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REDISTRIBUTION EQUILIBRIA INVOLVING FLUORO AND AZIDO GROUPS ON THE DIMETHYLSILICON MOIETY

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SUMMARY

Equilibrium constants are reported for scrambling of the fluoro and azido groups with chloro, cyanato, methoxyl, methylthio, and dimethylamino groups on the dimethylsilicon moiety. The ΔF^0 values obtained from these constants show that fluorine lies first in the halogen series (*e.g.* F, Cl, Br) with respect to exchange with various other substituents and that the azido groups acts as a pseudohalide. The mixed species $(CH_3)_2SiF(N_3)$, $(CH_3)_2SiF(NCO)$, $(CH_3)_2SiF(OCH_3)$, $(CH_3)_2SiF[N(CH_3)_2]_2$, $(CH_3)_2Si(N_3)(SCH_3)$, $(CH_3)_2Si(N_3)(OCH_3)$, and $(CH_3)_2Si(N_3)[N(CH_3)_2]$ observed in this work are all new compounds.

INTRODUCTION

Within the extensive web of experimental data[1-3] now available for equilibria involving exchange of monofunctional substituents on the dimethylsilicon moiety, there is still only one piece of information available for exchange of the fluoro group[4] and none for the azido group. In this paper, equilibrium constants are presented for the exchange of these substituents with each other, the exchange of the fluoro with chloro, cyanato, methoxyl, and dimethylamino groups and the exchange of the azido with chloro, methoxyl, methylthio, and dimethylamino groups.

According to an apparently quite general rule[1,5], the deviation from random scrambling of a pair of given substituents is, to a first order, independent of the central moiety. Thus, the equilibrium constants obtained from exchange on dimethylsilicon can be applied with reasonable accuracy to other moieties and should be useful for predicting yields of products from reactions involving either of these substituents.

EXPERIMENTAL

Reagents

Dichlorodimethylsilane was purchased from Eastman Organic Chemicals, Rochester, N.Y.; and dimethoxydimethylsilane and difluorodimethylsilane from Peninsular Chemical Research, Inc., Gainesville, Fla. The first two of these chemicals were carefully distilled before use. Bis(dimethylamino)dimethylsilane[6], bis(methylthio)dimethylsilane[7], dicyanatodimethylsilane[8], and diazidodimethylsilane[9] were prepared according to the literature.

Procedures

The experimental procedures for obtaining the data were carried out according to previous descriptions[10,11]. The reagents and catalysts were placed in the correct proportions (in the case of difluorodimethylsilane, by vapor condensation at −78°) into medium-thick-walled NMR tubes (0.75 mm wall thickness, purchased from NMR-Specialties, New Kensington, Pa.) and the tubes were then sealed. In each case, pilot runs were undertaken to find out the appropriate reaction conditions and the length of time needed for cessation of all changes in overall composition, at which point equilibrium is assumed to have barely been reached. Proof that a state of equilibrium or of pseudoequilibrium was really attained came from checking for no further composition changes in periods several times longer than this equilibration time. The amount of catalyst, when used, represented about 1% of the total weight.

Measurement of the relative concentrations of the species at equilibrium was performed by electronic integration or by the cut-and-weight method. Generally, the areas of the peaks corresponding to the $(CH_3)_2Si\langle$ signals were used for calculating the equilibrium constants. In the system $(CH_3)_2Si(SCH_3)_2$ *vs.* $(CH_3)_2Si(N_3)_2$ the SCH_3 signals were also employed because of overlapping of the $(CH_3)_2Si\langle$ peaks. In the systems $(CH_3)_2Si(NCO)_2$ *vs.* $(CH_3)_2SiF_2$ and $(CH_3)_2Si(N_3)_2$ *vs.* $(CH_3)_2SiF_2$ only the area of the peak at the highest field of the $(CH_3)_2SiF_2$ triplet, could be measured independently; all others had to be obtained by subtraction of superimposed peaks.

For each system, equilibration was carried out at three different compositions (R values ≈0.5, 1.0, and 1.5), with three or four tubes being used for each R value, which is defined as the mole ratio of one of the exchangeable groups to the total silicon. However in Table 2, only a single randomly selected example is shown for each R value. The equilibrium-constant calculations were, of course, carried out using all of the data.

A Varian A-60 analytical NMR spectrometer operating at a frequency of 60 MHz was employed for the NMR-determination, using a sweep time of 100 or 250 sec per full scale (sweep width generally 50 cycles for the entire scale). The final NMR determinations were carried out after about twice the time required to reach equilibrium. The proton NMR chemical shifts of the neat equilibrated mixtures for $R = 1.0$ with internal TMS and, for comparison, of the neat unmixed species with internal TMS as standard are listed in Table 1.

New compounds and incomplete equilibration

The mixed species $(CH_3)_2SiF(N_3)$, $(CH_3)_2SiF(NCO)$, $(CH_3)_2SiF(OCH_3)$, $(CH_3)_2SiF[N(CH_3)_2]$ $(CH_3)_2Si(N_3)(SCH_3)$, $(CH_3)_2Si(N_3)(OCH_3)$, and $(CH_3)_2Si(N_3)[N(CH_3)_2]$ are new compounds. However, the species $(CH_3)_2SiFCl$[12] and $(CH_3)_2SiCl(N_3)$[13] have been described previously.

In addition to the systems of compounds which were successfully studied to give the data of Tables 2 and 3, several systems were not amenable to investigation, primarily because of incomplete equilibration. There was failure to reach equilibrium in the following systems even after holding for several months at elevated tem-

TABLE 1

^{1}H NMR CHEMICAL SHIFTS[a] (τ-values in ppm) AND COUPLING CONSTANTS (in cps) FOR THE UNDILUTED SYSTEMS $(CH_3)_2SiZ_2$ *vs.* $(CH_3)_2SiT_2$

Z	T	$(CH_3)_2SiZ_2$		$(CH_3)_2SiZT$		$(CH_3)_2SiT_2$	
		$\tau(CH_3Si)$	$\tau(Z)$	$\tau(CH_3Si)$	$\tau(Z)$	$\tau(CH_3Si)$	
Cl	F	9.276 (9.242)[b]		9.496 $J=6.36$		9.746 (9.747) $J=6.12$	(6.06)
N_3	F	9.620 (9.612)		9.663 $J=6.12$		9.737 $J=6.30$	
NCO	F	9.625 (9.646)		9.684 $J=5.70$		9.743 $J=6.06$	
OCH_3	F	9.973 (9.976)	6.56 (6.54)	9.863 $J=5.88$	6.48	9.728 $J=6.15$	
$N(CH_3)_2$	F	10.000 (10.013)	7.56 (7.99)	9.867 $J=5.64$	7.47 $J=2.4$(F)	9.745 $J=6.18$	
SCH_3	N_3	9.522 (9.532)	7.98 (7.99)	9.548	7.88	9.578	
Cl	N_3	9.238		9.438		9.596	
OCH_3	N_3	9.963	6.49	9.759	6.42	9.592	
$N(CH_3)_2$	N_3	10.007	7.52	9.772	7.40	9.607	

[a] Values relative to internal TMS, tetramethylsilane, for which τ is set equal to 10.000 ppm. [b] Shifts measured for the neat unmixed species are shown in parentheses.

peratures: $(CH_3)_2Si(SCH_3)_2$ *vs.* $(CH_3)_2SiF_2$ [catalysts tried: $AlCl_3$, $(C_2H_5)_4NF$]; as well as $(CH_3)_2SiF_2$, $(CH_3)_2Si(OCH_3)_2$, and $(CH_3)_2Si[N(CH_3)_2]_2$ *vs.* $(CH_3)_2SiH_2$ [catalysts tried: $AlCl_3$, $(C_2H_5)_4NF$, $LiAlH_4$, $(CH_3)_2SiCl_2$]. The systems $(CH_3)_2Si(SCH_3)_2$ *vs.* $(CH_3)_2SiH_2$ (catalyst: $AlCl_3$) and $(CH_3)_2Si(N_3)_2$ *vs.* $(CH_3)_2Si(NCO)_2$ could not be evaluated since, in the first case, the reaction time was too painfully slow (probably many years for completion at 100°) and, in the second case, the ^{1}H NMR chemical shifts are so close that the signals cannot be separated properly.

Data handling

Calculation of the weighted-average equilibrium constants and their standard errors was carried out according to Groenweghe[14,15] for all systems except for those in which $(CH_3)_2SiF_2$ was one of the reactants. In these fluoro systems, the ^{1}H NMR signal for $(CH_3)_2SiF_2$ is split into a triplet because of coupling with the two fluorines attached to the silicon and the ^{1}H NMR signal for the mixed compound $(CH_3)_2SiFT$ is split into a doublet. In this situation, a better calculation of the weighted-average equilibrium constant should be obtained by a method in which only the smallest peak is considered for the weighting of the individual constants obtained from each sample.

According to introductory studies carried out as a part of this investigation, the error in measuring the area of a peak by the cut-and-weigh method or by using an average value of several electronic integrations is less than 1.0% of that area (*i.e.* 1% absolute). Thus, when integrating, the relative error for an individual peak must be larger when the peak is smaller. Therefore, the reciprocal value of the relative error for the smallest peak of the spectrum is used as the weighting, *W*, for the individual equilibrium constant:

$$\text{Relative error} = 1.0\%\ \text{abs./Area of smallest peak (in } \%\ \text{abs.)} \tag{1}$$

$$W = 1/\text{Rel. error} = \text{Abs. } \%\ \text{of smallest peak} \tag{2}$$

The weighted-average equilibrium constant is then calculated from the equation

$$K_{\text{av.}} = \Sigma K \cdot W/\Sigma W \tag{3}$$

and the standard error from

$$s = \Sigma[K - K_{\text{av.}}] \cdot W/\Sigma W \tag{4}$$

RESULTS AND DISCUSSION

Redistribution equilibria from scrambling on dimethylsilicon of two kinds of monofunctional, exchangeable substituents (Z and T) can be described by the equation:

$$2\,(CH_3)_2SiZT \rightleftarrows (CH_3)_2SiZ_2 + (CH_3)_2SiT_2 \tag{5}$$

In agreement with previous results[1-3], no exchange is found for the methyl groups attached to the silicon under any of the experimental conditions employed.

The equilibrium constant describing the reaction of eqn. (5) is given by the following relationship:

$$K = \frac{[(CH_3)_2SiZ_2]\cdot[(CH_3)_2SiT_2]}{[(CH_3)_2SiZT]^2} \tag{6}$$

In Table 2, examples of the experimental data are presented. These values plus those from the replicate determinations were employed to calculate the weighted-average equilibrium constants given in Table 3. The equilibrium constants thus obtained were then used to calculate[14] the theoretical compositions given in parentheses in Table 2. The *R*-value was determined from the ingredients and the corresponding value in parentheses in Table 2 was calculated from the peak areas in the NMR spectrum. Good agreement is seen between the experimental and the calculated equilibrium compositions in Table 2. The derivation from randomness (expressed as the difference in free energy, $\delta\Delta F^0$, between the real state and the ideally random one) is about equal to the enthalpy per mole of eqn. (6) for those case in which the entropy change in the reaction is mainly due to the scrambling and not to other factors such as preferential solvation. The $\delta\Delta F^0$ corresponds to the weighted-average equilibrium constant [eqn. (3)] in the relationship:

$$\delta\Delta F^0 = -(R\cdot T/2)\cdot \ln K_{\text{obs.}}/K_{\text{rand.}} \tag{7}$$

Table 3 shows the weighted-average equilibrium constants and their standard errors, as well as the reaction conditions (time required for reaching equilibrium, reaction temperature, catalyst) and the $\delta\Delta F^0$ values. It should again be noted that the equilibrium constants are calculated from all replicates, not only from the single examples presented in Table 2.

In a previous paper[2] a diagramatic representation has been given for the values

TABLE 2

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA (in mole per cent) FOR SINGLE DETERMINATIONS IN THE SYSTEMS $(CH_3)_2SiZ_2$ *vs.* $(CH_3)_2SiT_2$

A. System $(CH_3)_2SiCl_2$ *vs.* $(CH_3)_2SiF_2$

R = Cl/Si	$(CH_3)_2SiCl_2$	$(CH_3)_2SiClF$	$(CH_3)_2SiF_2$
0.515[a]	11.78	26.47	61.75
(0.500)[b]	(12.55)[c]	(26.40)	(61.05)
1.014	36.11	31.51	32.38
(1.037)	(34.56)	(32.28)	(33.16)
1.569	67.84	23.83	8.33
(1.595)	(66.93)	(23.04)	(10.03)

B. System $(CH_3)_2Si(N_3)_2$ *vs.* $(CH_3)_2SiF_2$

R = N_3/Si	$(CH_3)_2Si(N_3)_2$	$(CH_3)_2Si(N_3)F$	$(CH_3)_2SiF_2$
0.511	10.80	26.17	63.03
(0.478)	(11.75)	(27.59)	(60.66)
1.032	34.35	33.60	32.05
(1.023)	(34.58)	(34.03)	(31.39)
1.588	67.37	24.91	7.72
(1.596)	(67.16)	(24.48)	(8.36)

C. System $(CH_3)_2Si(NCO)_2$ *vs.* $(CH_3)_2SiF_2$

R = NCO/Si	$(CH_3)_2Si(NCO)_2$	$(CH_3)_2Si(NCO)F$	$(CH_3)_2SiF_2$
0.493	8.18	32.74	59.08
(0.491)	(8.01)	(33.29)	(58.70)
1.010	27.44	43.72	28.84
(0.986)	(28.78)	(43.43)	(27.79)
1.587	66.05	28.41	5.54
(1.605)	(64.50)	(29.70)	(5.80)

D. System $(CH_3)_2Si(OCH_3)_2$ *vs.* $(CH_3)_2SiF_2$

R = OCH_3/Si	$(CH_3)_2Si(OCH_3)_2$	$(CH_3)_2Si(OCH_3)F$	$(CH_3)_2SiF_2$
0.477	55.97	41.84	2.19
(0.462)	(54.43)	(43.43)	(2.14)
0.988	17.06	67.45	15.49
(0.984)	(17.19)	(66.81)	(16.00)
1.477	2.69	47.35	49.96
(1.473)	(2.69)	(46.92)	(50.39)

E: System $(CH_3)_2Si[N(CH_3)_2]_2$ *vs.* $(CH_3)_2SiF_2$

R = $N(CH_3)_2$/Si	$(CH_3)_2Si[N(CH_3)_2]_2$	$(CH_3)_2Si[N(CH_3)_2]F$*	$(CH_3)_2SiF_2$
0.454	0.30	36.93	62.77
(0.375)	(0.56)	(44.28)	(55.16)
1.008	8.49	78.54	12.97
(0.955)	(10.63)	(79.54)	(9.83)
1.518	48.96	50.16	0.88
(1.481)	(52.46)	(46.88)	(0.66)

TABLE 2 (*continued*)

F. System $(CH_3)_2Si(SCH_3)_2$ *vs.* $(CH_3)_2Si(N_3)_2$

$R=N_3/Si$	$(CH_3)_2Si(SCH_3)_2$	$(CH_3)_2Si(SCH_3)(N_3)$	$(CH_3)_2Si(N_3)_2$
0.577	51.29	35.71	13.00
(0.617)	(52.62)	(37.05)	(10.33)
1.042	25.93	45.51	28.56
(1.026)	(25.80)	(44.21)	(29.99)
1.504	8.42	30.82	60.76
(1.523)	(7.83)	(33.93)	(58.24)

G. System $(CH_3)_2SiCl_2$ *vs.* $(CH_3)_2Si(N_3)_2$

$R=N_3/Si$	$(CH_3)_2SiCl_2$	$(CH_3)_2SiCl(N_3)$	$(CH_3)_2Si(N_3)_2$
0.481	57.30	39.86	2.84
(0.455)	(54.91)	(42.08)	(3.01)
1.055	17.25	62.02	20.73
(1.035)	(16.32)	(61.86)	(21.82)
1.471	4.20	47.78	48.02
(1.438)	(3.77)	(45.36)	(50.87)

H. System $(CH_3)_2Si(OCH_3)_2$ *vs.* $(CH_3)_2Si(N_3)_2$

$R=N_3/Si$	$(CH_3)_2Si(OCH_3)_2$	$(CH_3)_2Si(OCH_3)(N_3)$	$(CH_3)_2Si(N_3)_2$
0.528	1.30	47.34	51.36
(0.499)	(1.48)	(49.84)	(48.68)
0.953	11.09	73.83	15.08
(0.960)	(10.52)	(74.26)	(15.22)
1.485	48.12	50.30	1.58
(1.465)	(49.88)	(48.73)	(1.39)

I. System $(CH_3)_2Si[N(CH_3)_2]_2$ *vs.* $(CH_3)_2Si(N_3)_2$

$R=N_3/Si$	$(CH_3)_2Si[N(CH_3)_2]_2$	$(CH_3)_2Si[N(CH_3)_2]_2(N_3)$	$(CH_3)_2Si(N_3)_2$
0.532	0	56.71	43.29
(0.567)	(0.02)	(53.17)	(46.81)
1.026	4.13	94.95	0.92
(1.032)	(3.37)	(95.86)	(0.77)
1.527	54.08	45.92	0
(1.541)	(52.71)	(47.28)	(0.01)

[a] From the ingredients. [b] From the NMR Spectra. [c] Calculated from the weighted-average equilibrium constants.

of $\delta\Delta F^0$ corresponding to various pairs of exchangeable substituents on the dimethylsilicon moiety. In this representation the sequence of Z-substituents was arbitrarily chosen so as to give reasonably smooth curves for the majority of the T-substituents. Using the $\delta\Delta F^0$ values presented herein, it was found that the azido group conveniently inserts itself between the chloro and the thiocyanato group, and the fluoro group

TABLE 3

WEIGHTED-AVERAGE EQUILIBRIUM CONSTANTS AND RELATED VALUES FOR INTERCHANGE OF PAIRS OF SUBSTITUENTS ON THE DIMETHYLSILICON MOIETY

Substituents Z	 T	$K = \frac{[(CH_3)_2SiZ_2]\cdot[(CH_3)_2SiT_2]}{[(CH_3)_2SiZT]^2}$		Time[a] (h)	Temp. (°C)	Catalyst[b]	$\delta\Delta F^0$ (kcal/mole)
Cl	F	1.097 ± 0.075[c]	(1.079 ± 0.093)[d]	5	70	$[N(C_2H_5)_4]F$[f]	−0.50
N_3	F	0.937 ± 0.049	(0.917 ± 0.052)	<0.2	25	[j]	−0.39
NCO	F	0.424 ± 0.034	(0.422 ± 0.038)	100	70	$AlCl_3$[g]	−0.18
OCH_3	F	$(6.16 \pm 0.83)\cdot 10^{-2}$	$[(5.77 \pm 0.84)\cdot 10^{-2}]$	100	70	$AlCl_3$[h]	+0.48
$N(CH_3)_2$	F[e]	$(1.58 \pm 0.16)\cdot 10^{-2}$	$[(1.51 \pm 0.23)\cdot 10^{-2}]$	50	100	$AlCl_3$[i]	+1.02
SCH_3	N_3	0.396 ± 0.067[c]		1	25	[j]	−0.14
Cl	N_3	$(9.32 \pm 0.19)\cdot 10^{-2}$		1	25	[j]	+0.29
OCH_3	N_3	$(2.90 \pm 0.16)\cdot 10^{-2}$		<0.1	25	[j]	+0.64
$N(CH_3)_2$	N_3	$(2.7 \pm 1.0)\cdot 10^{-4}$		6	25		+2.02
Randomness		0.25					

[a] Approximate time for reaching equilibrium (the reported constants correspond to data taken after holding many times longer than this. [b] Concentration of added catalyst is ca. 1 %. [c] Weighted-average equilibrium constants and their standard errors obtained as described in the text. [d] Weighted-average equilibrium constants and their standard errors obtained according to Groenweghe[14]. [d] Some decomposition observed in this system. [f−i] Other but less effective catalysts: *f*, $AlCl_3$; *g*, $[N(C_2H_5)_4]F$; *h*, $LiOCH_3$; and *i*, $[N(C_2H_5)_4]F$. [j] Use of $AlCl_3$ increases the reaction time considerably.

between the cyanato and the thiomethyl group. This gives the expanded sequence[2] shown below, with the largest $\delta\Delta F^0$ values coming from the more widely separated pairs in this series:

$$CN > Br > Cl > N_3 > NCS(?) > NCO(?) > F > SCH_3 > H(?) > OCH_3 > N(CH_3)_2 .$$

Fig. 1 shows the diagram in which the azido and the fluoro group are included. As

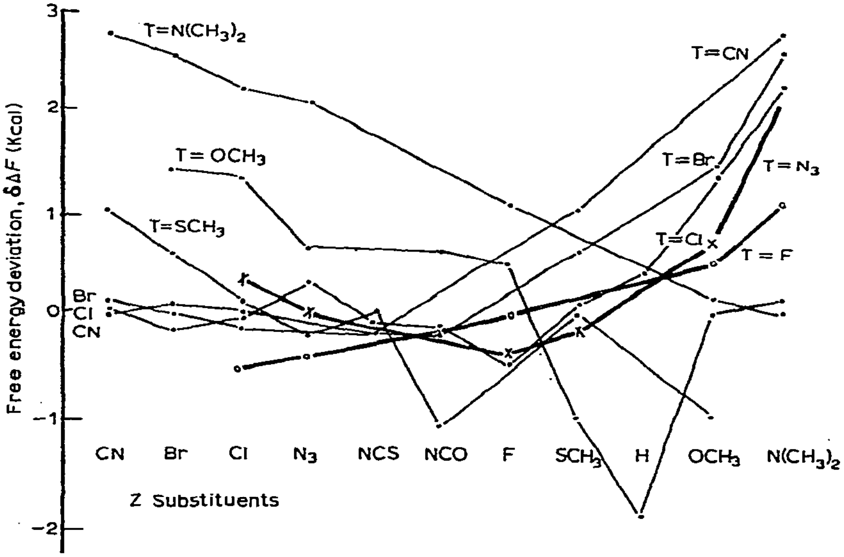

Fig. 1. Systematic plots of the deviation from randomness in the scrambling of Z and T substituents on the dimethylsilicon group, given as a function of the particular Z substituent for different kinds of T substituents. The sequence of Z substituents was chosen arbitrarily to give reasonably smooth curves.

expected, both of these groups belong to the class of substituents exhibiting increasing $\delta\Delta F^0$ values when going from left to right along the above series. Other substituents of this group are CN, Br, and Cl, so that on the grounds of quantitative thermodynamics NNN may be considered to be a pseudohalide. The azido group exhibits a small minimum in $\delta\Delta F^0$ at the position of the fluoro group in Fig. 1.

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