A STUDY OF THE EQUILIBRIA AND RATES OF EXCHANGE OF SECONDARY AMINES WITH SILYLAMINES

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ABSTRACT

EQUILIBRIA AND RATES OF EXCHANGE OF
SECONDARY AMINES WITH SILYLAMINES

by Charles A. Roth

The labile exchange of electronegative groups on organosilicon compounds has long been recognized as an important difference between silicon and carbon chemistry.

One example of this is the exchange of the nitrogen moiety of an aminosilane with another amine.

$$R_3SiNR'_2 + HNR''_2 \rightleftharpoons R_3SiNR''_2 + HNR'_2$$

There are numerous examples in the literature pertaining to the use of this reaction to prepare new silylamines. Generally, a readily available silylamine containing a low boiling amine group such as $-NH_2$, $-NHCH_3$, etc. is refluxed with another amine to give the desired silylamine. The volatile amine which is displaced is driven off.

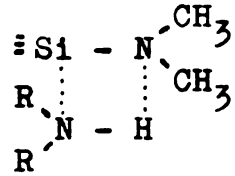
In this investigation the equilibrium constants for the reactions of a number of aliphatic and aromatic amines with several dimethylaminosilicon compounds in benzene were measured.

It was found that the ability of an aliphatic amine to displace the $(CH_3)_2N-$ group bonded to silicon was

governed by several factors. Firstly, for aliphatic amines the steric effect of the groups on nitrogen appears to be very important. Secondly, primary amines are more readily exchanged on silicon than secondary amines. Thirdly, aromatic amines exchange much more completely with a dimethylamino group on silicon than do aliphatic amines. This is probably due to d_{π}-p_{π} bonding of the aromatic nitrogen with the unfilled orbitals of silicon, giving a lower energy state in the resulting silylamine. Electron donating groups increase the extent to which exchange occurs. Finally, it is interesting to note that N-substituted anilines do not exchange.

The rate of exchange was also measured for some amines with a few silylamines. The reaction was found to be second order overall and is probably first order with respect to both amine and silylamine.

Although the mechanism has not been rigorously established, a four centered intermediate of the type shown below has been used to rationalize the data.



Both the equilibrium measurements and the rate studies were conducted by means of proton magnetic resonance spectroscopy.

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By

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I. Objectives

The exchange of an amine with a silylamine is a useful technique for the preparation of new silylamines.

$$\equiv SiNR_2 + HNR'_2 \rightleftharpoons \equiv SiNR'_2 + HNR_2$$

For synthetic use this reaction is forced to the right by removing the amine which is liberated.

One objective of this study was to measure equilibrium constants of this reaction and to show both the effects of the substituents on the amine nitrogen and the effect of various groups attached to silicon. A second objective was to measure the rate constants for representative examples of this reaction. Such studies should lead to an understanding of the nature of this reaction and the effect that the structures of the reagents have upon the course of the reaction.

II. Background

In 1949 Larsson et al. (1) demonstrated that N-(triethylsilyl)ethylamine underwent an exchange reaction when heated with primary amines according to the equation:

$$Et_3SiNHEt + H_2NR \longrightarrow Et_3SiNHR + H_2NEt$$

This discovery led to a widely used method of preparing many new silylamines from readily available silylamines. Larsson reported (2) that $Me_2Si(NHMe)_2$ "decomposed" on heating to give methylamine as one of the products. This was undoubtedly a condensation of the type

$$2\ Me_2Si(NHMe)_2 \xrightleftharpoons{\Delta} MeNHMe_2SiNMeSiMe_2NHMe + MeNH_2 + \text{some } \{Me_2SiNMe\}_x$$

From this it is clear why the compound Me_3SiNH_2 eluded isolation. Rather, the reaction of Me_3SiCl with ammonia led to the condensed product hexamethyldisilazane (3).

$$2\ Me_3SiCl + \text{excess } NH_3 \longrightarrow 2\left[Me_3SiNH_2\right] \longrightarrow Me_3SiNHSiMe_3 + 2\ NH_4Cl + NH_3$$

Since Larsson's work, there are many literature references to the preparation of silylamines by this route. An excellent review of the chemistry of silicon-

nitrogen compounds including a section on silylamine-amine exchange appeared in 1961 (4). Reference is made to more than fifty silylamines prepared by this exchange reaction.

Abel and Bush (5) found that symmetrically substituted ethylenediamines reacted with a bis-aminosilane to give cyclic compounds.

$$HRNCH_2CH_2NRH + Me_2Si(NHEt)_2 \longrightarrow \underset{(I)}{\begin{matrix} H_2C & \text{——} & CH_2 \\ | & & | \\ RN & & NR \\ & \diagdown\ \diagup & \\ & Si & \\ & Me_2 & \end{matrix}} + 2\ H_2NEt$$

At room temperature compound (I) formed a polymer which reverted to the starting material upon heating.

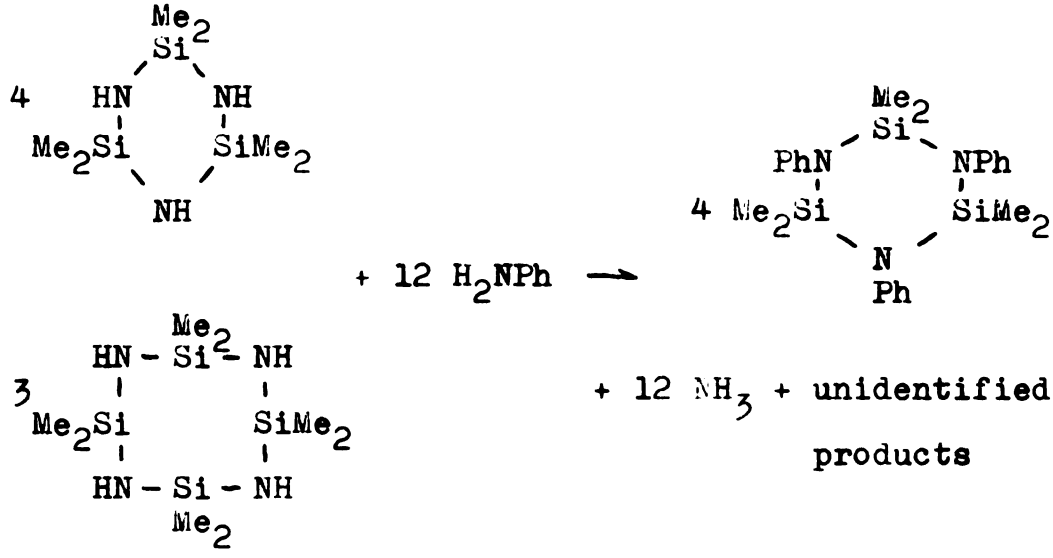
$$(I) \underset{200^\circ}{\overset{25^\circ}{\rightleftharpoons}} \text{polymer}$$

The exchange of (I) (R is Ethyl) with tetrakis-dimethylaminosilane formed a spirane.

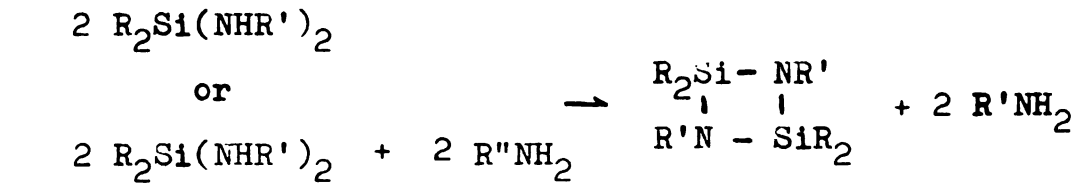
$$2\ (I) + (Me_2N)_4Si \longrightarrow \begin{matrix} & Et & & Et & \\ CH_2- & N & & N & -CH_2 \\ | & & Si & & | \\ CH_2- & N & & N & -CH_2 \\ & Et & & Et & \end{matrix} + 2\ Me_2Si(NMe_2)_2$$

Andrianov (6) has examined the reaction of aniline with octamethylcyclotetrasilazane and hexamethylcyclotrisilazane and found in each case that the products included N,N',N"-triphenylhexamethylcyclotrisilazane. In this reaction silicon-nitrogen bond cleavage took place with the formation of a six-membered ring from

an eight-membered ring.



Fink (7) has shown that heating $R_2Si(NHR')_2$ or allowing it to exchange with a primary amine in which R or R' are bulky groups led to a cyclodisilazane.



The exchange is reported (4,8) to be acid catalyzed but it has also been shown to proceed in the absence of a catalyst (9). Ammonium salts are commonly used as catalysts.

In 1961 Fessenden showed (9) that hexamethyldisilazane lost ammonia when refluxed with some secondary aliphatic and aromatic amines. In addition, the reversible nature of the reaction was demonstrated.

$$Me_3SiNHSiMe_3 + 2\ HNBu_2 \longrightarrow 2\ Me_3SiNBu_2 + NH_3$$

$$Me_3SiNBu_2 + \text{excess } NH_3 \xrightarrow[25^\circ,\ 12 \text{ hrs.}]{\text{press.}} Me_3SiNHSiMe_3 + HNBu_2 \quad 100\%$$

N-Trimethylsilylpyrrole and ammonia likewise formed pyrrole and hexamethyldisilazane. Data were also obtained concerning the effect of solvent on the extent of exchange of piperidine with hexamethyldisilazane.

Solvent	% Yield of N-trimethylsilyl piperidine
Ether	0
p-Dioxane	35
Toluene	54
Decalin	54
Quinoline	61

Several reports concerning silylamine-amine exchange reactions appear to be anomolous. Hexamethyldisilazane (II) is reported not to exchange with diethylamine, because no products boiling above the starting materials were found (10). Later (9) II (b.p. 126°) was shown to be separated only with difficulty by distillation from N,N-diethylaminotrimethylsilane (b.p. 128°). Ammonia was a product of thisreaction. Another example of an unusual result in the aminolysis of silicon compounds involved the use of N-substituted anilines. N-Methylaniline did not exchange with hexamethyldisilazane (9) and N-ethyl-

aniline did not exchange with hexamethylcyclotrisilazane (6). Contrary to these reports Panslo (11) found that tris-(ethylamino)propylsilane does exchange with N-methylaniline.

$$n\text{-}PrSi(NHEt)_3 + 2\ PhMeNH \longrightarrow n\text{-}PrSiNHEt(NMePh) + 2\ H_2NEt$$

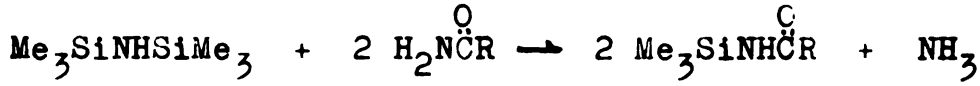
The divergences in these results may in some way be due to the extent to which the substituted aniline can approach the silicon-nitrogen bond. In 1962 Sergeeva (12) found that hydrazines will exchange with silylamines. Up to four amino groups on silicon could be exchanged, giving a series of compounds of the structure $R_{4-x}Si(NHNR'_2)_x$. This was the first example in which a silicon hydride i.e. R is H was present in the exchange of an amine with a silylamine. In 1965 Goldin and Ivanova (13) studied this aminolysis reaction with other hydrazines.

Alkoxy groups attached to silicon are not attacked during these amine-silylamine reactions as shown by the work of Larsson (14) in which benzylamine reacted with tributoxy-N-ethylaminosilane.

$$(BuO)_3SiNHEt + H_2NCH_2Ph \longrightarrow (BuO)_3SiNHCH_2Ph + H_2NEt$$

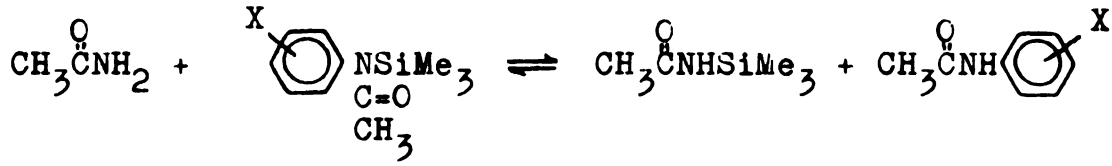
Amides react with amino groups on silicon. Wannagat (15) has shown that hexamethyldisilazane and

organic amides or imides, including urea, liberate ammonia and form an N-silylated amide.



$$Me_3SiNHSiMe_3 + 2\ H_2N\overset{O}{\overset{\|}{C}}R \longrightarrow 2\ Me_3SiNH\overset{O}{\overset{\|}{C}}R + NH_3$$

Klebe and Bush (16) quantitatively measured the equilibria of substituted trimethylsilylacetanilides with acetamide.



$$CH_3\overset{O}{\overset{\|}{C}}NH_2 + \underset{C{=}O\ CH_3}{X\text{-}C_6H_4\text{-}NSiMe_3} \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}NHSiMe_3 + CH_3\overset{O}{\overset{\|}{C}}NH\text{-}C_6H_4\text{-}X$$

An electron withdrawing group (X) shifted the equilibrium as written above to the right while an electron donating group had the opposite effect. This study used nuclear magnetic resonance spectroscopy to measure the concentration of the various species at equilibrium. It was decided to use this same method to evaluate the equilibrium constants in the reaction of amines with silylamines, described below.

III. Discussion of Results and Conclusions

The equilibrium between aliphatic primary and secondary amines or aromatic amine with each of three dimethylaminosilanes (RMe_2SiNMe_2, R=Me, Ph and $CH=CH_2$) was studied by means of nuclear magnetic resonance spectroscopy and the equilibrium constants for the reactions were calculated.

$$RMe_2SiNMe_2 + HNR'R'' \rightleftharpoons RMe_2SiNR'R'' + HNMe_2$$

With a few exceptions the equilibria were studied in benzene solutions. In most cases good reproducibility of the equilibrium constants was achieved at various concentrations of the reagents and also independently of the direction from which the equilibrium was approached.

Using ^1H n.m.r. the rates of the above reaction for a representative number of amines were also measured.

A. Equilibrium Studies

The data for the equilibrium studies can be found in Tables I, II and III.

The equilibrium constant K_c for the reaction is dependent upon several factors. In order to simplify the discussion consider first the aliphatic amines. Primary amines exchange more completely than secondary amines (9). The present work substantiates this

Table 1

Equilibrium Data for the Exchange at 38° of Amines with Trimethylsilyldimethylamine.

$$Me_3SiNMe_2 + R_2NH \rightleftharpoons Me_3SiNR_2 + HNMe_2$$

A B C D

Stoichiometry A:B	R_2NH	Moles Me_3SiNMe_2 at equil.	Moles $HNMe_2$ at equil.	K_c
1:1	Et_2NH	1.71	0.29	0.026
2:1	"	3.57	0.43	0.036
1:1	$(iso\text{-}Pr)_2NH$	1.69	0.31	0.034
1:1	$tert\text{-}BuNH_2$	1.42	0.58	0.17
2:1	"	3.14	0.86	0.21
1:1	"	1.48	0.52	0.15*
1:1	piperidine	1.06	0.94	0.78
2:1	"	2.75	1.25	0.76
1:1	"	1.29	0.71	0.30*
1:1	$PhCH_2(Me)NH$	1.09	0.91	0.70
2:1	"	2.78	1.22	0.69
1:1	aniline	0.65	1.35	4.32
2:1	"	2.28	1.72	4.62
1:1	p-chloroaniline	0.52	1.48	8.19
2:1	"	2.18	1.82	8.45
1:1	m-chloroaniline	0.61	1.39	5.20
2:1	"	2.27	1.73	4.75
1:1	m-toluidine	0.54	1.46	7.16
2:1	"	2.20	1.80	7.38
1:1	p-toluidine	0.43	1.57	13.3
1:1	Ph_2NH	No evidence of exchange		
1:1	N-methylaniline	" "	" "	

* No solvent

Table II

Equilibrium Data for the Exchange at 38° of Amines with Phenyldimethylsilyldimethylamine.

$$PhMe_2SiNMe_2 + HNR_2 \rightleftharpoons PhMe_2SiNR_2 + HNMe_2$$

A	B	C	D	
Stoichiometry A:B	R_2NH	Moles $PhMe_2SiNMe_2$ at equil.	Moles $HNMe_2$ at equil.	K_c
1:1	Et_2NH	1.62	0.38	0.05
1:1	$(iso\text{-}Pr)_2NH$	1.85	0.15	0.007
2:1	"	3.81	0.19	0.005
1:1	$PhCH_2(CH_3)NH$	1.18	0.82	0.434
2:1	"	2.91	1.09	0.448
1:1	$tert\text{-}BuNH_2$	1.49	0.51	0.117
2:1	"	3.32	0.68	0.105
1:1	aniline	0.70	1.30	3.49
2:1	"	2.32	1.68	3.80
1:1	p-toluidine	0.37	1.53	16.9
2:1	"	2.08	1.92	21.2
1:1	m-toluidine	0.54	1.46	7.30
2:1	"	2.20	1.80	7.35

Table III

Equilibrium Data for the Exchange at 38° of Amines with Vinyldimethylsilyldimethylamine.

$$ViMe_2SiNMe_2 + R_2NH \rightleftharpoons ViMe_2SiNR_2 + HNMe_2$$

A B C D

Stoichiometry A:B	R_2NH	Moles $ViMe_2SiNMe_2$ at equil.	Moles $HNMe_2$ at equil.	K_c
1:1	Et_2NH	1.64	0.36	0.047
1:1	piperidine	0.99	1.01	1.014
1:1	"	1.01	0.99	0.953
1:1	aniline	0.70	1.30	3.45
1:1	m-toluidine	0.51	1.49	8.53
2:1	"	0.20	1.80	7.35
1:1	p-toluidine	0.45	1.55	12.0
1:1	tert-$BuNH_2$	1.37	0.64	0.21

in showing that tert-butylamine exchanged by a factor of about ten times more completely than diethyl- or di-iso-propylamine. This was true regardless of the nature of the group on silicon. For similar reasons N-methylbenzylamine gave a much higher value of K_c than might have been expected. Since by definition, the exchange of dimethylamine with RMe_2SiNMe_2 would yield an equilibrium constant of 1.0, substitution of only one methyl hydrogen with phenyl in N-methylbenzylamine only slightly reduced the value of K_c. The values of K_c for the two silylamines used with piperidine seem to be inordinately high, compared to those obtained for other secondary amines. In piperidine, however, the two alkyl moieties on nitrogen are not free to rotate due to the cyclic structure of the compound. Therefore, these groups apparently do not have a large deactivating effect.

A second factor which undoubtedly also influences the reaction is the relative base strengths of the amines. Table IV gives the dissociation constants in water for the amines used in this study. In discussing the effect of the base strengths of the amines, substituted anilines as well as the aliphatic amines were considered. Only meta and para substituted anilines (substituents = CH_3 and Cl) were used in order that the steric effect of these groups on the

Table IV

Dissociation Constants of Organic Amines in Water at 25

Amine	pKa	Ka
Me_2NH	3.28	5.2×10^{-4}
Et_2NH	3.02	9.6×10^{-4}
$(iso\text{-}Pr)_2NH$	1.95	1.1×10^{-3}
$tert\text{-}BuNH_2$	3.55	2.8×10^{-4}
piperidine	2.79	1.6×10^{-3}
N-benzylmethyl-amine	4.42	3.8×10^{-5}
aniline	9.42	3.8×10^{-10}
m-chloroaniline	10.54	2.9×10^{-11}
p-chloroaniline	10.07	8.5×10^{-11}
m-toluidine	9.31	4.9×10^{-10}
p-toluidine	8.92	1.2×10^{-9}
Ph_2NH	13.12	7.6×10^{-14}
N-methylaniline	9.30	5.0×10^{-10}

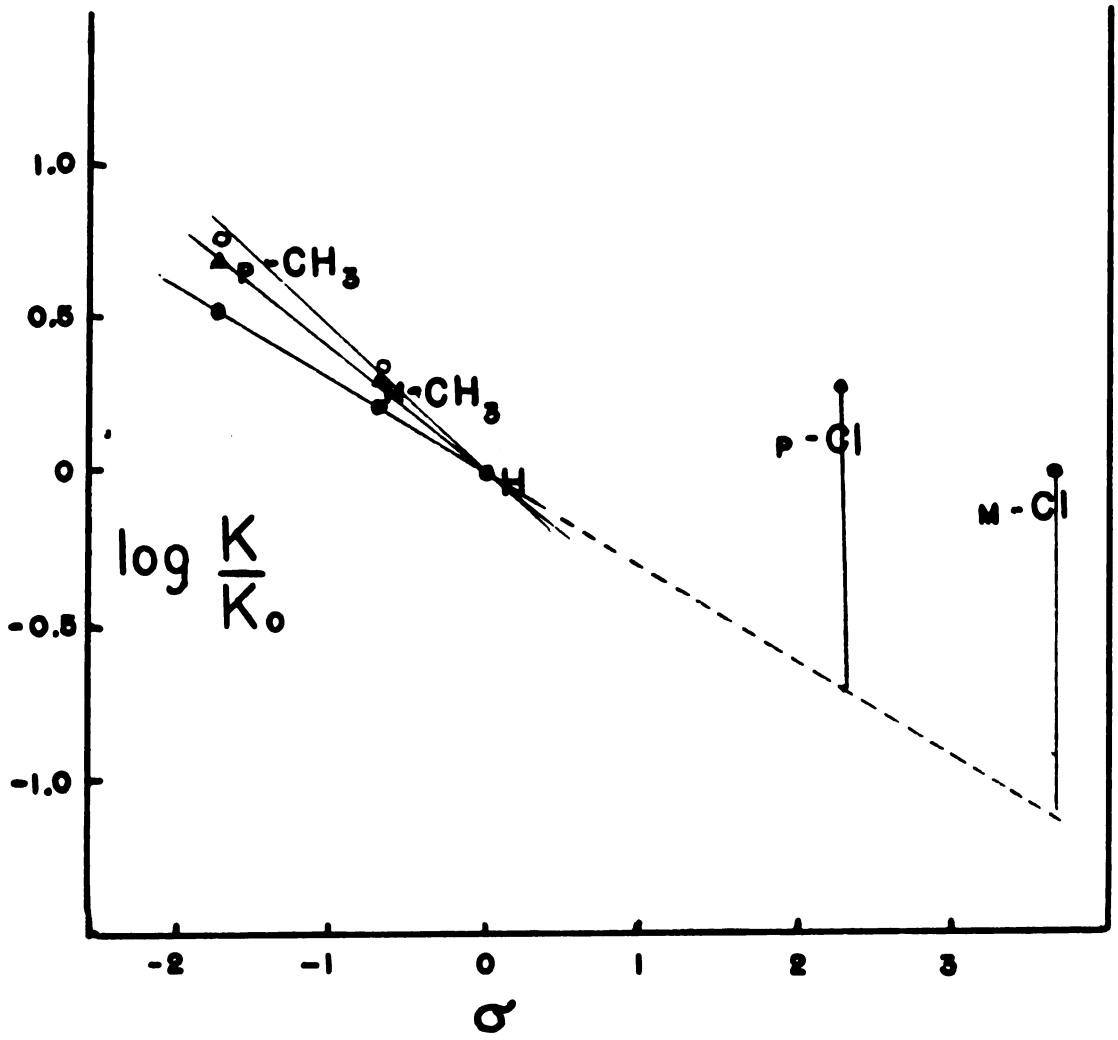
energy of the transition state would be of the same order of magnitude. The values of the equilibrium constants for all of the amines studied were grouped into two sets, those greater than 1.0 and those less than 1.0. The aliphatic amines with pKa values ranging from 2.8 to 3.5 fall into the set having $K_c < 1.0$. The aromatic amines, with the exception of N-substituted anilines which will be discussed later, all have $K_c > 1.0$. However, only qualitative conclusions can be drawn because attempts to establish a linear relationship between K_c or log K_c and K_a or pK_a failed. Thus, it was concluded that both the steric nature of the incoming amine as well as its base strength relative to the amine attached to silicon effected the position of equilibrium.

The ability of the nitrogen lone pair electrons to enter into bonding with the vacant d orbitals of silicon suggests that amines which can facilitate such bonding by making the electron pair more available sterically as in piperidine or through conjugative effects such as in the anilines ought to increase the magnitude of the equilibrium constant.

Electron donating substituents on aniline increased the equilibrium constant. A plot of log K_c/K_o*

* K_o is the equilibrium constant for the reaction of aniline with RMe_2SiNMe_2

versus σ (See below) for the meta- and para-toluidines and aniline with the three silylamines yielded a straight line.



log K/K_0 for the reaction:

$$RMe_2SiNMe_2 + H_2N\text{-}C_6H_4\text{-}X \rightleftharpoons RMe_2SiNH\text{-}C_6H_4\text{-}X + HNMe_2$$

where R is CH_3- ● , CH_2=CH- ▲ and phenyl o .

The σ values used for the substituents are:

Substituents (X)	σ
p-chloro	0.227
m-chloro	0.373
p-methyl	-0.170
m-methyl	-0.069
hydrogen	0.0

The chloroanilines were not consistent with this linear free energy relationship. More data must be collected concerning the electronic effects of substituents, but it is possible to venture a few predictions based on the available data. Only hyperconjugative structures can be written for the toluidines. Thus the resonance contribution for this group is relatively small and a linear relationship of log K/K_o can be obtained. However, resonance structures involving the amino group can be written for the chloroanilines. Therefore, the Hammett relationship fails. Taft (17) has shown that the Hammett equation usually does not hold when the substituents are capable of direct conjugation with the reaction site. This strongly supports the existence of a pseudo double bond (d_π-p_π) between the silicon and the nitrogen of the arylaminosilane. The negative value of ρ indicates that the reaction is favored by a high electron density on the nitrogen of the aniline (18). An attempt was

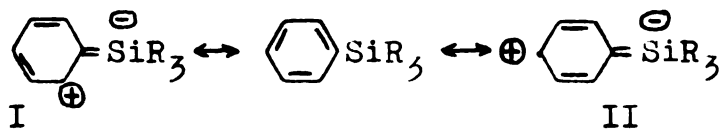
made to determine the effect of the strongly electron withdrawing nitro group on the exchange reaction. This was foiled by the fact that both meta- and para-nitroaniline are only sparingly soluble in benzene. Since all other exchanges were measured in benzene at a concentration of 1.5 M silylamine, it was not possible to include these two compounds. The exchanges were performed in nitrobenzene but the separation of the peaks necessary for a measurement of the equilibrium constant was considerably less in nitrobenzene than in benzene and no reliable results could be obtained. Others (19) have shown that this exchange reaction is solvent dependent. This work has also shown that the equilibrium constants for the exchange of aliphatic amines with silylamines in nitrobenzene were markedly different from those obtained for identical reactions in benzene as the solvent. Generally, higher values of K_c were obtained in nitrobenzene. This is probably due to increased solvation of the amine by nitrobenzene.

N-substituted anilines showed no exchange with dimethylaminosilanes. The base strengths of these amines cannot be used as criteria in this case since N-methylaniline is a stronger base than aniline. The observation that N-substituted anilines do not exchange has also been reported by others (6,9).

In addition to the amines listed in Tables I, II and III, exchange reactions involving di-n-butylamine, di-n-propylamine and ethyleneimine were also studied. In these three cases, however, the ^1H n.m.r. spectra were too complex to interpret.

The equilibrium constants obtained for the reactions of vinyldimethylsilyldimethylamine were not significantly different from those obtained with trimethylsilyldimethylamine. From these data it was concluded that the vinyl group exerts on influence similar to that of methyl on the silicon-nitrogen bond.

The equilibrium constants obtained in the reactions of phenyldimethylsilyldimethylamine were somewhat lower than those obtained for trimethylsilyldimethylamine when aliphatic amines were used. The usual effect of a phenyl group on silicon is that $d_\pi - p_\pi$ bonding of the π electrons of the ring and the vacant d orbitals of silicon causes the silicon to become less electronegative due to contributions from structures I and II.



I II

Thus, the normal electron releasing character (positive inductive effect) of the Me_3Si group is compensated by the electron donating ability of the phenyl group of $PhMe_2Si$. The result is a strengthening of the silicon-

nitrogen bond and a reduction in the ease with which exchange takes place. On the other hand, a less basic amine would prefer to displace the dimethylamino group. It was found that indeed aniline and substituted anilines exchanged with phenyldimethylsilyldimethylamine to the same extent as trimethylsilyldimethylamine.

B. Reverse Equilibrium Reactions

Although this reaction of amines with silylamines was long thought to be an equilibrium reaction, Fessenden (9) was first to experimentally show this to be true. He found that hexamethyldisilazane and di-n-butylamine liberated ammonia by the reaction:

$$Me_3SiHNSiMe_3 + 2(n\text{-}Bu)_2NH \longrightarrow 2Me_3SiN(n\text{-}Bu)_2 + NH_3$$

Upon treating trimethylsilyldibutylamine with ammonia in a bomb at room temperature for 12 hrs., hexamethyldisilazane was formed.

$$2\ Me_3SiN(n\text{-}Bu)_2 + NH_3 \longrightarrow Me_3SiHNSiMe_3 + HN(n\text{-}Bu)_2$$

In order to establish the validity of the equilibrium constants determined in the present study a number of trimethylsilyl- N,N-dialkylamines were synthesized and allowed to react with dimethylamine in benzene.

$$Me_3SiNR_2 + HNMe_2 \rightleftharpoons Me_3SiNMe_2 + HNR_2$$

The compounds prepared were:

Me_3SiNEt_2	Me_3SiNBu_2
$Me_3SiNHCMe_3$	$Me_3SiN(CH_2)_5$

Trimethylsilyldibutylamine underwent exchange with dimethylamine but, as noted earlier, the spectrum was too complex to interpret. In the other cases the values obtained for K_c^{-1} for the above reaction were in good agreement with these for K_c. See Table V.

Table V

Equilibrium Data for the Exchange at 38° of Dimethyl amine with Substituted Trimethylsilylamines.

$$Me_3SiNR_2 + HNMe_2 \rightleftharpoons Me_3SiNMe_2 + HNR_2$$

A B C D

Stoichiometry A:B	Me_3SiNR_2	Moles Me_3SiNR_2 at equil.	Moles HNR_2 at equil.	K_c	K_c^{-1}
1:1	Me_3SiNEt_2	1.72	0.28	19	0.05
2:1	"	Difficult to measure			0.03-0.04
1:1	Me_3SiNBu_2	Too complex to measure			
1:1	Me_3SiN⬡	1.07	0.93	1.33	0.75
1:1	Me_3SiNHtertBu	0.61	1.39	5.26	0.19

C. Kinetic Studies

With respect to the kinetics of this reaction it should be noted that these data are relative and not absolute measurements. In the kinetic experiments no external catalysts were used while in the equilibrium studies a small amount of $(NH_4)_2SO_4$ was added. The role of this salt only as a catalyst is indicated by the fact that the same concentrations of reagents are found in the presence and absence of the salt. The silylamines were all prepared from chlorosilanes and amines so that the possibility exists that even after distillation they may have been contaminated with trace amounts of amine hydrochloride. To compensate for this a portion of the silylamine was set aside and used exclusively for the kinetic determinations. Inthis way the salt concentration in each run was constant.

The exchange reaction follows second order kinetics and therefore is likely to be first order with respect to each reagent. The reaction probably proceeds through a four centered intermediate. The reactions of silylamines with silanols (19) and with alcohols (20) are thought to proceed by such a mechanism. Although mechanisms involving four centered intermediates are relatively uncommon in

organic chemistry, they have been postulated for a variety of reactions of silicon compounds (21).

$$\equiv SiNMe_2 + HNR'_2 \rightleftharpoons \left[\begin{matrix} \equiv Si- & NMe_2 \\ \vdots & \vdots \\ R'_2N- & H \end{matrix} \right] \rightleftharpoons \equiv SiNR'_2 + HNMe_2$$

In considering the kinetic results one observes that aniline exchanges by a factor of at least ten times faster than any of the aliphatic primary or secondary amines. The rate may be enhanced in part by the ability of the silicon nitrogen bond to achieve partial double bond character (d_π-p_π) and thus be conjugated with the aromatic ring. The initial rate of the reaction of m-chloroaniline with trimethylsilyldimethylamine substantiated the fact that arylamines react faster than aliphatic amines. This experiment was not reported here in detail since the magnetic field of the A-60 collapsed a short time after the reaction was initiated.

The rates of the reactions of vinyldimethylsilyldimethylamine and trimethylsilyldimethylamine with tert-butylamine were approximately equal. This is in accord with the results of the equilibrium studies in which little effect was noted on the magnitude of K_c when these two silylamines were compared with an amine.

The effect of solvent on this reaction is

difficult to explain. Tert-butylamine and trimethylsilyldimethylamine reacted slightly faster in benzene than when no solvent was used.

The rate of the reaction of trimethylsilyldimethylamine with piperidine at two different temperatures gave data from which it was possible to estimate an activation energy of 4.9 kcal. $mole^{-1}$ using the equation

$$\log \frac{k_2}{k_1} = \frac{E_a (T_2 - T_1)}{2.303\ R\ T_1T_2}$$

A summary of the kinetic data is presented below.

Silylamine	Amine	Temp. °C	k ($l.moles^{-1}sec.^{-1}$)
Me_3SiNMe_2	tert-$BuNH_2$	38	6.4×10^{-5}
"	" [a]	38	1.9×10^{-5}
"	piperidine[a]	0	1.5×10^{-5}
"	" [a]	38	4.6×10^{-5}
"	aniline	38	5.0×10^{-4}
$ViMe_2SiNMe_2$	tert-$BuNH_2$	38	7.8×10^{-5}

[a] No solvent

D. Summary

In summarizing the observations of this study of the reaction of amines with silyldimethylamines, one can draw the following conclusions.

With regard to the equilibrium constants for this reaction, the steric effect of groups on the amine nitrogen as well as the base strength of the amines are important. Primary aromatic amines exchange more completely than aliphatic amines. Electron donating groups on the aromatic ring increases the extent of exchange. The reaction of aromatic amines with silyldimethylamines is favored by a high electron density on the nitrogen. On the basis of this study, the influence that the groups on silicon have on the reaction is not clear. Perhaps, a detailed study of the effect of the groups on silicon would provide more information on the mechanism of this reaction as well as the nature of the silicon-nitrogen bond in general. The effect of solvent on this reaction is another area which requires more investigation.

With regard to the kinetic study of this reaction, it is clear that aromatic amines react faster than aliphatic amines with silyldimethylamines. The reaction which is second order overall is believed to be first order with respect to each reactant. The effect of the catalyst and the solvent on the rate of this

reaction is also not clear at the present time. By analogy to other similar reactions, the exchange probably proceeds through a four centered intermediate.

The above observations, although limited in scope, represent the first attempt to quantitatively measure equilibrium constants and rates of the reaction of amines with silylamines. With the growing interest in the chemistry of silylamines, it is hoped that this study will contribute to an understanding of the nature of silicon-nitrogen compounds.

IV. Experimental

A. Materials

Trimethylsilyldimethylamine and vinyldimethylsilyldimethylamine were provided by the Dow Corning Corporation. These materials were distilled through a 30 in. X 0.5 in. column packed with glass helices.

Trimethylsilyldimethylamine had b. 86°, n_D^{25} 1.3953-1.3955, d^{25} 0.733, R_D(calcd) 0.327, R_D(found) 0.324 (22). Anal. Calcd. for $C_5H_{15}SiN$: % Si, 23.93; % N, 11.93. Found: % Si, 23.8; % N, 11.92, 11.97.

The 'H n.m.r. spectrum of this compound in benzene showed two peaks one (CH_3Si) at 2 cps., the other (CH_3N) at 150 cps. relative to TMS in the ratio of 9.10/5.95. The theoretical values are 9.0/6.0.

Vinyldimethylsilyldimethylamine had b. 107-8°, n_D^{25} 1.4171, d^{25} 0.7725, R_D(calcd) 0.326, R_D(found) 0.326. Anal. Calcd. for $C_6H_{15}SiN$: % Si, 21.72; % N, 10.83. Found: % Si, 21.68; % N 10.69.

B. Preparation of Phenyldimethylsilyldimethylamine

A one liter, three-necked flask fitted with condenser, stirrer and gas inlet tube was charged with 600 cc. of pentane 341.2 g. phenyldimethylchlorosilane (2.0 moles). At room temperature dimethylamine was introduced with vigorous stirring. When the mixture became too thick to stir, it was filtered to remove the dimethylamine hydrochloride. The salt was washed several times with pentane and the washings combined and added to the original filtrate. This was treated with more dimethylamine and again filtered. This process was repeated until dimethylamine hydrochloride no longer precipitated. The solvent was removed from the liquid portion of this reaction by means of a Rinco rotating evaporator. The material was then distilled at 30 mm. Hg through a 27 X 1.5 cm. column packed with glass helices. The following product fractions were collected:

Fraction	Wt. (g.)	B.P. (C at 30 mm Hg)	n_D^{25}
1	24	103	1.4950
2	85	105	1.4958
3	101	105	1.4958
4	28	105	1.4949

Fractions 2 and 3 were pure by v.p.c. and had the following properties: b_{30} 105°, n_D^{25} 1.4958, d^{25} 0.904, R_D (calc'd) 0.323, R_D (found) 0.323.

Anal. Calc'd. for $C_{10}H_{17}SiN$: % Si, 15.66; % N, 7.82. Found: % Si, 15.70; % N, 7.86.

Fraction three was used for all the amine exchange reactions.

C. Preparation of Trimethylsilyldiethylamine

A 500 ml., three-necked flask fitted with stirrer, condenser and addition funnel was charged with trimethylchlorosilane (0.3 moles, 32.5 g.), triethylamine (0.3 moles, 30.3 g.) and 200 mls. of hexane. At room temperature diethylamine (0.3 moles, 21.9 g.) was added slowly with stirring. The resulting slurry was heated at reflux for 30 min. The triethylamine hydrochloride was filtered from the product and washed thoroughly with hexane. The hexane was removed on a water aspirator and the concentrated product distilled at atmospheric pressure through a 1.5 X 27 cm. column packed with glass helices. The following fractions were taken

Fraction	Temp.	Wt. (g.)	n_D^{25}
1	113-23	5.0	1.4062
2	124	4.0	1.4089
3	124	5.5	1.4092
4	124	11.2	1.4091

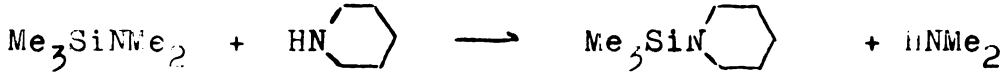
Fractions 2-5 (20.7 g. 0.142 moles were combined and v.p.c showed these to be a single component. This represents a 48% yield. The low yield is probably due to the product being lost into the crystalline

amine hydrochloride. Trimethylsilyldiethylamine had b_{745} 124°, n^{25}_D 1.4091, d^{25} 0.7627, R_D(calcd.) 0.325, R_D(found) 0.324.

Anal. Calcd. for $C_7H_{19}SiN$: % Si, 19.33; % N, 9.65. Found: % Si, 19.26; % N, 9.64.

The ^1H n.m.r. spectrum showed a triplet, J = 3 cps. at 60 cps. and a quarter, J = 3 cps. at 173 cps. These were in the ratio of 9.0/6.2/4.0. The theoretical values are 9.0/6.0/4.0.

D. Preparation of Trimethylsilylpiperidine



A 100 ml. flask fitted with a condenser and drying tube was charged with trimethylsilyldimethylamine (0.1 mole, 11.7 g.), piperidine (0.1 mole, 8.6 g.) and a small amount of NH_4Cl. The solution was refluxed for 14 hours and distilled at 30 mm Hg. The following fractions were taken:

Fraction	Wt.(g.)	Temp.	n_D^{25}
1	1.4	63	-
2	1.6	65	1.4392
3	5.6	66	1.4402
4	4.7	66	1.4401

Small amounts of dimethylamine and piperidine were found in the Dry Ice trap. Fractions 3 and 4 (10.3 g., 0.064 m., 64%) were analyzed by v.p.c. and found to be greater than 98% pure. These fractions had n_D^{25} 1.4402, d^{25} 0.837, R_D (calcd.) 0.317 R_D (found) 0.315. For this compound Birkhofer reports (23) b.p. 161° and n_D^{20} 1.4423. Anal. Calcd. for $C_8H_{19}SiN$: % Si, 17.85: % N, 8.91. Found: % Si, 17.37: % N 8.91.

The ^1H n.mr. spectrum showed a sharp CH_3Si peak at 2.0 cps., a broad $(CH_2)_3$ resonance at 87 cps. and also a broad $(CH_2)_2N$ peak at 165 cps. These were in the ratio of 9.1/5.9/4.0 the theoretical values being 9.0/6.0/4.0.

E. Preparation of Trimethylsily-tert-butylamine

A 500 cc., three necked flask fitted with a condenser, stirrer, thermometer, and addition funnel was charged with 200 cc. pentane, 60 g. triethylamine (0.6 moles), and 36.6 g. tert-butylamine (0.5 moles). At room temperature there was slowly added with stirring 54.3 g. trimethylchlorosilane (0.5 moles). The reaction mixture was stirred one hour and filtered. The amine hydrochloride was washed several times with pentane and the combined filtrates distilled through a 1.5 X 27 cm. column packed with glass helices. After removing the solvent there was obtained 26 g. (36 % yield) of pure trimethylsilyl-tert-butylamine b. 118-20°, n_D^{25} 1.4049-51, d^{23} 0.7625, R_D(calcd) 0.324 and R_D(found) 0.322.

Anal. Calcd. for $C_7H_{19}SiN$: % Si, 19.32; % N, 9.65. Found: % Si, 19.4; % N,9.63.

The ^1H n.m.r. spectrum of this compound in benzene showed two singlets one at 9 cps. (CH_3Si) and another at 64 cps. (CH_3C) in the ratio of 9/9.1. The theoretical values are 9.0/9.0.

V. Analyses of Materials

A. Organic amines

All liquid amines were analyzed for purity by vapor phase chromatography (v.p.c.) and by comparing their refractive indices with published values. The amines were stored over potassium hydroxide pellets to maintain dryness. Para-toluidine was recrystallized from water and para-chloroaniline and meta- and para-nitroaniline were recrystallized from ethanol. These amines were dried *in vacuo* and their melting points agreed favorably with literature values.

B. Silylamines

After distillation the silylamines were also analyzed for purity by v.p.c. and by comparing their physical properties with published values.

1. Silicon analyses

The silicon analyses were performed by conventional methods by the Analytical Department of the Dow Corning Corporation, Midland, Michigan.

2. Nitrogen analyses

The silylamines were analyzed for nitrogen by the non-aqueous titration method of Fritz (24). Weighed samples (0.2-0.3g.) were placed in 30 to 50 cc. of glacial acetic acid and several drops of a methyl violet indicator solution added*. This solution was

* A solution of approximately 0.1 g. methyl violet in 10 cc. of chlorobenzene

then titrated with a solution of $HClO_4$ in glacial acetic acid previously standardized with potassium hydrogen phthalate. The amount of nitrogen was calculated by means of the expression

$$\% N = \frac{\text{Vol. } HClO_4 \text{ (l.) X Norm. of } HClO_4 \text{ X } 14.01}{\text{Sample Weight}} \text{ X } 100$$

VI. Method of Conducting Equilibrium Experiments

With few exceptions the equilibrium studies were conducted as follows: 8 mm X 200 mm Pyrex glass tubes sealed on one end were charged with 2.00 millimoles of a silylamine by means of a syringe. Exactly 1.00 ml. (2.00 millimoles) of a 2.0 M solution of an amine in benzene was then added together with a few grains of $(NH_4)_2SO_4$. When the ratio of reagents was raised from 1:1 to 2:1, 4.00 millimoles of the silylamine was used with 1.00 ml. of the amine solution. An additional amount of benzene was then added to maintain a constant molarity of the silicon species. The tubes were shaken thoroughly and sealed with rubber septa. After standing a minimum of 12 hours at room temperature, a sample was withdrawn with a syringe and placed directly into an n.m.r. sample tube. The ^1H n.m.r. spectrum was recorded at a sweep width of 250 cps. This allowed both the peaks of CH_3Si at about 0 cps. and the CH_3N of the dimethylaminosilane and dimethylamine at 130 to 150 cps. to be recorded with maximum separation. In all cases the spectra were redetermined after 24 hours and no significant change was noted. It was found that in benzene solutions the $(CH_3)_2NSi$ showed a resonance at 145 cps. while $(CH_3)_2NH$ was found at 135 cps. This separation

of 10 cps. was sufficient to easily integrate the peaks and determine the amount of each moiety present. Generally, the amount of Me_2NH present was found by simple proportion relative to the total amount of CH_3Si, although the position of the CH_3Si peak varied slightly depending on the remaining groups on silicon. This allowed the total CH_3Si peaks to be integrated and set equal to the initial concentration of silylamine. The number of protons and hence the number of moles of dimethylamine could be determined. Figure 1 shows the ^1H n.m.r. spectra of (a) Me_2NH, (b) Me_2NH containing tetramethylsilane (TMS) and (c) Me_2NH containing TMS and Me_3SiNMe_2 all in benzene. A typical spectrum obtained in the equilibrium studies is reproduced in Fig. 2.

Reverse Equilibrium Reactions

$$Me_2NH + Me_3SiNR_2 \rightleftharpoons Me_3SiNMe_2 + HNR_2$$

A solution of dimethylamine (Matheson, dried in a KOH train) in benzene was prepared and found to be 2.28 M by titration with 0.1721 N $HClO_4$ in acetic acid. The correct amount of this solution and also the silylamine was loaded into a sample tube by means of a 1.00 cc. syringe. Additional benzene was then added to bring the molar concentration of the silicon

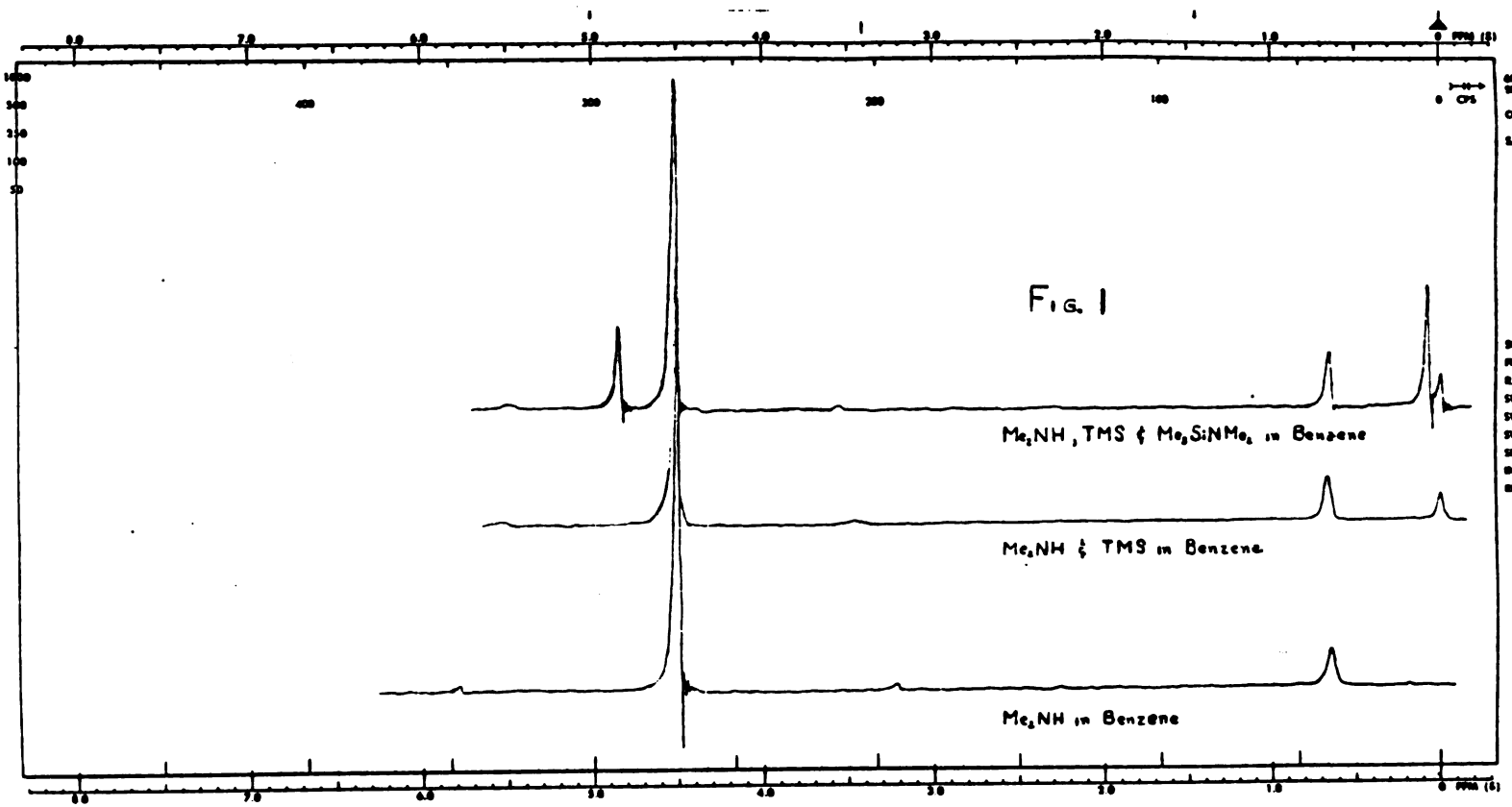
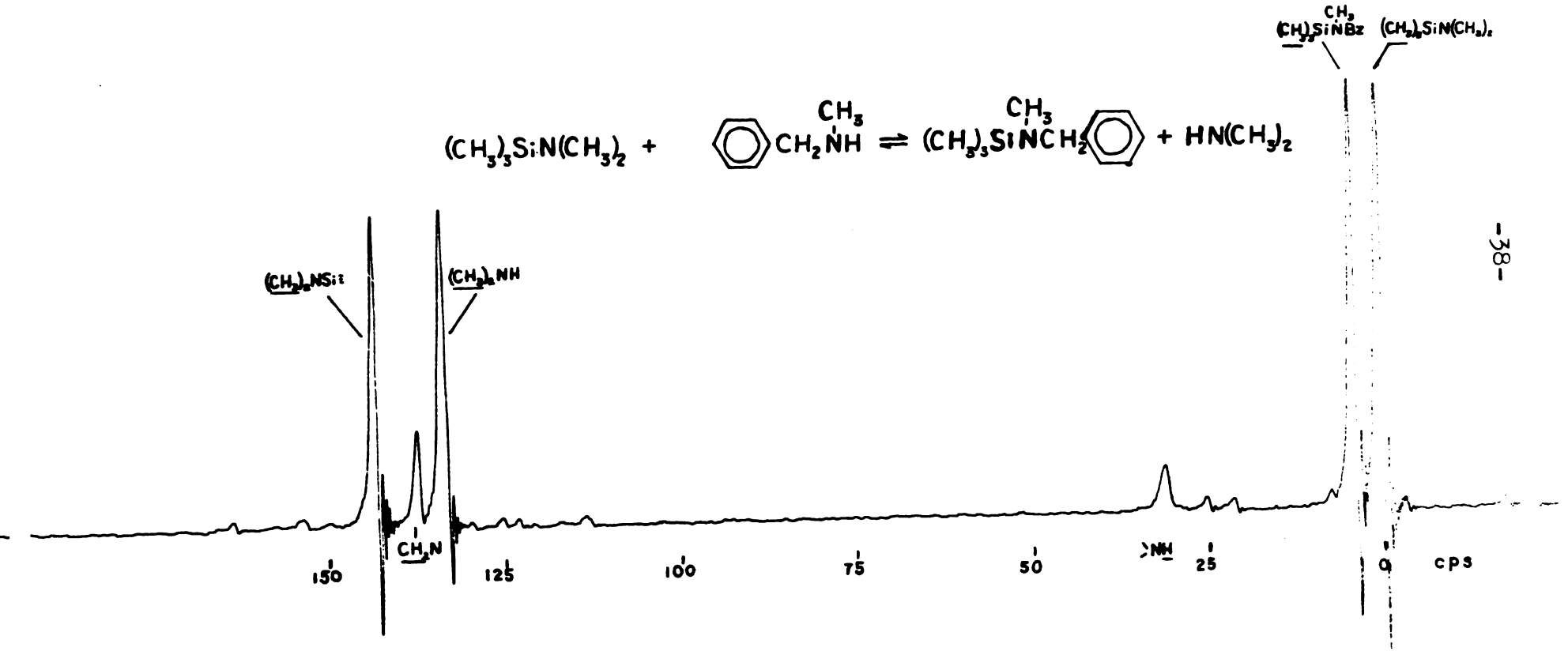

Me₂NH, TMS & Me₃Si:NMe₂ in Benzene
Me₂NH & TMS in Benzene
Me₂NH in Benzene

FIG. 1

FIG. 2


(CH3)3SiN(CH3)2 + C6H5CH2NHCH3 ⇌ (CH3)3SiNCH2C6H5 + HN(CH3)2
(CH3)3SiNBz
(CH3)3SiN(CH3)2
(CH3)3NSi
(CH3)2NH
CH2N
>NH
150
125
100
75
50
25
0
cps

species to the same value used in studying the reverse of this reaction. A few crystals of $(NH_4)_2SO_4$ were added and the system allowed to equilibrate. The position of equilibrium was then measured in a manner analogous to that described earlier. The values of K_c and K_c^{-1} are given in Table 5. The good agreement of K_c for this reaction and K_c for the reverse reaction (Cf. Table 1) verify the condition of equilibrium. An attempt was made to prepare N-anilinotrimethylsilane and p-chloroanilinotrimethylsilane in order that they might be included in this series of reactions with dimethylamine. Both of these syntheses were fraught with difficulties and pure materials were not obtained. In both cases the isolation of the anilinosilane free from traces of the aniline was difficult.

Kinetic Measurements

The kinetics of the exchange

$$\equiv SiNMe_2 + HNR_2' \rightleftharpoons \equiv SiNR_2' + HNMe_2$$

for a number of amines and silylamines was followed by ^1H n.m.r. The 10 cps. separation of the methyl protons of $(CH_3)_2NSi\equiv$ and $(CH_3)_2NH$ allowed the disappearance of the former and the appearance of the latter to be measured at various time intervals. This was done by placing the correct amount of silylamine into an n.m.r. sample tube after maximizing the magnetic field of the instrument according to standard procedures (25). The

tube was placed into the probe and the offset control adjusted so that the $(CH_3)_2NSi\equiv$ protons were as far to the left of the chart paper as possible. Adjustment of the instrument required sufficient time for the sample to reach the temperature of the probe. The correct amount of amine was then added to the n.m.r. tube and the time (T_o) recorded. After shaking the solution vigorously the tube was replaced in the probe. The spectrum amplitude was then adjusted for maximum peak heighth. A region of about 20 cps. (ca. 5 cps. on either side of the peaks) containing the methyl protons of $(CH_3)_2NSi$ and $(CH_3)_2NH$ was recorded. The offest adjustment was then increased 10 cps. (upfield) and again scanned at various time intervals from T_o. Repeating this procedure resulted in spectra of the type shown in Fig. 3 .

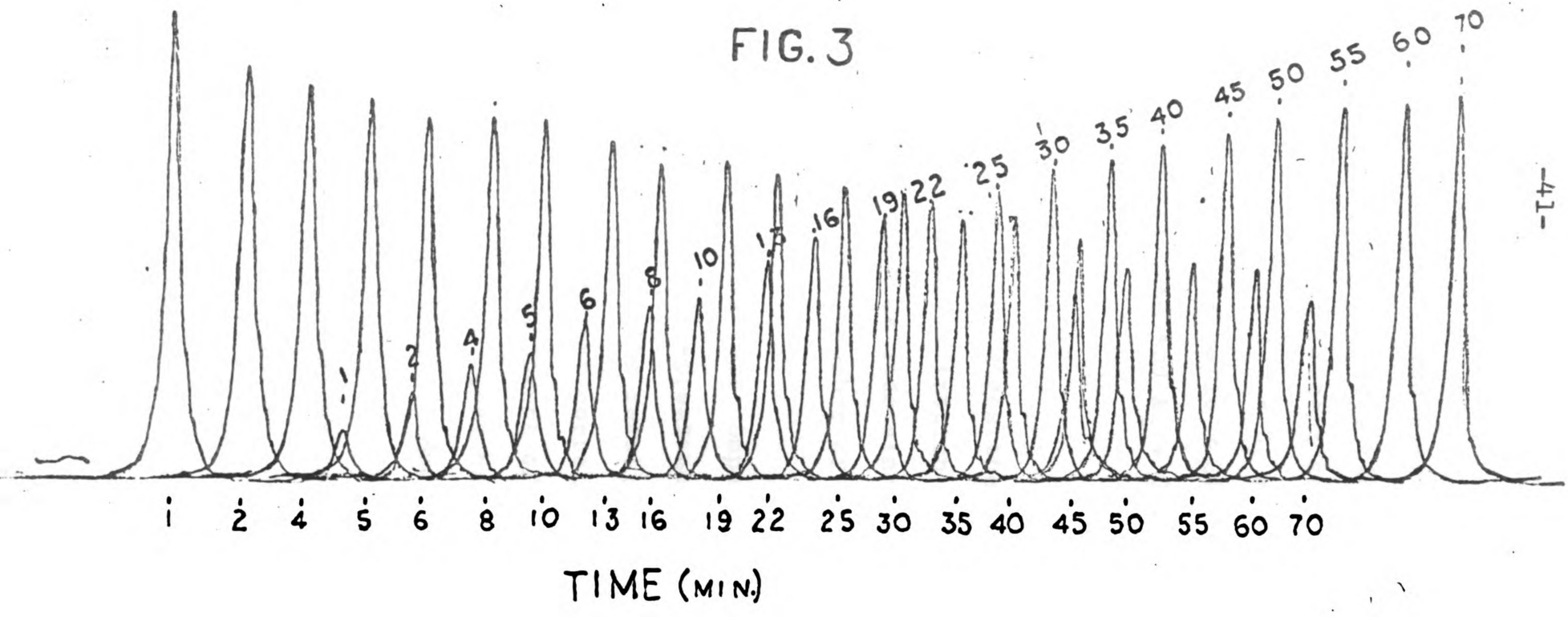
Fig.9 shows the kinetic results of such a measurement for the exchange:

$$Me_3SiNMe_2 + H_2N\langle\bigcirc\rangle \rightleftharpoons Me_3SiNH\langle\bigcirc\rangle + HNMe_2$$

The concentration of Me_3SiNMe_2 at each point can be determinded in two ways. The area of each peak can be measured by means of a planimeter and related to the (area) concentration at equilibrium. The second methcd of determing concentrations involves relative peak height measurements. The peak height ratio N of $\equiv SiN\underline{Me}_2/HN\underline{Me}_2$ can be found and the absolute concentra-


(CH3)3SiN(CH3)2 + H2N
38°
(CH3)3SiNH
+ HN(CH3)2
LOWER TIME SCALE
UPPER TIME SCALE

FIG. 3


1
2
4
5
6
8
10
13
16
19
22
25
30
35
40
45
50
55
60
70
TIME (MIN.)

tion of $\equiv SiNMe_2$ can be determined from a knowledge of the initial concentration of $\equiv SiNMe_2$. Thus if A_o moles of $\equiv SiNMe_2$ are initially present and A_t moles present at time t then $(A_o - A_t) = C_t$ moles of $HNMe_2$ must have formed. Since the ratio $\equiv SiNMe_2/HNMe_2$ or $A_t / C_t = N$ can be measured and $A_t + C_t = A_o$ then:

$$C_t = A_o - A_t$$

or

$$A_t = N (A_o - A_t)$$

Solving this expression for A_t then gives the concentration of $\equiv SiNMe_2$ at time t. A normalization of the peak heights per proton need not be made since both peaks in question contain an equal number of protons, namely six.

The two types of measurements were compared in several cases. Fig. 4 shows the disappearance of Me_3SiNMe_2 done by both methods for the reaction of Me_3SiNMe_2 with aniline. The excellent correlation of these two methods prompted the abandonment of the tedious area measurements and adoption of the peak height ratio method exclusively in later experiments. Such peak height measurements are valid when peaks corresponding to the same nuclei in the same chemical environment are being compared since identical nuclei have identical spinspin relaxation times (26). Legrow (27) showed that excellent kinetic data can be obtained in this fashion when he examined the base catalyzed rearrange-

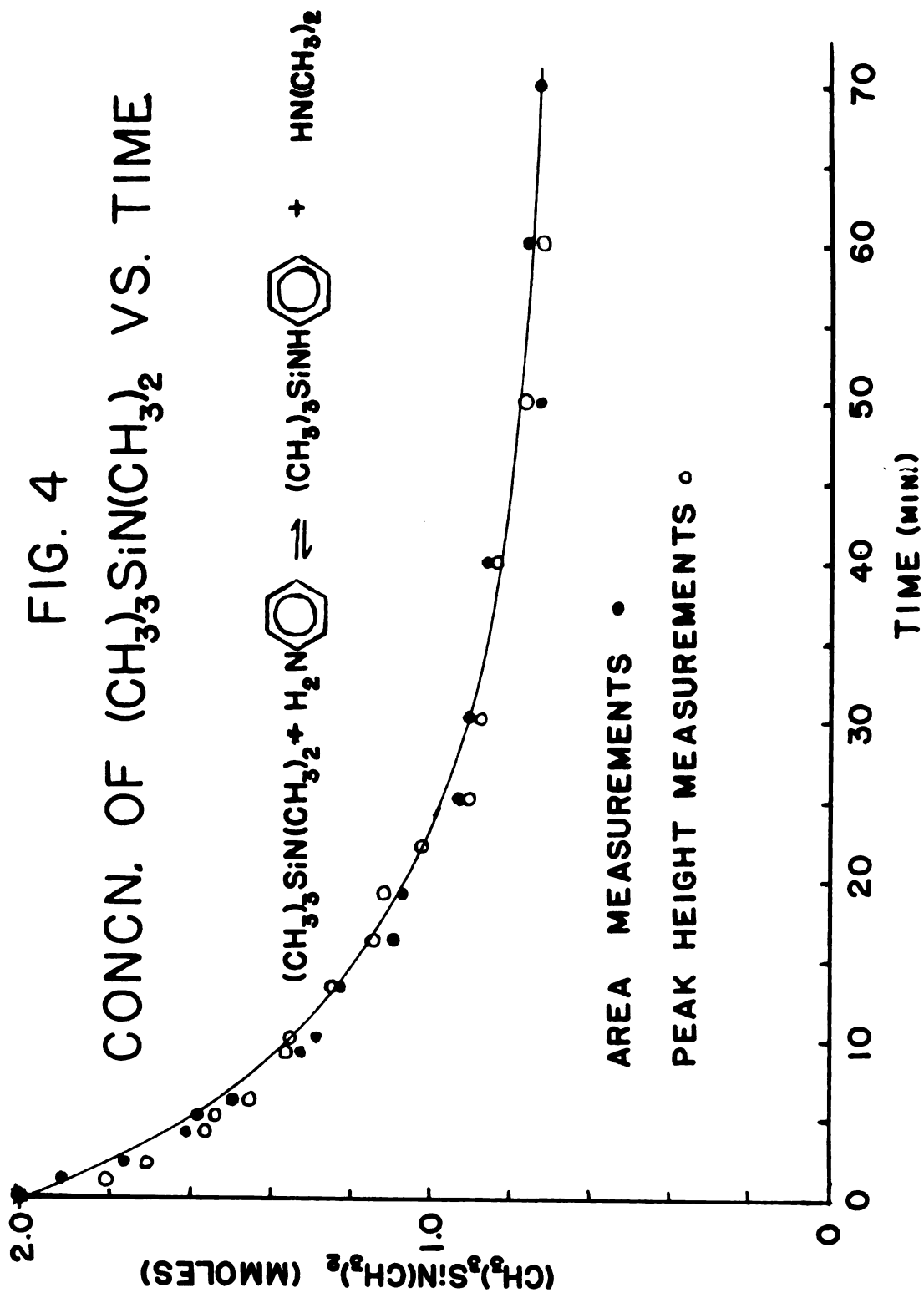
ments of silylcarbinols.

$$Ph_2MeSiC(OH)Ph_2 \xrightarrow{B:} Ph_2MeSiOCH_2Ph_2$$

The CH_3Si peak is shielded significantyly differently in each compound to allow kinetic measurements by ^1H n.m.r.

FIG. 4

CONCN. OF $(CH_3)_3SiN(CH_3)_2$ VS. TIME



VII. Treatment of Data for Kinetic Reactions

The above discussion described how the concentration of silylamine was determined at various time intervals. These data were then treated in a manner used for second order equilibrium kinetics for a system of two components (2B). For a reaction of the type:

1) $$A + B \underset{k'}{\overset{k}{\rightleftharpoons}} C + D$$

2) $$-\frac{dA}{dt} = k(AB) - k'(CD)$$

If A_o and B_o are the initial concentrations then

3) $$-\frac{dA}{dt} = kA(B_o - A_o + A) - k'(A_o - A)^2$$

This expression can then be integrated by the method of partial fractions giving

4) $$\ln \frac{(A_o - A_e)(A - A_e + \mathcal{Q})}{(A - A_e)(A_o - A_e + \mathcal{Q})} = (k - k')\mathcal{Q}t$$

where $$\mathcal{Q} = \left[\frac{1}{(K-1)}\right]\sqrt{K^2(B_o - A_o)^2 + 4A_oB_oK},$$

$$K = \frac{k}{k'} \quad \text{and} \quad A_e = \frac{-[K(B_o - A_o) + 2A_o] + \mathcal{Q}(K-1)}{2(K-1)}$$

In all experiments equal concentrations of A and B or $\equiv SiNMe_2$ and HNR_2 were used. Therefore, equation 4) becomes

$$\ln \left[\frac{(K - \sqrt{K})[A(K-1) + A_o(\sqrt{K}+1)]}{(K + \sqrt{K})[A(K-1) - A_o(\sqrt{K}-1)]}\right] = (k - k')\left[\frac{2A_o\sqrt{K}}{K-1}\right]t$$

or $\frac{dx}{dt} = k(a - x)^2 - k'x^2$.

Using reaction variable notation i.e.

$$x = A_o - A,\ a = A_o \text{ and } x_e = A_o - A_e$$

the following form of the expression is obtained

$$\ln \frac{x(a - 2x_e) + ax_e}{a(x_e - x)} = k \frac{2a(a - x_e)}{x_e} t$$

Thus a plot of

$$\frac{\ln \dfrac{x(a - 2x_e) + ax_e}{a(x_e - x)}}{\dfrac{2a(a - x_e)}{x_e}} \quad \text{versus time } t$$

should give a straight line with slope equal to the second order rate constant k.

* Throughout the remainder of this dissertation this expression is referred to as ln Z/A.

VIII. Discussion of Error

Since nuclear magnetic resonance spectroscopy was used to measure both the equilibrium constants and the rates of reaction, the discussion of error centers itself upon the inherent errors of the instrument.

Equilibrium Studies

The temperature at which equilibrium measurements are made will alter the equilibrium constant. In these experiments the temperature was necessarily that of the probe of the A-60. This was checked frequently and found not to vary more than two degrees from 38°C. With such small temperature changes the expression giving the dependence of K_c on temperature,

$$\ln K_c = \frac{\Delta H^\circ}{RT} + \text{Constant}$$

indicates that this is a small scource of error, provided that ΔH° is not large.

The solutions used to measure the equilibrium constants were examined at 12 to 16 hours after mixing. To show that the equilibrium condition had indeed been achieved many were rechecked after 24 hours and some after four days. No significant change was noted in any of those tested. From this it was con-

cluded that 12 to 16 hours at room temperature was sufficient time for the solutions to reach equilibrium.

The largest error present in this study was the area measurement of peaks by the automatic integrator of the A-60. The accurate measurement of a peak by n.m.r. is most difficult and subject to the largest error when that peak is very small. The area deviation commonly associated with n.m.r. integrals is $\pm$ 5%. In the equilibrium studies reported here the constant $CH_3Si\equiv$ peak was related to the methyl protons of dimethylamine. Thus, if a reaction formed very little dimethylamine, this peak was very small and difficult to measure unequivocally. When the equilibrium was far to the right the amount of dimethylamine was large. The expression for calculating the equilibrium constant is:

$$K_c = \frac{[Me_2NH]\quad[\equiv SiNR_2]}{[Me_2NSi\equiv]\quad[HNR_2]}$$

However, since by the equation for the reaction, each mole of dimethylamine which is formed also forms a mole of $\equiv SiNR_2$ this reduces to:

$$K_c = \frac{[Me_2NH]^2}{[Me_2NSi\equiv]\quad[HNR_2]}$$

Consequently a variation in a rather large value of the dimethylamine concentration appreciably alters the value of K_c. The optimum conditions for having the smallest error in the equilibrium constant occur when the numerator and denominator are nearly unity. That is when the peak areas for both Me_2NH and $Me_2NSi\equiv$ are nearly equal.

The reactions in which no solvent was used are probably least reliable since the dimethylamine was not very soluble in these solutions. Evidence to this effect was observed by a slight pressure of dimethylamine on the ampules. Benzene was a good solvent for these reactions since dimethylamine is soluble in it and the aromatic protons were far enough downfield in the n.m.r. not to interfere with the spectrum of the reactants.

The measurement of exact amounts of reagents by means of a syringe is probably reproducible within one per-cent.

Kinetic Studies

In addition to the errors discussed above the kinetic determinations were effected by descrepancies in measuring the time of each succesive point. In an attempt to reduce this contribution to the error it was found that at a sweep time of 250 sec. (full chart)

15-20 sec. were required for the pen to scan the two peaks in question. The pen was started approximately 10 sec. prior to the time of measurement thus reducing this error to about ± 10 sec.

In some cases the magnetic field collapsed after a portion of the kinetic run was made and the experiment had to be terminated.

IX. Kinetics of the Reaction of Trimethylsilyldimethylamine with tert-Butylamine in the Absence of Solvent at 38° C

$$Me_3SiNMe_2 + H_2NCMe_3 \rightleftharpoons Me_3SiNHCMe_3 + HNMe_2$$

The exchange reaction in the absence of a solvent led to a lower equilibrium constant. Values of 0.17, 0.18 and 0.21 were obtained when the reaction was performed in benzene. With no solvent a value of 0.126 was found for K_c. Of the initial 3.77 moles/l. of Me_3SiNMe_2, 2.78 moles/l. was present at equilibrium. The following data were obtained for this system.

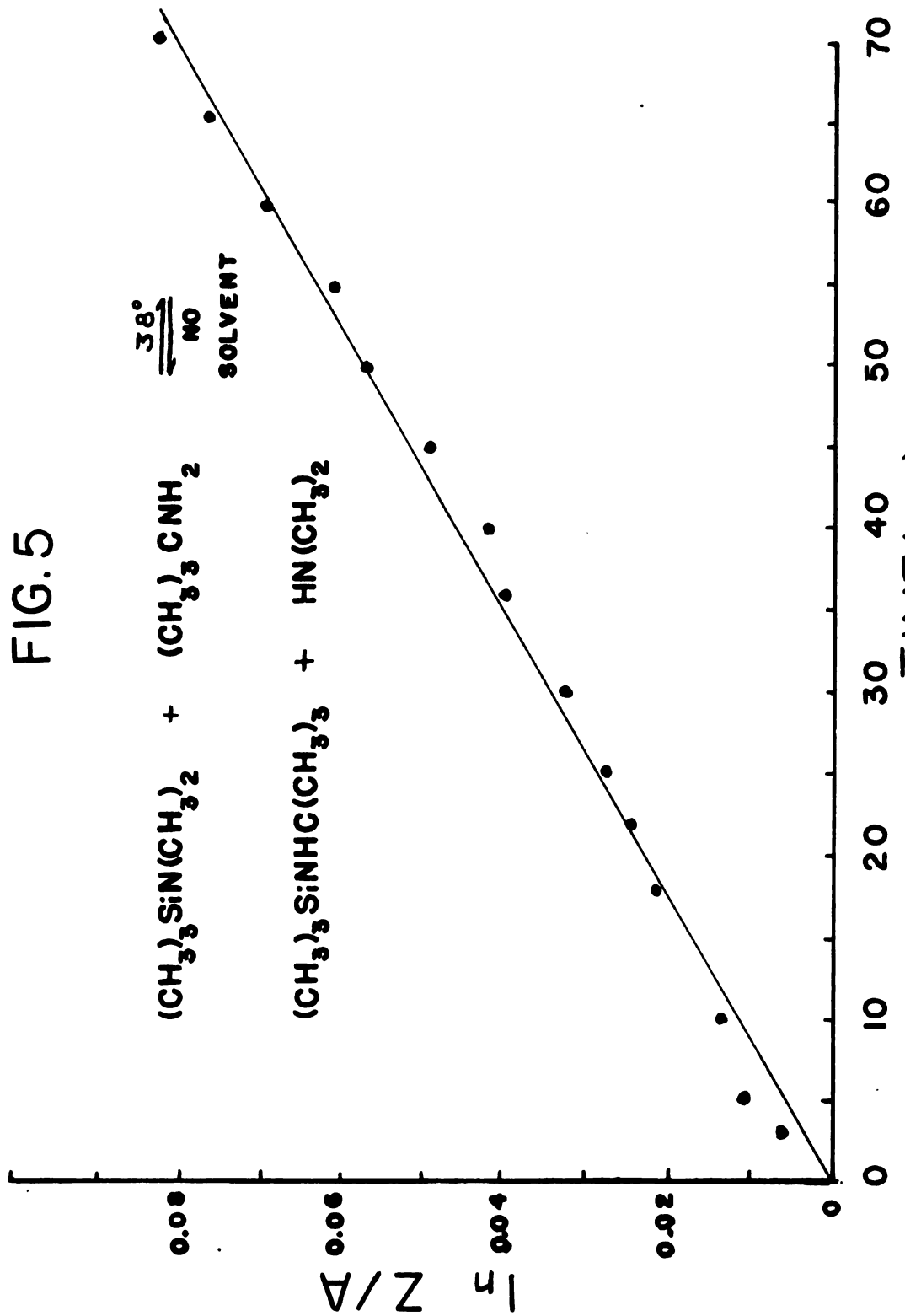
Time (min.)	Me_3SiNMe_2 (moles/l.)	ln Z/A*
0	3.77	0
3	3.68	0.0065
5	3.62	0.0110
10	3.59	0.0134
18	3.49	0.0217
22	3.45	0.0252
25	3.42	0.0279
30	3.37	0.0328
36	3.30	0.0401
40	3.28	0.0423
45	3.22	0.0495

* See footnote bottom of page 46

50	3.16	0.0575
55	3.13	0.0618
60	3.08	0.0700
65	3.04	0.0775
70	3.01	0.0837

When the terms in the last row were plotted versus time a straight line was obtained as shown in Fig. 5. The slope of this line was found to be 1.94 X 10^{-5} l. $moles^{-1}sec.^{-1}$.

FIG. 5


$(CH_3)_3SiN(CH_3)_2$ + $(CH_3)_3CNH_2$ $\rightleftharpoons$ $(CH_3)_3SiNHC(CH_3)_3$ + $HN(CH_3)_2$
38°
NO
SOLVENT
$\ln Z/A$
0.08
0.06
0.04
0.02
0
0
10
20
30
40
50
60
70
TIME (MIN.)

X. Kinetics of the Reaction of Trimethylsilyldimethylamine with tert-Butylamine at 38° C in Benzene

$$Me_3SiNMe_2 + H_2NCMe_3 \rightleftharpoons Me_3SiNHCMe_3 + HNMe_2$$

At equilibrium 1.076 moles/l. of Me_3SiNMe_2 remained of the initial 1.515 moles/l.. This kinetic experiment gave a value for K_c of 0.18 which is in agreement with the two values of 0.17 and 0.21 obtained in the equilibrium studies. The data collected for the reaction are compiled below.

Time (min.)	Me_3SiNMe_2 (moles/l.)	ln Z/A*
0	1.515	0
3	1.492	0.0101
8	1.439	0.0350
10	1.417	0.0461
15	1.394	0.0581
25	1.334	0.0932
35	1.273	0.1360
75	1.159	0.2640

The plot of the terms in the last column versus time gave a straight line with slope k equal to 6.4 X 10^{-5} l. $moles^{-1}sec.^{-1}$. See Fig. 6.

* See footnote bottom of page 46.

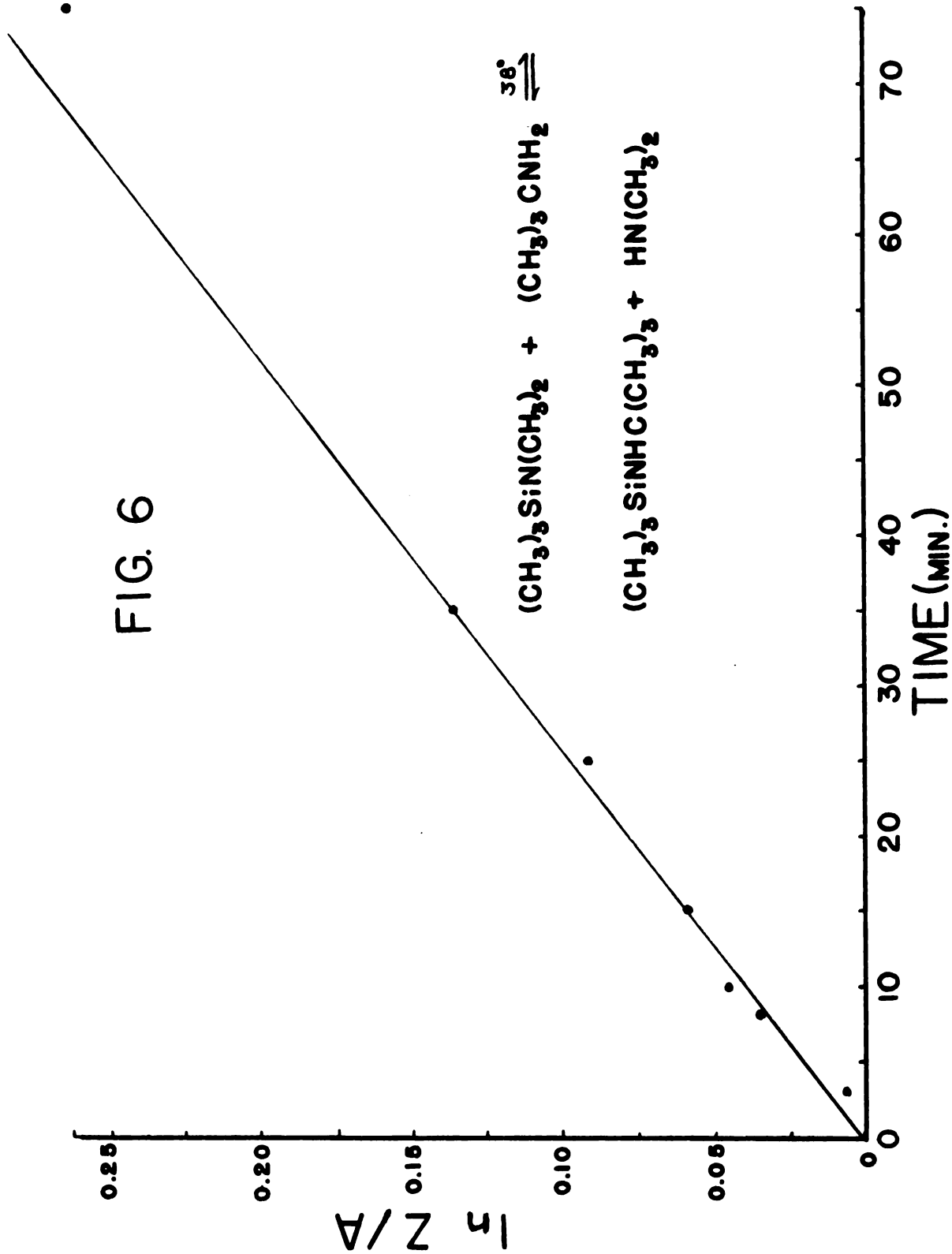

$(CH_3)_3SiN(CH_3)_2 + (CH_3)_3CNH_2 \xrightleftharpoons{38^\circ} (CH_3)_3SiNHC(CH_3)_3 + HN(CH_3)_2$
ln Z/A
TIME (MIN.)
0.25
0.20
0.15
0.10
0.05
0
10
20
30
40
50
60
70

FIG. 6

XI. Kinetics of the Reaction of Vinyldimethylsilyldimethylamine with tert-Butylamine at 38° C in Benzene

$CH_2{=}CHMe_2SiNMe_2 + H_2NCMe_3 \rightleftharpoons CH_2{=}CHMe_2SiNHCMe_3 + HNMe_2$

Of the initial 1.510 moles/l. of $ViMe_2SiNMe_2$ for this reaction there was found 1.035 moles/l. remaining at equilibrium. This results in an equilibrium constant of 0.19 which is in agreement with the value of 0.21 obtained in the equilibrium study. The data for this reaction are shown below.

Time (min.)	$ViMe_2SiNMe_2$ (moles/l.)	ln Z/A*
0	1.510	0
4	1.455	0.0251
6	1.411	0.0469
10	1.388	0.0588
12	1.373	0.0675
15	1.359	0.0752
19	1.343	0.0849
25	1.298	0.1132
30	1.261	0.1402
35	1.238	0.1589
40	1.208	0.1862
45	1.185	0.210
50	1.163	0.236

* See footnote bottom of page 46.

55	1.148	0.257
60	1.139	0.270

When the last column was plotted versus time a straight line with slope equal to the second order rate constant k of 7.75×10^{-5} l. moles^{-1}sec.$^{-1}$ was obtained. See Fig. 7.

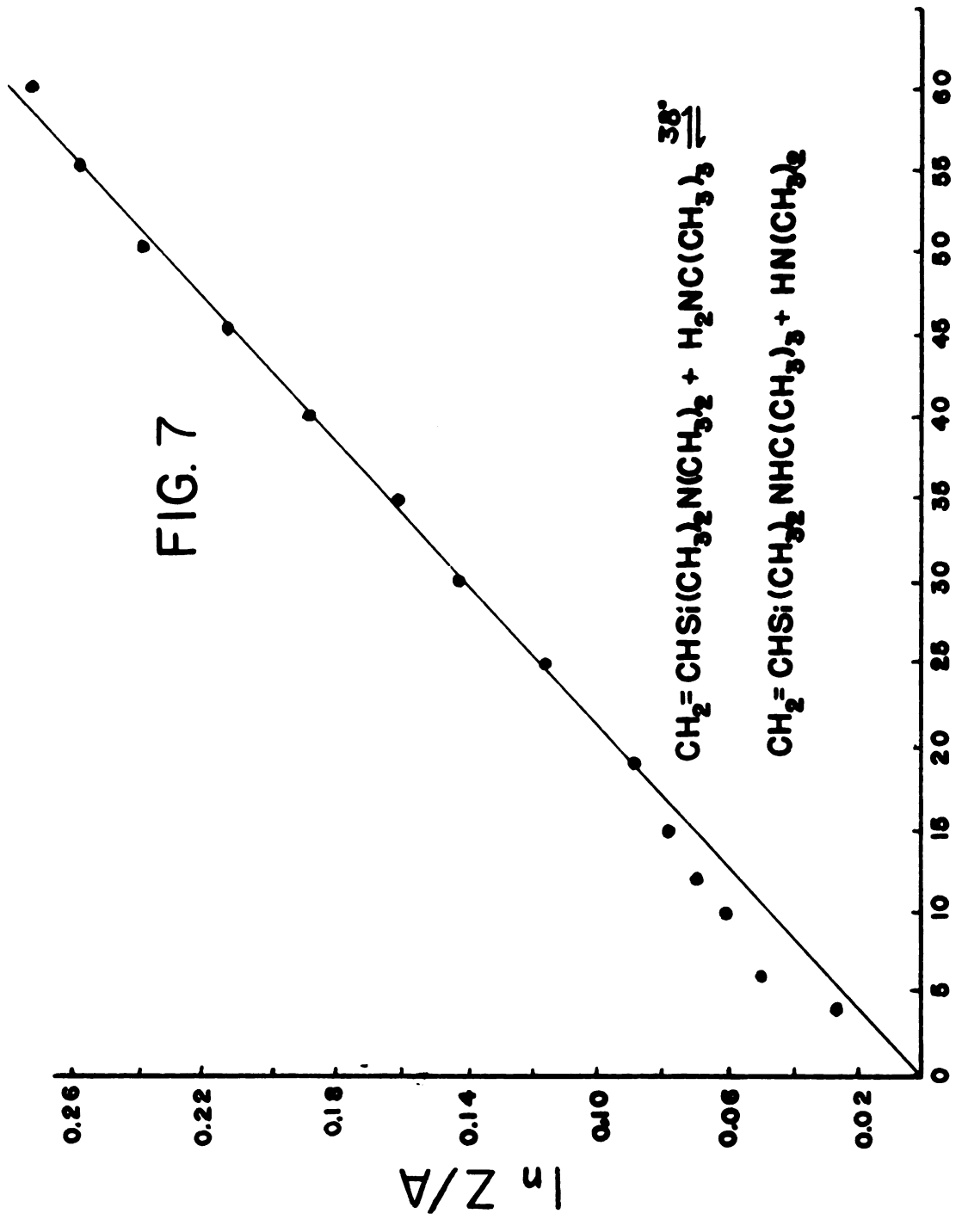
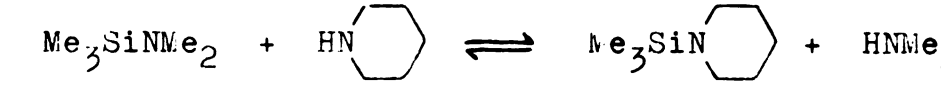

ln Z/A
0.26
0.22
0.18
0.14
0.10
0.06
0.02
0
5
10
15
20
25
30
35
40
45
50
55
60
TIME (MIN.)
$CH_2=CHSi(CH_3)_2N(CH_3)_2 + H_2NC(CH_3)_3 \xrightleftharpoons{38°}$
$CH_2=CHSi(CH_3)_2NHC(CH_3)_3 + HN(CH_3)_2$

FIG. 7

XII. Kinetics of the Reaction of Trimethylsilyldimethylamine with Piperidine at 0° and 38° with No Solvent



In an attempt to determine the energy of activation for this reaction the exchange of piperidine with trimethylsilyldimethylamine was examined in the absence of any solvent. Unfortunately, because of mechanical difficulties with the n.m.r. instrument, measurements could only be taken at two temperatures. 0° and 38° C. Thus, there is considerable ambiguity in the activation energy. A value of 4.9 kcal. mole $^{-1}$ has been estimated on the basis of the available data. After these data were obtained, a second error was discovered. It will be noted that the intercept is not zero for either the kinetic measurements. Apparently some error was made in either the initial amount of one of the reagents or in the measurement of x_e, the amount of Me_3SiNMe_2 which has reacted. Since both plots intercept the ordinate at 0.012 the error was probably consistent in both experiments. Therefore the important aspect of these measurements, the slope, will be correct.

At 0°C

Initially the concentration of Me_3SiNMe_2 was 3.864 moles/l.; at equilibrium it was 2.420 moles/l.

Time (min.)	Me_3SiNMe_2 (moles/l.)	ln Z/A*
0	3.86	0
4	3.67	0.0135
7	3.62	0.0173
11	3.57	0.0213
15	3.48	0.0289
19	3.46	0.0306
23	3.45	0.0314
29	3.39	0.0368
35	3.28	0.0476
43	3.24	0.0519
48	3.21	0.0550
55	3.18	0.0585
65	3.06	0.0733

A plot of ln Z/A yielded a straight line with slope k equal to 1.5×10^{-5} l. $moles^{-1} sec.^{-1}$. See Fig. 8.

* See footnote bottom of page 46.

At 38°C

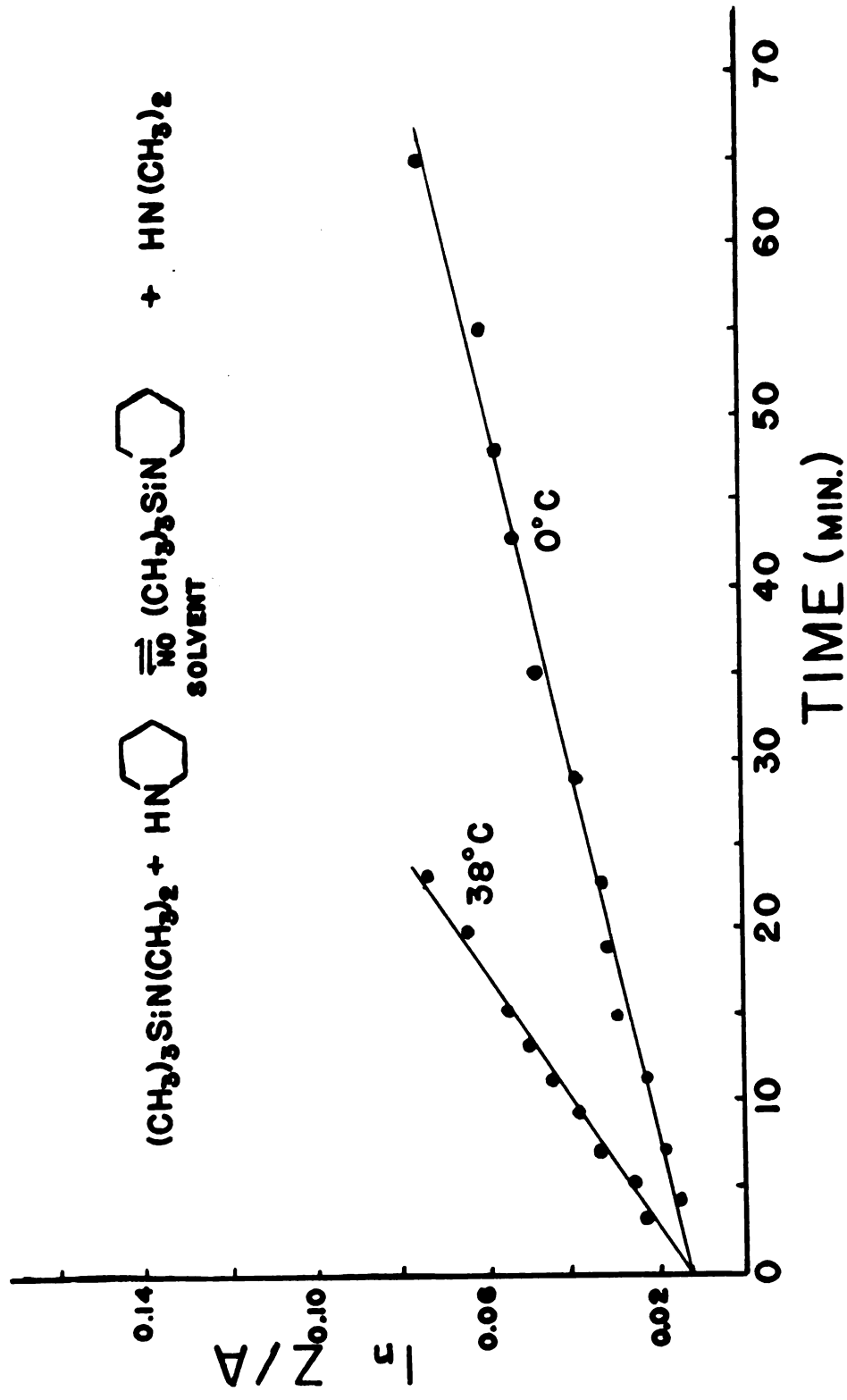
Initially the concentration of Me_3SiNMe_2 was 3.86 moles/l.; at equilibrium it was 2.50 moles/l..

Time (min.)	Me_3SiNMe_2 (moles/l.)	ln Z/A*
0	3.86	0
3	3.55	0.0227
5	3.48	0.0286
7	3.42	0.0338
9	3.36	0.0395
11	3.31	0.0443
13	3.24	0.0517
15	3.22	0.0539
20	3.13	0.0644
23	3.05	0.0749
30	3.00	0.0824
35	2.93	0.0939

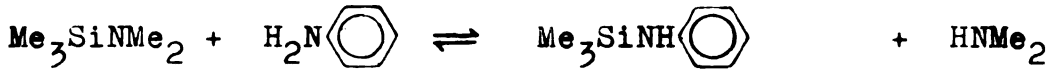
A plot of ln Z/A yielded a straight line with slope k equal to 4.6×10^{-5} l. $moles^{-1} sec.^{-1}$. The above two plots are shown in Fig. 8.

* See footnot bottom of page 46.

FIG. 8


(CH3)3SiN(CH3)2 + HN
(CH3)3SiN
+ HN(CH3)2
SOLVENT
38°C
0°C
0.14
0.10
0.06
0.02
0
10
20
30
40
50
60
70
TIME (MIN.)
ln Z/A

XIII. Kinetics of the Reaction of Trimethylsilyldimethylamine with Aniline at 38° C in Benzene



It was found that at equilibrium there was 0.537 moles/l. of Me_3SiNMe_2 remaining. Since initially there was 1.515 moles/l., x_e becomes 0.978 moles/l.. The following data were collected from these values.

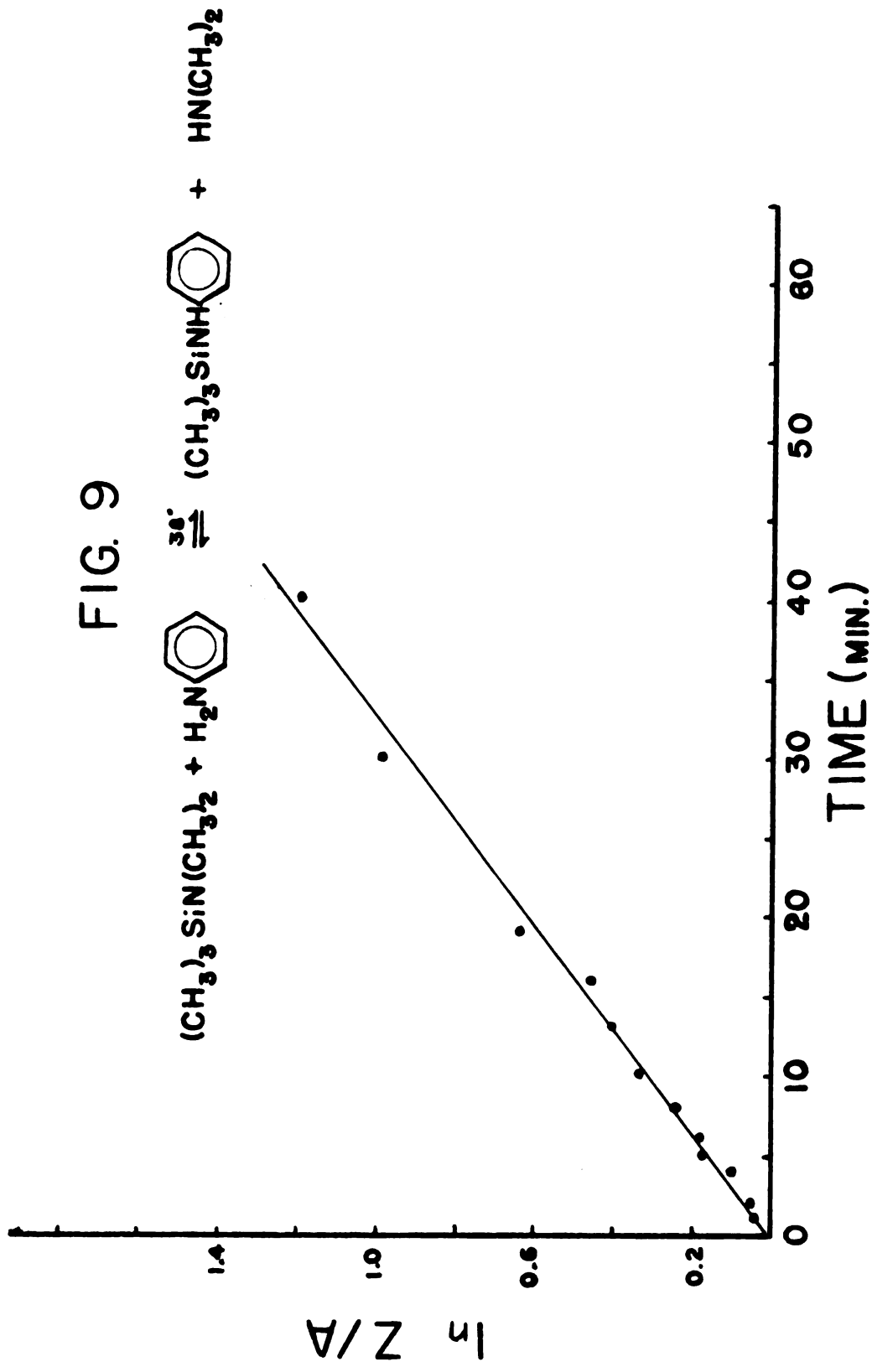
Time (min.)	Me_3SiNMe_2 (moles/l.)	ln Z/A*
0	1.515	0
2	1.438	0.035
4	1.318	0.098
5	1.204	0.171
6	1.180	0.188
8	1.113	0.241
10	1.022	0.326
13	0.955	0.400
16	0.918	0.448
19	0.804	0.631
30	0.678	0.989
40	0.637	1.185

Plotting the data from the last column versus time (Fig. 9) gave a straight line with slope k equal to the second order rate constant 5.0×10^{-4} l. $moles^{-1} sec.^{-1}$

* See footnote bottom of page 46.

$sec.^{-1}$. For this kinetic experiment the area of the peaks as well as the peak heights were determined. The data for this comparision are found in Fig. 4. The excellant agreement of the two methods will be noticed. The actual ^1H n.m.r. spectrum from which this data was compiled is reproduced in Fig. 3.

FIG. 9


(CH3)3SiN(CH3)2 + H2N
38°
(CH3)3SiNH
+ HN(CH3)2
ln Z/A
1.4
1.0
0.6
0.2
0
10
20
30
40
50
60
TIME (MIN.)

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