiCl$

R ≡ Br/Si	R′ ≡ Q/Si	QBr_2	QBrCl	QCl_2	MBr	MCl
0.334[a] (0.364)[b]	0.167[a] (0.204)[b]	1.0 (0.8)[c]	8.0 (5.8)	11.4 (10.0)	26.4 (25.9)	53.2 (57.4)
0.647 (0.658)	0.324 (0.364)	6.4 (6.1)	18.3 (15.8)	11.7 (10.5)	34.7 (36.8)	29.0 (30.8)
0.978 (1.004)	0.489 (0.506)	20.8 (19.0)	22.7 (22.9)	7.1 (7.0)	36.1 (36.9)	13.4 (14.2)
1.378 (1.409)	0.689 (0.704)	47.1 (44.6)	20.7 (21.6)	2.6 (2.7)	26.0 (26.9)	3.7 (4.2)
1.658 (1.632)	0.829 (0.827)	65.6 (67.7)	15.7 (14.4)	1.4 (0.8)	16.3 (16.0)	1.1 (1.1)

B. System $(CH_3)_2Si(OCH_3)_2$ vs. $(CH_3)_3SiCl$

R ≡ Cl/Si	R′ ≡ Q/Si	QCl_2	QCl(OMe)	$Q(OMe)_2$	MCl	M(OMe)
0.167[a] (0.207)[b]	0.833[a] (0.814)[b]	-- (0.0)[c]	14.0 (10.3)	67.4 (72.9)	6.7 (6.4)	11.9 (10.4)
0.340 (0.354)	0.660 (0.649)	-- (0.0)	14.7 (14.9)	50.2 (51.0)	20.7 (19.0)	14.5 (15.0)
0.509 (0.530)	0.491 (0.471)	-- (0.0)	16.1 (16.1)	31.0 (32.9)	36.9 (34.6)	16.1 (16.3)
0.668 (0.664)	0.332 (0.350)	-- (0.1)	14.8 (14.7)	20.2 (18.4)	51.6 (51.8)	13.4 (14.9)
0.837 (0.818)	0.163 (0.195)	-- (0.2)	10.7 (10.0)	8.8 (6.1)	71.1 (73.4)	9.5 (10.3)

C. System $(CH_3)_2Si(SCH_3)_2$ vs. $(CH_3)_3SiCl$

R ≡ Cl/Si	R′ ≡ Q/Si	QCl_2	QCl(SMe)	$Q(SMe)_2$	MCl	M(SMe)
0.177[a] (0.187)[b]	0.823[a] (0.823)[b]	0.2 (0.2)[c]	11.8 (10.7)	70.3 (71.4)	6.5 (6.6)	11.3 (11.1)
0.346 (0.358)	0.654 (0.661)	0.7 (0.7)	16.3 (14.7)	49.1 (50.1)	18.1 (18.5)	15.9 (16.0)
0.504 (0.508)	0.496 (0.509)	1.2 (1.1)	16.9 (15.5)	32.8 (33.0)	31.5 (32.7)	17.6 (17.7)
0.674 (0.677)	0.326 (0.336)	1.6 (1.6)	13.9 (13.5)	18.1 (17.5)	50.6 (50.7)	15.9 (16.7)
0.839 (0.834)	0.161 (0.182)	1.6 (1.9)	8.4 (8.5)	8.2 (5.7)	71.8 (71.6)	9.9 (12.3)

D. System $(CH_3)_2Si(SCH_3)_2$ vs. $(CH_3)_3SiBr$

R ≡ Br/Si	R′ ≡ Q/Si	QBr_2	QBr(SMe)	$Q(SMe)_2$	MBr	Me(SMe)
0.186[a] (0.199)[b]	0.814[a] (0.810)[b]	-- (0.1)[c]	12.4 (12.0)	68.6 (69.3)	7.5 (6.5)	11.5 (12.1)
0.368 (0.403)	0.642 (0.620)	0.4 (0.2)	17.7 (17.3)	43.9 (46.7)	21.8 (19.1)	16.2 (16.7)
0.515 (0.534)	0.485 (0.483)	0.6 (0.3)	18.3 (17.7)	29.4 (30.5)	33.9 (33.1)	17.8 (18.4)
0.678 (0.696)	0.322 (0.325)	0.8 (0.5)	16.2 (15.7)	15.5 (15.9)	51.8 (51.1)	15.7 (16.8)
0.885 (0.908)	0.115 (0.113)	0.9 (0.7)	8.3 (7.9)	2.1 (2.9)	80.7 (79.2)	8.0 (9.3)

E. System $(CH_3)_2Si[N(CH_3)_2]$ vs. $(CH_3)_3SiCl$

R ≡ Cl/Si	R′ ≡ Q/Si	QCl_2	$QCl(NMe)_2$	$Q(NMe_2)_2$	MCl	$M(NMe_2)$
0.151[a] (0.161)[b]	0.849[a] (0.831)[b]	-- (0.0)[c]	14.8 (13.9)	68.3 (71.0)	1.3 (1.2)	15.6 (13.9)
0.324 (0.320)	0.676 (0.688)	-- (0.0)	25.1 (25.6)	43.7 (41.9)	6.9 (6.8)	24.3 (25.7)
0.450 (0.456)	0.550 (0.531)	-- (0.0)	29.3 (29.8)	23.8 (25.2)	16.3 (15.2)	30.6 (29.8)
0.635 (0.672)	0.365 (0.375)	-- (0.0)	30.3 (27.4)	7.2 (9.0)	36.9 (36.1)	25.5 (27.5)
0.819 (0.838)	0.181 (0.225)	-- (0.0)	19.9 (16.3)	2.6 (1.8)	63.9 (65.5)	13.5 (16.4)

F. System $(CH_3)_2Si[N(CH_3)_2]_2$ vs. $(CH_3)_3SiBr$

R ≡ Br/Si	R′ ≡ Q/Si	QBr_2	$QBr(NMe)_2$	$Q(NMe_2)_2$	MBr	$M(NMe_2)$
0.179[a] (0.155)[b]	0.821[a] (0.817)[b]	-- (0.0)[c]	15.1 (16.0)	66.6 (66.1)	0.4 (1.9)	17.9 (16.0)
0.346 (0.357)	0.654 (0.700)	-- (0.0)	28.0 (26.1)	42.0 (39.3)	7.7 (8.5)	22.3 (26.1)
0.514 (0.512)	0.486 (0.500)	-- (0.0)	30.0 (29.4)	20.0 (19.2)	21.2 (22.0)	28.8 (29.4)
0.689 (0.679)	0.311 (0.317)	-- (0.0)	24.5 (24.5)	7.2 (6.6)	43.4 (44.3)	24.9 (24.5)
0.838 (0.832)	0.162 (0.174)	-- (0.0)	14.9 (14.6)	2.5 (1.5)	68.3 (69.2)	14.3 (14.7)

[a] Determined from the ingredients. [b] Values in parentheses are calculated from the nmr data. [c] Values in parentheses are calculated from the equilibrium constants K_1 and K_I in Table II.

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(10) J. R. Van Wazer and K. Moedritzer, *J. Inorg. Nucl. Chem.*, **26**, 737 (1964).

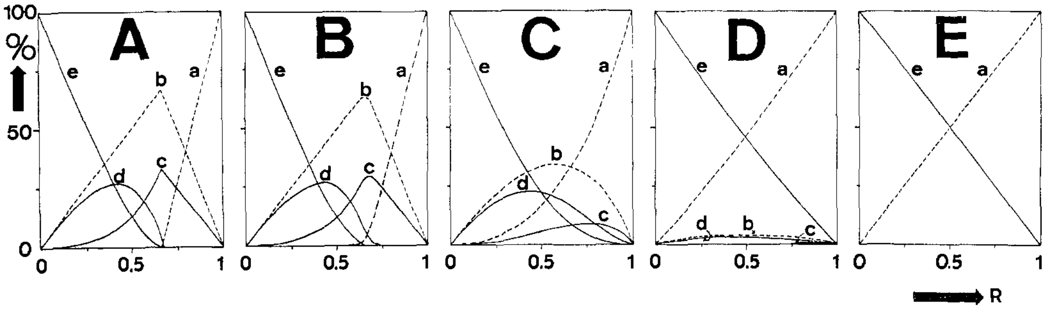

Figure 1.—Theoretically calculated equilibrium curves for systems QT_2 *vs.* MZ in which two kinds of monofunctional substituents, T and Z, are scrambled between a bifunctional central moiety, Q, and a monofunctional central moiety, M. The calculations correspond to $K_1 = 0.250$ (ideal randomness) and varying K_I: A, $K_I = 10^{-20}$; B, $K_I = 10^{-5}$; C, $K_I = 1.00$ (ideal randomness); D, $K_I = 10^{+5}$; E, $K_I = 10^{+20}$. Curve a corresponds to the concentration of the MZ molecule, b to the MT, c to the QZ_2, d to the QZT, and e to the QT_2 molecule, with the over-all composition being given by the parameter $R \equiv Z/(Q + M)$, $R' \equiv M/(Q + M)$.

methyl groups. Halogens also prefer the silicon moiety bearing the larger number of organic substituents when equilibrated with silanic hydrogen.[11]

Estimations of the enthalpy of the reaction of eq 1 based on the bond-energy approach[2] show that the values of ΔH, assuming only σ-bond contributions, differ considerably from ΔH values that were calculated from the intersystem constants K_I according to the approximation

$$\Delta H \approx \Delta F = -RT \ln [K_I/(K_I)_{rand}]$$

We attribute these differences to π-bonding effects which, therefore, appear to be the major driving force for the nonrandom equilibrations of eq 1. Quantum mechanical calculations[12] support the concept of the major influence of π contributions in these reactions.

Acknowledgment.—We wish to thank Ray E. Miller for obtaining the nmr spectra and for assistance in the data reduction.

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(11) D. R. Weyenberg, A. Bey, and P. J. Ellison, *J. Organometal. Chem.* (Amsterdam), **3**, 489 (1965).

(12) J. H. Letcher and J. R. Van Wazer, in preparation.

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Washington, D. C. 20390

The Mass Spectra of Volatile Hydrides. V. Silylarsine[1,2]

By F. E. SAALFELD and M. V. McDOWELL

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The mass spectra of silylarsine, H_2AsSiH_3, arsine, AsH_3, and diarsine, H_2AsAsH_2, have been studied. From appearance potential data, the heat of formation of several silylarsine positive ions and the following thermochemical values have been calculated (in kcal/mole): $\Delta H_f°(H_2AsSiH_3) = 37$; $D(H_2As\text{-}SiH_3) = 73$; $I(\cdot AsH_2) = 213$; $\Delta H_f°(\cdot AsH_2) = 60$; and $\Delta H_f°(\cdot SiH_2) = 81$.

Introduction

Silylarsine has been prepared by several investigators,[3,4] and although a mass spectrometer was employed in one of the studies[3] for the identification of this hydride, neither the fragmentation pattern nor any appearance potential measurements were reported. It is the purpose of this paper to report these data, the heat of formation of several of the positive ions of silylarsine, the silicon–arsenic bond dissociation energy, and the standard heat of formation of silylarsine.

Experimental Section

Silylarsine was prepared by the method of Drake and Jolly[3] in a vacuum system which contained no grease. Equimolar amounts of silane and arsine were circulated by an automatic Toepler pump through a silent electric discharge, operated at 6 kv ac, and a U trap cooled with an ethanol slush (−125°) for 6 hr. At 1-hr intervals, the discharge was stopped, the U trap was cooled with liquid nitrogen, and any volatile substances remaining in the system were quickly removed by evacuation. Silylarsine and tetrasilane, Si_4H_{10}, were separated from the other compounds formed in the discharge reaction by fractional distillation using conventional vacuum techniques.[5] It was not possible to separate completely silylarsine from tetrasilane by either distillation or with a gas–liquid chromatographic column (12 ft × 0.25-in. i.d.), packed with 10% Silicone 702 on Celite.

Several times during the course of this investigation, an explo-

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(1) Paper IV: F. E. Saalfeld and H. J. Svec, *J. Phys. Chem.*, **70**, 1753 (1966).

(2) Presented at the 14th Annual ASTM E-14 Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, May 22–27, 1966.

(3) J. E. Drake and W. L. Jolly, *Chem. Ind.* (London), 1470 (1962).

(4) B. J. Aylett, H. J. Emeléus, and A. G. Maddock, *J. Inorg. Nucl. Chem.* **1**, 187 (1955).

(5) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.