Barriers to Internal Rotation in *N,N*-Dimethylselenoamides

A Complete Line Shape Analysis

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The barriers to internal rotation around the central C—N bond in *N,N*-dimethylselenoacetamide and *N,N*-dimethylselenobenzamide have been studied over wide temperature ranges by a complete line shape method. The free energies of activation were found to be about 1 kcal/mol higher than for the corresponding thioamides, and the entropies of activation were close to zero. The barrier in tetramethylselenourea was too low to be measured by this method.

It has been shown in several instances [1-4] that the barriers to rotation around the central C—N bond in *N,N*-dimethylthioamides are considerably higher than in the corresponding amides. This phenomenon agrees with simple quantum-chemical models of the molecules, which reflect the fact that carbon and sulfur have a lower tendency than carbon and oxygen to form a double bond.[4] A natural extrapolation of these investigations is a study of the barriers in some *N,N*-dimethylselenoamides. In these, still higher barriers are expected, since the tendency of carbon and selenium to form a double bond is lower than that of carbon and sulfur. *N,N*-Dimethylselenoacetamide, *N,N*-dimethyl-selenobenzamide, and *N,N,N',N'*-tetramethylselenourea were available,[5,6] and they were chosen for an NMR investigation. While this work was in progress, Schwenker and Rosswag [7] published a note, describing the determination of the barriers in *N,N*-dimethylselenobenzamide, *N,N*-dimethylthio-benzamide, and *N,N*-dimethylbenzamide. These barriers were determined in chlorobenzene, whereas the high barrier in *N,N*-dimethylselenoacetamide caused us to use a solvent with a higher boiling point, namely *o*-dichlorobenzene. This difference clouds a quantitative comparison of their and our results (*cf.* Table 1). Schwenker and Rosswag used the peak separation method of Gutowsky and Holm,[8] which only permits rate constant measurements in a rather narrow temperature range below coalescence. This method and other approximate methods are now coming to be regarded as more or less hazardous,[9]

and we have preferred to evaluate the rate constants by fitting complete theoretical line shapes to the experimental ones by adjusting the parameters. The theoretical line shapes were obtained by the equation given by McConnell.[10]
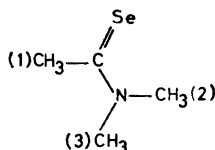
EXPERIMENTAL

The selenoamides were prepared by the methods given in Refs. 5 and 6 and stored under nitrogen. The melting points were in agreement with the literature values, and the NMR spectra showed no traces of impurities. The o-dichlorobenzene was purified by vacuum distillation and stored over molecular sieves. The selenoamide-solvent molar ratio was 1:4. Tetramethylselenourea was studied in methylene chloride solution.

The spectra were recorded using a Varian A-60 NMR spectrometer equipped with a Varian V-6031 variable temperature probe and temperature controller, with a sweep rate of 0.2 Hz/sec. The amplitude of the radiofrequency field was kept well below the level where saturation effects could be observed.

Determination of T_2. Since it is known that several different combinations of rate constants and transverse relaxation times can give the same or almost the same line shape,[11] it was considered advisable to determine T_2 directly from the spectrum at each temperature. This was done by measuring the line width of the reference hexamethyldisiloxane signal, W_{ref}, and that of the N-methyl signals, W_1, at a temperature considerably below that at which exchange effects were first noticed The W_1 values are slightly larger than the W_{ref} values, probably owing to ^{14}N quadrupole relaxation. At a temperature where the N-methyl signals are broadened by exchange, the width of the reference signal is W'_{ref}. The line width of the N-methyl signals at this temperature if no exchange had taken place would have been $W_1 + (W'_{ref} - W_{ref}) = W_1 + \Delta W_{ref}$. The quantity ΔW_{ref} gives the change in line width due to changes in viscosity and magnet homogeneity which applies to all lines in the spectrum.[12] Thus T_2 for each temperature is obtained from the expression:

$$T_2 = \frac{1}{2 \pi (W_1 + \Delta W_{ref})}$$

The spectrum of N,N-dimethylselenoacetamide is complicated by a long-range coupling between the C-methyl group (1) and the N-methyl group *trans* to it (2). As in N,N-dimethylthioacetamide,[4] the signal of (2) falls at lower field than the signal of (3), and the very large chemical shift between them (Table 1) shows that the anisotropy of the selenocarbonyl group is still stronger than that of the thiocarbonyl group. The identifica-

tion of (2) rests upon the fact that it gives rise to a quartet with a splitting of 0.7 Hz, whereas (3) gives a slightly broadened singlet and (1) a broadened doublet. Obviously the coupling (1)−(2) is stronger than (1)−(3), and it is generally conceded that *trans* couplings are stronger than *cis* ones. The different couplings result in greatly differing line widths for the two N-methyl signals at low rotation rates, and in order to be able to use the simple line shape equation we measured only the high field component of the exchanging doublet below coalescence. It was found that the influence of T_2 was large only below the temperature where broadening became appreciable, *i.e.* up to $W > 5 W_1$. This procedure is also justified by the good linearity of the Arrhenius plot over the entire temperature range.

Temperature measurement. The temperatures were monitored by the shifts between the OH and CH_2 signals in ethylene glycol samples contained in narrow capillaries placed coaxially in the test tubes. The shifts were determined by sidebands generated by a Hewlett-Packard model 200CD oscillator and measured by a model 3734A frequency counter from the same company. The shifts were calibrated against the standard Varian ethylene glycol sample, and a good linear relation between shift and temperature was obtained. In this way the temperature in the sample could be measured without removing the sample tube or changing the spinning rate. The temperature differences are believed to be accurate to $\pm 0.2°C$, whereas the absolute accuracy of the temperature measurements is probably somewhat less, owing to the uncertainty in the calibration standard. The selenoacetamide was studied over a temperature range of 40°C and the selenobenzamide, which has a larger nonexchanging chemical shift, over 50°C.

Comparison of experimental and theoretical spectra. With T_2 determined directly, the only parameters to be varied were $\Delta\nu_0$, the chemical shift in the absence of exchange, and the rate constant. After normalizing the areas of the experimental and theoretical curves, the experimental curves were given as 40—70 points so distributed as to give a reasonably detailed description of the curve. A set of estimated parameters were given to the computer, and the theoretical intensities were calculated for all given frequencies, as was the sum of the squared deviations between the theoretical and experimental intensities, $\sum \Delta^2$. New parameters were then tried in a systematic way until $\sum \Delta^2$ reached a true minimum. When this occurred, the root mean square deviation was less than 0.6 % of the maximum intensity, which meant that the experimental and theoretical curves were almost indistinguishable. With this method of calculation, $\Delta\nu_0$ values are obtained at all temperatures studied. They show a temperature dependence (Fig. 1), but below coalescence the change is small. This lack of variation gives good credibility to the parameters of Schwenker and Rosswag[7] since the peak separation method is known to give reliable results as long as $\Delta\nu_0$ is constant.

The calculations were performed on the electronic digital computer SMIL at the Data Center of the University of Lund.
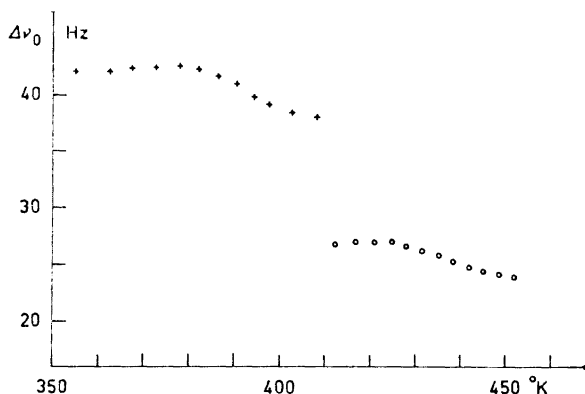

Fig. 1. Non-exchanging chemical shifts *versus* temperature for $R-CSe-N(CH_3)_2$. (O, R = CH_3; +, R = Ph).

RESULTS AND DISCUSSION

The thermodynamic parameters for *N,N*-dimethylselenoacetamide and -benzamide are found in Table 1. The barrier in tetramethylselenourea is probably very low, since it gave only one signal down to —120°C. The possibility of accidental overlap of the two signals is not very likely in view of the

Table 1. Thermodynamic parameters for $R-CSe-N(CH_3)_2$.

R	E_a kcal/mol	$\log A$	$\Delta G^{\neq}$ kcal/mol	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ e.u.	$\nu(2)$Hz	$\nu(3)$Hz
CH_3	26.0 ± 0.4^a	14.4 ± 0.2	22.8 ± 0.1	25.1 ± 0.4	$+5.1\pm1.3$	199.8	173.1
C_6H_5	19.5 ± 0.3	12.9 ± 0.2	19.3 ± 0.1	18.8 ± 0.3	-1.3 ± 1.2	206.0	164.0
$C_6H_5{}^b$	(21.1)		(19.1)	(20.3)	(+3.2)		
$(CH_3)_2N$			<7.9				

[a] The errors in E_a, $\log A$, and $\Delta H^{\neq}$ are standard deviations from the least squares plots, whereas the errors in $\Delta G^{\neq}$ are estimated from the Eyring equation, in which the main source of error is the temperature measurement.
[b] Calculated from the data in Ref. 7.

large shifts shown by the other selenoamides. Assuming a shift of at least 10 cps, the free energy of activation for this rotation must be less than 7.9 kcal/mol. This very low barrier can probably only in part be ascribed to the strong conjugative effect of the added dimethylamino group. It is evident that the two dimethylamino groups cannot be coplanar, and a considerable steric effect will raise the energy of the ground state and thus lower the barrier. Furthermore, in the transition state for the rotation of one dimethylamino group the other one can turn into a position with more effective conjugation, which further lowers the barrier. The free energies of activation for the other selenoamides are about 1 kcal/mol higher than for the corresponding thio-amides,[4] which is in the expected direction. It is possible that the difference is diminished by a small steric effect in the selenoamides, since the van der Waals radius of selenium is 2.00 Å, compared to 1.85 Å for sulfur.[13]

The free energy of activation for N,N-dimethylthioformamide is 26.6 kcal/mol (neat) or 24.0 kcal/mol (40 % in o-dichlorobenzene).[1] Walter et al.[14] have been able to isolate one of the stereoisomers of N-methyl-N-benzylthio-formamide in a pure state, but comparison of the free energies of activation of the N,N-dimethyl derivatives indicates that separation of the isomers will not be possible at room temperature with unsymmetrical N,N-dialkylseleno-acetamides. On the other hand, it is very likely that the corresponding seleno-formamides can be separated.

Neuman et al.[3,15] have recently performed accurate line shape investigations for two amides. They have found entropies of activation and frequency factors that are higher than those commonly encountered with more approximate methods but are regarded as more reliable, since they are in better agreement with results of spin-echo measurements.[16,17] However, the measurements described in Refs. 3 and 15 were performed in solvents other than ours, which precludes a direct comparison with our results. On considering the type of solvation to be anticipated in aromatic solvents,[18] one should except rather high activation entropies of rotation for the selenoamides. The lower value for N,N-dimethylselenobenzamide may be due to a different kind of solvation,

centered more at the aromatic ring than at the selenoamide group. This displacement should lead to less loss of order on rotation. That such a difference in solvation really does exist is corroborated by the solvent shifts of N,N-dimethylselenoacetamide and -benzamide, and also of their thio analogs, on dilution with o-dichlorobenzene. For the acetamides both N-methyl signals are shifted upfield, but the high field one is shifted most strongly, and a considerable increase in relative chemical shift results. This difference in behaviour is explained by the structure of the solvation complex proposed by Hatton and Richards.[18] For the benzamides, both signals are shifted upfield at the same rate, and the relative chemical shift remains nearly the same.

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