Internal Rotation in the Trimethylsilyl Esters of Dimethylcarbamic Acid and Thio Derivatives

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Abstract: The kinetic parameters for hindered rotation about the C–N bond for the trimethylsilyl esters of *N,N*-dimethylcarbamic acid and *N,N*-dimethylmonothiocarbamic acid have been determined by total line-shape analysis of their proton nuclear magnetic resonance spectra. Evidence is presented for the possible existence of a four-membered CSSiS ring in the trimethylsilyl ester of *N,N*-dimethyldithiocarbamic acid.

It is now reasonably well accepted that total line-shape analysis, of nuclear magnetic resonance spectra obtained from systems undergoing exchange processes, is the most reliable method for obtaining consistent activation parameters.[1-6]

Unfortunately the list of compounds studied by the line-shape method is both short and patchy, and this suggested to us that a systematic study of a series of similar compounds might provide some useful comparative information. Carbamate[7] and thiocarbamate[8,9] esters have received less attention than amides, although some initial studies by Valega[10] suggest that the results may well be more interesting. Some earlier work on silylcarbamates[11] indicated that a useful series for study would be the carbamate esters of derivatives of the elements of group IV. We have previously reported our results for a series of methyl esters;[12] in this paper we discuss the trimethylsilyl derivatives; in a later paper we shall report results for trimethylgermyl- and trimethylstannylcarbamates.

Experimental Section

(a) Methods. The techniques for obtaining and analyzing the nmr spectra have been described previously.[12] Temperatures were measured using the methanol and ethylene glycol standards supplied by Varian Associates, and employing the relationships between peak separation and temperature reported by Van Geet.[13,14] Temperatures are believed to be accurate to ±0.3°K when using the glycol method and to ±0.8°K when using methanol. Dilute solutions in hydrocarbon solvents were used to minimize solvent–solute and solute–solute interactions. The solutions were prepared by distilling the compound and solvent into nmr tubes under vacuum. Values of T_2* were obtained for each spectrum from the resonance of the $SiMe_3$ protons. All nmr spectra were obtained from a Varian A56-60D nmr spectrometer.

(b) Preparation of Compounds. (1) **$Me_2NC(O)OSiMe_3$.** This compound was prepared from $Me_2NC(O)OH–HNMe_2$ and Me_3SiCl by procedure C of Tilles,[15-17] using hexane as a solvent. Because the compound is air sensitive, all operations were carried out under a nitrogen atmosphere. Purification was by repeated vacuum distillation.

(2) **$Me_2NC(S)SSiMe_3$.** This compound was prepared and purified as above from $Me_2NC(S)SH–HNMe_2$ and Me_3SiCl by procedure C of Tilles.[15-17]

(3) **$Me_2NC(S)OSiMe_3$.** This compound was prepared and purified as above from $Me_2NC(O)SH–HNMe_2$ and Me_3SiCl by procedure C of Tilles.[15] It is of interest to note that this preparative procedure yields the sulfur ester in the methyl ester series. However, the absence of any C=O stretching band in the ir of $Me_2NC(S)OSiMe_3$ as opposed to the strong C=O stretch at 1653 cm^{-1} in $Me_2NC(O)SMe$ suggests that in this case the oxygen ester is being formed; this reflects, perhaps, the greater strength of silicon–oxygen *vs.* silicon–sulfur bonds.

The direct reaction of Me_2NSiMe_3 with COS also yields the oxygen ester.[18]

Results

(A) $Me_2NC(O)OSiMe_3$. Both the neat liquid and *n*-hexane solutions exhibit a singlet for the *N*-methyl protons. However, this singlet splits into a doublet below room temperature.

The spectra of the neat liquid showed considerable broadening at low temperatures (probably because of viscosity effects), and hence were not considered suitable for analysis.

Kinetic parameters were, however, obtained from a variable temperature study of an 11 mol % solution of $Me_2NC(O)OSiMe_3$, in *n*-hexane. The parameters were $E_a = 15.0 \pm 0.8$ kcal/mol, $\Delta H^{\ddagger}_{298.2} = 14.4$ kcal/mol, $\Delta G^{\ddagger}_{298.2} = 16.1$ kcal/mol, $\Delta S^{\ddagger} = -5.7$ eu.

Because of the small value of the nonexchanging chemical shift (1.92 cps at −41.5°), the limits of error in these parameters are high. In particular, the error in the entropy of activation may be at least as large as the value itself.

(B) $Me_2NC(S)OSiMe_3$. The neat liquid exhibits a doublet for the *N*-methyl protons at room temperature. On raising the temperature, the doublet gradually collapses to a singlet with the coalescence temperature being ~99°.

Kinetic studies were carried out on the neat liquid and on a 37 mol % solution in *n*-hexane. As described previously rate constants were obtained by a compari-

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Table I. Activation Parameters

Compd	Solvent	E_a, kcal/mol	log A	$\Delta G^{\ddagger}_{298.2}$, kcal/mol	$\Delta H^{\ddagger}_{298.2}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Ref
$Me_2NC(O)OSiMe_3$	11 mol % in n-hexane	15.0 ± 0.8	12.0 ± 0.8	16.1	14.4	−5.7	This work
$Me_2NC(S)OSiMe_3$	Neat	20.8 ± 0.4	13.6 ± 0.3	19.7	20.2	+1.68	This work
	37 mol % in n-hexane	19.5 ± 0.5	12.9 ± 0.3	19.3	18.9	−1.3	This work
$Me_2NC(S)OMe$	Neat	14.5 ± 0.4	10.7 ± 0.3	17.4	13.9	−11.7	a
	1.5 mol % in cyclohexane	14.2 ± 0.5	10.6 ± 0.3	17.1	13.6	−11.7	
$Me_2NC(S)SMe$	n-Hexane	13.0 ± 0.6	11.6 ± 0.5	14.7	12.5	−7.4	a
	n-Hexane	10.3 ± 0.3	9.6 ± 0.18	14.7			b
$Me_2NC(O)CD_3$	Neat	19.6 ± 0.3	13.8 ± 0.2	18.2	19.0	+2.7	c
	9.5% in DMSO-d_6	20.6 ± 0.3	14.3 ± 0.3	18.6	20.0	+4.7	
$Me_2NC(O)H$	Neat	20.5 ± 0.2			20.2 ± 0.2	−1.7	d
	Neat	20.8 ± 0.6				0 ± 1	e
$Me_2NC(S)H$	Neat			26.6			f

[a] Reference 12. [b] Reference 8. [c] Reference 5. [d] Reference 3. [e] Reference 4. [f] Reference 18.

son between computer-generated and experimental spectra; a pictorial comparison is shown in Figure 1.

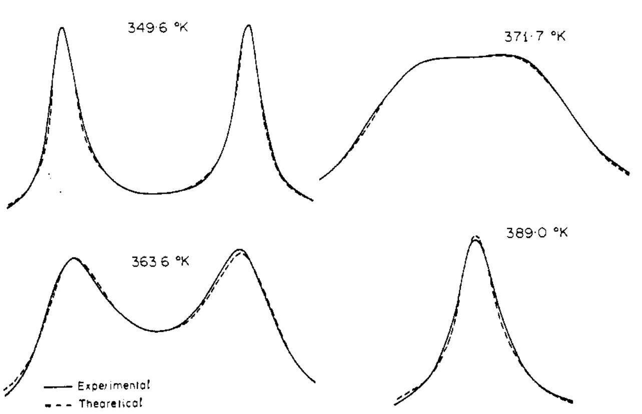


Figure 1. Experimental (———) and theoretical (— — —) spectra for neat $Me_2NC(S)OSiMe_3$.

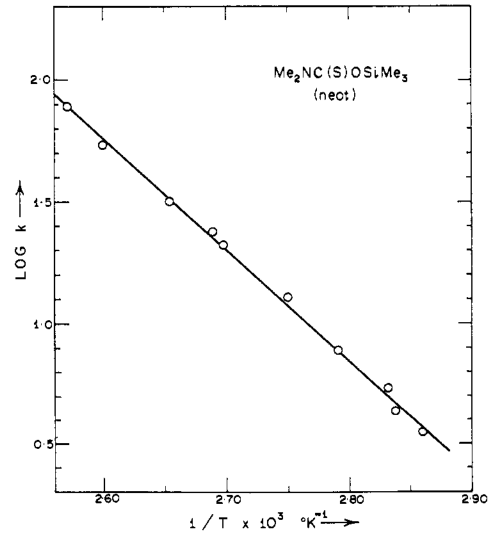


Figure 2. Arrhenius plot for the process of internal rotation in $Me_2NC(S)OSiMe_3$ (neat).

Arrhenius plots yielded the following activation parameters. For the neat liquid, $E_a = 20.8 \pm 0.4$ kcal/mol, $\Delta H^{\ddagger}_{298.2} = 20.2$ kcal/mol, $\Delta G^{\ddagger}_{298.2} = 19.7$ kcal/mol, $\Delta S^{\ddagger} = 1.68$ eu. The Arrhenius plot is shown in Figure 2

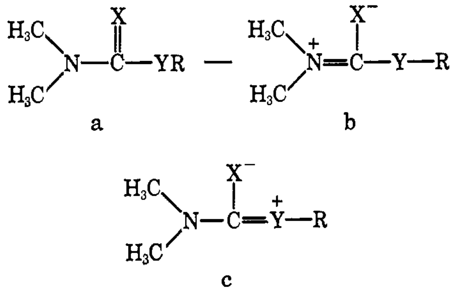
For the 37 mol % solution in n-hexane, $E_a = 19.5 \pm 0.5$ kcal/mol, $\Delta H^{\ddagger}_{298.2} = 18.9$ kcal/mol, $\Delta G^{\ddagger}_{298.2} = 19.3$ kcal/mol, $\Delta S^{\ddagger} = -1.3$ eu.

(C) $Me_2NC(S)SSiMe_3$. The N-methyl protons of $Me_2NC(S)SSiMe_3$ in n-hexane solution exhibit a singlet at room temperature. No splitting of the singlet was observed at temperatures down to −23.5°. Spectra were not obtained below this temperature because of solubility problems.

Discussion

The activation parameters obtained for these and similar compounds are summarized in Table I.

Generally the barriers to rotation in carbamate and thiocarbamate esters have been found to be lower than in the corresponding amides and thioamides. This has been ascribed by Middaugh, *et al.*,[9] to the "cross-conjugation" of the -Y-R group as shown in I.



I, X,Y = O,S

Contributions from form Ic will weaken the barrier to rotation in carbamates relative to amides, since for -OR or -SR substituents the loss of C–N π-bonding energy in the transition state is partially compensated for by an increase in the C–Y–R (Y = O, S) π bonding. The effect of the R group has not been widely studied. Valega[10] found that for R = phenyl, electron-withdrawing substituents on the phenyl ring will reduce the contribution of Ic and hence raise the barrier to rotation in the C–N bond.

We shall first consider the results obtained from the O-SiMe₃ monothiocarbamate. The energy barrier to rotation is lower than in the corresponding thioamide, dimethylthioformamide,[19] but higher than in the methyl ester.[12] The $SiMe_3$ group thus acts as an electron withdrawer as compared with the Me group. Two ways in which this might happen are shown in Figure 3. Process 1 leads toward 5-coordinate silicon, which reflects a situation similar to that found for the trimethylstannyldithio analog whose structure has been determined by X-ray.[20,21] Process 2 involves (p → d) π bonding between oxygen and silicon. Cross-conjugation as in Ic would tend to reduce the barrier to rotation if the $SiMe_3$ group were electron releasing. Similarly the barrier to rotation in the trimethylsilyl carbamate is higher than that in the methyl ester but lower than that in dimethylacetamide.[5] No splitting of the *N*-methyl protons was observed in the methyl ester in hexane solution down to $-58°$,[7,12] but the absence of splitting must not be taken as firm evidence for the lack of hindered rotation, since the chemical-shift difference between the *N*-methyl protons may be too small to be observed. The little evidence available for $Me_2NC(O)OSnMe_3$[7] suggests that it does not have a structure involving 5-coordinate tin, and hence we believe that the apparently higher barrier to rotation in the $SiMe_3$ ester, compared with the Me ester, is real and due to processes 1 or 2 as in Figure 3. The barrier in this ester is lower than in the monothio derivative discussed above. However a similar trend was also found in the methyl esters and has been attributed to a greater ability of sulfur to stabilize the polar form $S^{-}-C{=}N^{+}$.[22]

The dithio esters represent the most unexpected part of this work, since no splitting was observed in the $SiMe_3$ ester down to $-24°$ (the lowest temperature that could be reached due to solubility problems), whereas the methyl ester was split at $+5°$.[8,12] This could perhaps mean that the barrier to rotation in the $SiMe_3$ ester is lower than that in the methyl ester.

To explain this, one might postulate that the $SiMe_3$ group may act as either an electron-releasing group (because of the difference in electronegativity between silicon and sulfur or oxygen) or as an electron-withdrawing group (because of the empty orbitals on silicon).

In the sulfur ester, the $SiMe_3$ group is acting as an electron releaser and thus lowers the barrier by increasing the contribution of resonance form Ic.

In the oxygen ester, the electron-withdrawing capacity predominates with donation of the lone pair on oxygen into empty silicon orbitals.

However in view of the results for the $SnMe_3$ ester,[18,20,21,23] which also shows a single peak for the *N*-methyl protons, an alternative explanation may be given postulating a similar type of interaction in the $SiMe_3$ ester.

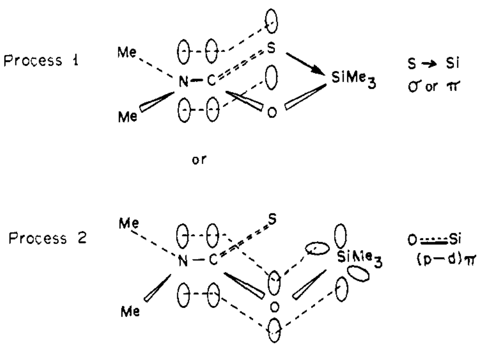
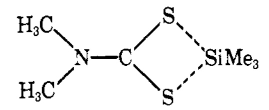


Figure 3. Processes influencing the barrier to rotation in $Me_2NC(S)OSiMe_3$.



Such a structure might well make the chemical shift between the *N*-methyl protons too small to be observed whether restricted rotation is important or not. Previous workers have considered such a structure unlikely,[17] but the evidence here is at least inconclusive, and it has been suggested that the presence of sulfur atoms might facilitate the formation of small rings.[17]

Further splittings are observed in different solvents, particularly chloroform, and our results from these studies and from studies of Me_3Ge and Me_3Sn esters will be reported later.

The entropy of activation values lie close to the theoretical value at zero; however, these are especially sensitive to error; indeed, it has been pointed out that an error of ± 0.4 kcal in $\Delta G^{\ddagger}$ would lead to an uncertainty of about 5 eu in $\Delta S^{\ddagger}$. Thus any discussion in terms of entropy seems premature and the best comparisons between compounds are still most safely made in terms of the free-energy values.

Our results thus show that the $SiMe_3$ group has a significant effect on the barrier to rotation in these molecules and that when bonded to oxygen it apparently serves to withdraw electrons, thus increasing the barrier. A compound of considerable interest is the S-bonded monothio $SiMe_3$ ester, for which a preparation has yet to be found. The barrier in the S-bonded methyl ester is lower than that in the O-bonded isomer, and we would predict that the S–$SiMe_3$ ester would show an even lower barrier.

Acknowledgments. The authors thank the National Research Council of Canada and the Ontario Department of University Affairs for financial assistance and Dr. W. F. Reynolds for many helpful discussions. One of us (A. E. L.) gratefully acknowledges the financial support provided by a Province of Ontario Graduate Fellowship Award.

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