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Synthesis and Characterization of Sodium Polyselenides in Liquid Ammonia Solution

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Received July 26, 1976 AIC60543R

Solutions of sodium polyselenides in liquid ammonia have been studied using UV–visible spectroscopy. The results of the investigation indicate that Na_2Se_3, Na_2Se_4, and Na_2Se_6 are isolatable, spectroscopically identifiable species. Na_2Se_5 was found to be a 1:1 mixture of Na_2Se_4 and Na_2Se_6 and no evidence was found to indicate a higher polyselenide than Na_2Se_6. Na_2Se_2 could be prepared only in equilibrium with Na_2Se_3 and Na_2Se and was not isolated in a pure state from solution. The value of the constant ($K' = K_{eq}/K_{sp}$) for the equilibrium $2Na_2Se_2 \rightleftharpoons Na_2Se_3 + Na_2Se$ was found to be ca. 5×10^6 M^{-3}. The spectra of Na_2Se and H_2Se in liquid ammonia were quite similar. Both spectra have a single band ca. 2900 Å which, in each case, shows an energy vs. temperature dependence. The slope for Na_2Se is −40 cal/deg and for H_2Se is −45 cal/deg. The spectrum of each polyselenide consisted of several overlapping bands. All spectra were submitted to curve resolution and the results are as follows: Na_2Se_3 (2780, 3170, 3860, 5925 Å), Na_2Se_4 (2560, 3040, 3440, 4160, 5515 Å), Na_2Se_6 (2660, 3060, 3820, 4360, 5810 Å), and Na_2Se_2 (based on difference spectra, ca. 2300, 3200, 4750, 5600 Å).

Introduction

Hugot[1] was one of the first to investigate the action of alkali metal–ammonia solutions on electronegative elements. His results on the sodium–selenium system indicated the formation of Na_2Se_4 as the highest polyselenide. Further work by Bergstrom[2] revealed a series of sodium and potassium selenides, from the di- through the tetraselenide, and a higher polyselenide. Bergstrom's results are in good agreement with those of Mathewson[3] who based his conclusions on thermal analysis. The color of the polyselenide ions in ammonia was described by Bergstrom as transparent red for the Se_2^{2-}, deep green for Se_3^{2-}, red for Se_4^{2-}, and red-brown for a higher, uncharacterized species.

Potentiometric titration data obtained by Zintl[4] on the sodium–selenium system indicated the existence of the diselenide through the hexaselenide. The colors of the ions reported by Zintl do not correspond to those given by Bergstrom. Zintl attributed the green color to the Se_4^{2-} species whereas Bergstrom attributed this color to Se_3^{2-}. Also, Zintl reported the penta- and hexaselenides whereas Bergstrom did not identify the highest polyselenide (but suggested that the hexaselenide was the highest selenium-containing species in solution).

A report by Klemm[5] and co-workers complicates the study of sodium polyselenides in ammonia. The potassium di-, tri-, tetra-, and pentaselenides were prepared; however, the corresponding sodium polyselenides were reported as being nonexistent. A significant result of Klemm's work was obtained from magnetic investigations on the various polyselenides. Klemm found no evidence to suggest the presence of paramagnetic species; this finding precludes the formation of radical anions of the type found in some polysulfide solutions.

Based on the investigations of the polyselenide ions in liquid ammonia, the reported species include Na_2Se_2, Na_2Se_3, Na_2Se_4, Na_2Se_5, and Na_2Se_6. Some confusion exists over the formation of Na_2Se_5 vs. Na_2Se_6 and Na_2Se_3 vs. Na_2Se_4. Other than early papers, which first reported the various stoichiometries, no further investigation has been made into the behavior of the polyselenides in liquid ammonia.

Because of the lack of information and understanding of the polyselenides, the study of the polyselenides of sodium was undertaken and the results are the subject of this paper. Ammonia was selected as the solvent because it is the most widely used solvent for the synthesis of compounds containing polyatomic anions such as polyselenides. The systematic approach to the problem includes synthesis, isolation, and analysis of all stoichiometries followed by a comparative ultraviolet–visible spectroscopic investigation of all the isolated compounds and mixtures.

Experimental Section

Chemicals. Anhydrous ammonia (Matheson Gas Products) was vacuum distilled from a 5-L steel cylinder containing sodium metal. Additional purification of the ammonia was accomplished by distillation from sodium on the vacuum line. Ultrapure sodium metal (Alfa Inorganics) was obtained in ampules and used without further purification. Selenium powder (99.95%, Alfa Inorganics) was rinsed with ammonia, degassed under vacuum, and stored in a drybox.

Preparation of Sodium Polyselenides. A drawing of the glassware used in the synthesis of all polyselenides is shown in Figure 1. A waste flask was attached to the collection flask and was used primarily as a container for ammonia used in rinsing.

All sodium polyselenides were prepared following the same basic procedure. The entire system was first rinsed with liquid ammonia. Following this, the reaction flask was charged with stoichiometric weights of sodium and selenium. The total weight of reactants was approximately 2 g. All weighings were done in the drybox on a Cahn Electrobalance and were accurate to ±0.1 mg. After the evacuation of the reaction flask, 200–300 mL of ammonia was condensed into the reaction flask. When the condensation of ammonia was completed, the 2-propanol–dry ice bath was removed and the solution warmed to the boiling point. The solution was allowed to boil for several hours. Ammonia was added, if needed, to keep the solution volume around 200 mL. After boiling for several hours, the solution was cooled and allowed to settle. The quiet solution was checked for any unreacted or insoluble material. If the reaction was incomplete, the solution was allowed to boil again. Upon completion of the reaction, the solution was cooled in preparation for liquid transfer.

At this point, the collection flask (Figure 1) was cooled, and an atmosphere of helium was introduced into the reaction flask. Just prior to the transfer of the solution, the filtration assembly was cooled by swabbing with an alcohol–dry ice slurry. Transfer of the solution was accomplished by opening the stopcock on the side arm of the reaction flask and simultaneously evacuating the collection flask.

Once the transfer was complete, the ammonia was boiled off leaving the product on the walls and frit of the collection flask. The collection flask was evacuated for several hours to assure complete removal of absorbed ammonia. When evacuation was complete, the flask was closed, detached from the vacuum line, and taken into the drybox.

Preparation of Sodium Selenide. The procedure for weighing the reactants was the same as that used in the synthesis of polyselenides. The total weight of the reactants was approximately 1–2 g. In addition to the sodium and selenium in the reaction flask, a small piece of sodium was attached to a glass spear contained in the winch assembly (Figure 2).

After condensing ammonia (ca. 150 mL) onto the reactants, the solution was warmed to boiling and allowed to boil until the blue coloration from the sodium disappeared. At this point, the solution had either a faint blue tint, due to a slight excess of sodium, or a faint pink tint, due to trace amounts of polyselenide. In the case of the blue solution, the only product formed was the normal selenide (Na_2Se) contaminated with a very small amount of sodium which could be removed by rinsing with ammonia. In the case of the pink solution, the product formed was the normal selenide contaminated with a small amount of polyselenide. If polyselenide formation was evident,

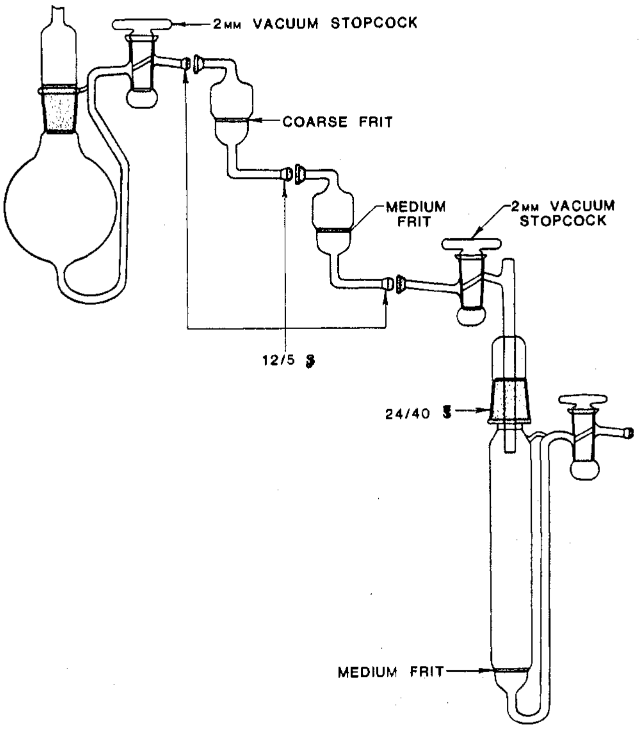

Figure 1. Glassware for polyselenide synthesis.

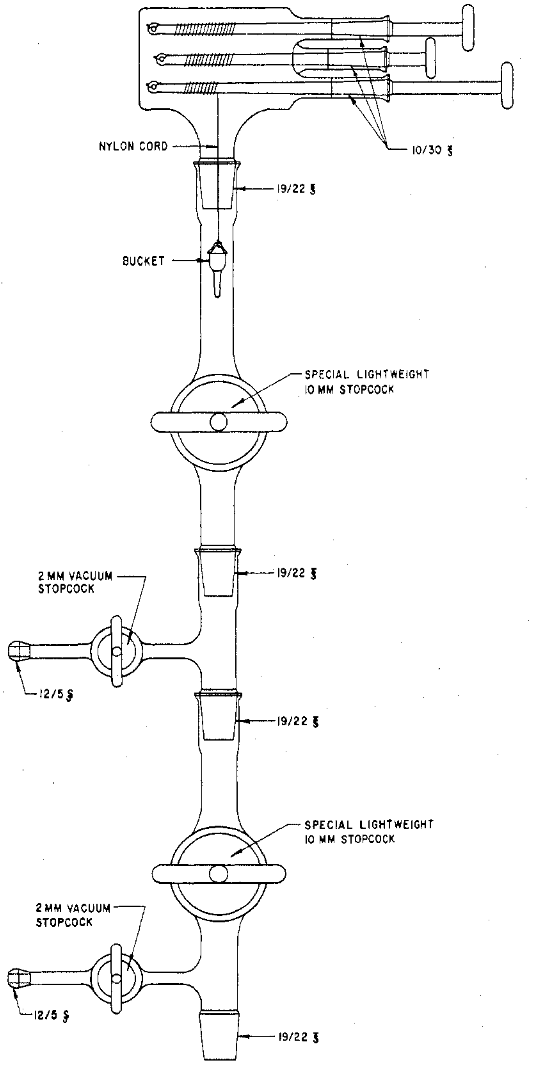

Figure 2. Winch assembly.

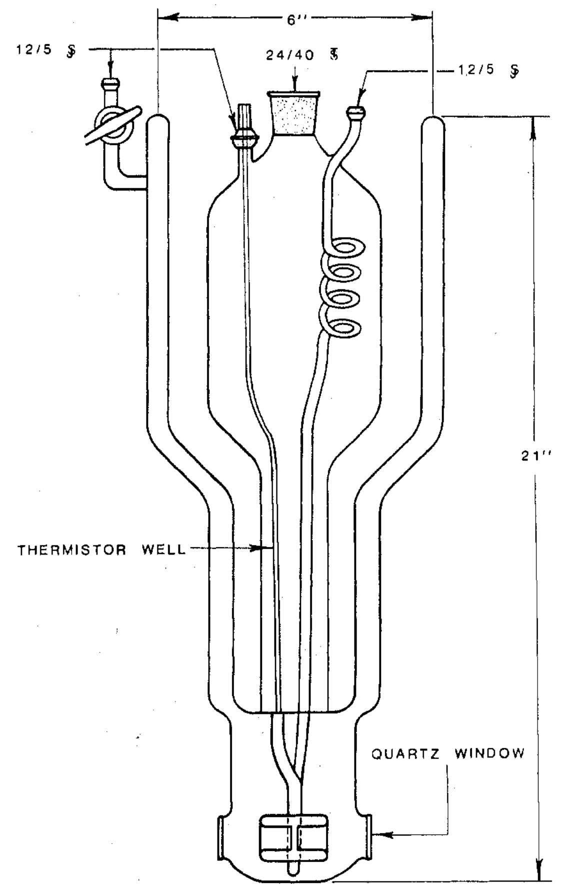

Figure 3. Optical Dewar and cell assembly.

additional sodium was added to the solution until the pink color vanished. The ammonia was boiled off and the reaction flask was evacuated for several hours to remove all traces of ammonia.

Preparation of Hydrogen Selenide. The method for preparing hydrogen selenide was one previously reported.[6]

Analytical Procedure. For analysis, a weighed polyselenide sample was digested in a solution of sulfuric acid, nitric acid, and water (1:1:1) below the boiling point until all the nitrogen oxides had been expelled. After cooling and dilution, the selenium content was determined using the procedure for refined selenium in Scott's Standard Methods.[7]

UV–Visible Spectroscopy. UV–visible spectra were obtained with a Cary Model 15 spectrophotometer (Varian Corp.). Because of the nature of the solutions to be studied, a specialized optical cell had to be used. The cell design used was similar to that of Burrow[8] and Nelson[9] and is shown in Figure 3. The Dewar assembly was set into a metal box and seated with polyurethane foam.

The winch assembly (Figure 2) could be connected to both the optical Dewar assembly and the preparative reaction vessel and was used for lowering salts or metals into the solution. The top part of the winch assembly could be removed and reassembled without contamination of the solution.

Temperature measurements were made using a bead thermistor (Veco 32A8, Springfield, N.J.) housed in a well which extended to the entrance of the optical cell. The thermistor was calibrated against slush baths in the range −90 to 0 °C.

Two methods were used to control temperature. If the temperature was to be controlled for only a short time, dry ice was judiciously added to a 2-propanol–dry ice bath in the optical Dewar. For extended temperature control, a low-temperature controller was used which recirculated cold methanol through the Dewar.

Solutions were prepared in the optical cell assembly by condensing a known weight of ammonia into the cell and adding a known weight of compound via the winch assembly. The winch assembly was equipped with three buckets, thus allowing three separate additions to be made. Weighing and loading of the compounds was done in the drybox.

Solutions of hydrogen selenide in liquid ammonia were prepared from a known weight of hydrogen selenide in a gas measuring bulb.

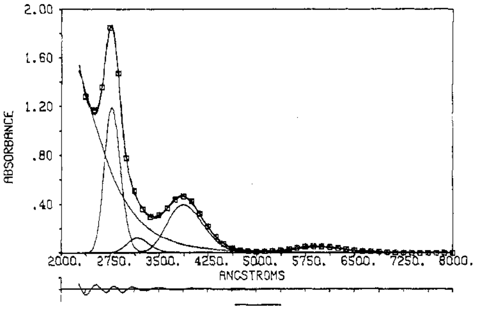

Figure 4. Na_2Se_3 (5.57 mM) at −41 °C.

Prior to the addition of any compounds to the ammonia, a baseline spectrum was recorded at several temperatures. After the first addition of compound, the solution was agitated by bubbling helium through the backside of the cell. A spectrum of the solution was recorded (at various temperatures) with intermittent agitation. More concentrated solutions were prepared by successive additions of the compound. After the addition of each solute charge, the solution was stirred and the spectrum recorded in a similar manner.

Data Treatment. In a homologous series such as the polyselenides, the spectra of the various species show a high degree of similarity and are characterized by multiple overlapping bands. Comparison of such a series of spectra based strictly upon the gross spectral features can be inconclusive. Thus, the spectra were subjected to resolution into component bands.

The Gaussian function has been used to describe spectra arising from electronic transitions,[10–16] and the form used in this work is given in eq 1, where Y_0 is the maximum intensity, x_0 is the position of

$$G_i = Y_0 \exp(-4 \ln 2((x_i - x_0)/W)^2) \qquad (1)$$

maximum intensity, x_i is any abscissa point, and W is the width of the band at half-height. The method of "nonlinear, damped least squares" was used to resolve the overlapping spectral bands encountered in this study, and the F test was used to test the significance of the parameter set.[17–21]

Results and Discussion

Liquid Ammonia Spectrum. The ultraviolet spectrum of gas-phase ammonia has been studied by several workers[22–25] and has been found to have a low-energy ultraviolet transition at ca. 2200 Å along with other transitions at higher energies. The spectrum of liquid ammonia in the ultraviolet region has not been reported; however, it might be expected to have an intense band around 2200 Å. Burrow and Lagowski[26] present data which indicate an overlap of the low-energy wing of the ammonia band and the charge-transfer band of the iodide ion. The overlap of the ammonia wing with the CTTS band appears to increase with increasing solute concentration; this suggests a perturbation of the ammonia band to lower energy with increasing concentration of solute. The same effect is evident in the spectrum of the amide ion.[27]

Similar behavior is observed in the ultraviolet bands of the polyselenides. The wing of the ammonia band at ca. 2200 Å appears to shift to lower energy with increasing polyselenide concentration. Because of the overlap of the ammonia wing and the polyselenide bands, the curve-fitting procedure allowed parameters describing the ammonia "wing" to be included in the least-squares adjustment.

The ammonia spectrum also exhibited a small temperature dependence. As the temperature increased, the intensity increased in the region below 2400 Å. This behavior suggests broadening in the ammonia band with increasing temperature.

Na_2Se_3, Na_2Se_4, and Na_2Se_6 Spectra. A 2:3 mole ratio of sodium to selenium was reacted in liquid ammonia to form the Na_2Se_3 species.[4,28] Initially, the solution was blue, due to unreacted sodium, and a white solid (Na_2Se) was evident. As the reaction proceeded, the solution became multicolored with zones of white, blue, red, and green. Upon completion of the reaction, all traces of the white solid and color variation were gone leaving a brilliant emerald green solution.

Table I. Band Parameters

Species	Concn, mM	Position, Å	Absorbance (Abs)	Half-width, Å
Na_2Se_3	5.57 at	2781	1.174	282
	−41 °C	3164	0.112	410
		3877	0.393	638
		5927	0.050	915
Na_2Se_4	5.47 at	2553	1.394	330
	−57 °C	3036	1.207	556
		3444	0.266	302
		4162	0.652	736
		5528	0.118	1113
Na_2Se_6	3.30 at	2656	0.979	251
	−69 °C	3061	0.458	492
		3863	0.408	1032
		4339	0.368	581
		5795	0.146	1324

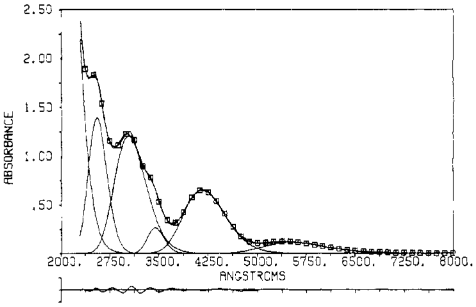

Figure 5. Na_2Se_4 (5.47 mM) at −57 °C.

Analysis of the product collected from the green solution indicated a selenium content of 83.9% as compared to a theoretical value of 83.7%.

Spectral data were collected at several concentrations and temperatures.[29] A typical, resolved spectrum appears in Figure 4. The resolved band parameters are presented in Table I.

A 2:4 mole ratio of sodium to selenium was reacted in liquid ammonia to form the Na_2Se_4 species.[4,28] The reaction proceeded in a manner visually similar to the formation of Na_2Se_3; the final solution was bright red.

Analysis of the product collected from the red solution indicated a selenium content of 86.4%; this value compared to a theoretical value of 87.3%.

Spectral data were collected at several concentrations and temperatures.[29] A typical, resolved spectrum appears in Figure 5. The resolved band parameters are included in Table I.

A 2:6 mole ratio of sodium to selenium was reacted to form the Na_2Se_6 species.[4,28] The reaction proceeded in the manner previously described. Upon completion of the reaction, the solution was dark red-brown in color. An additional preparation, in which the selenium was in excess of the amount required for Na_2Se_6, also resulted in the formation of a dark red-brown solution.

Analysis of the product isolated from the first solution indicated a selenium content of 91.6%. Analysis of the product isolated from the second solution indicated a selenium content of 91.4%. These values compare to a theoretical value of 91.2%.

Spectral data were collected at several concentrations and temperatures.[29] A typical, resolved spectrum appears in Figure 6. The resolution data are presented in Table I.

Because of the limited number of previous investigations, the availability of spectral data pertaining to polyselenides is indeed limited. The spectrum of Na_2Se_6, in aqueous solution, has been reported[30] and shows three bands at approximately 5250, 3650, and 3100 Å; the intensities of the three bands increase with increasing energy. A similar trend is observed

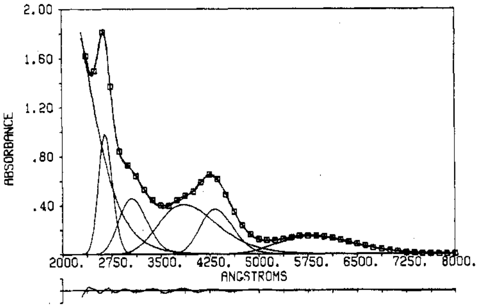

Figure 6. Na_2Se_6 (3.30 mM) at −69 °C.

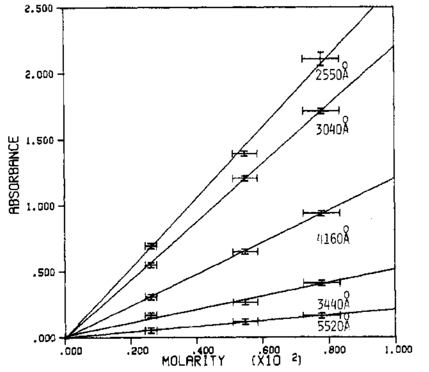

Figure 7. Absorbance vs. concentration of Na_2Se_4 at −57 °C.

for Na_2Se_6 in ammonia; however, the positions and number of bands do not correlate well between the two solvents.

Spectra obtained during the course of this investigation comprise the majority of the spectral data on polyselenides and the spectra of the polysulfides become important as a basis for comparison. In general, the reported spectra of the polysulfides consist of one to three bands in the near-UV–visible range. However, the position, intensity, and number of bands vary with solvent. In ammonia solutions of polysulfides, band assignments have been made for three stoichiometries. Na_2S has a single band at 2700 Å,[9] Na_2S_2 has bands at 2560 and 2820 Å,[9] and Na_2S_4 has bands at 3230 and 4000 Å.[9]

Comparison of the spectra of ammonia solutions of polyselenides with the spectra of ammonia solutions of polysulfides immediately shows a discrepancy; that is, the low-energy band, located between 5500 and 5900 Å and present in each polyselenide spectrum, is not observed in the polysulfide spectra. Although a low-energy band at 6180 Å is reported for polysulfides in Me_2SO,[31] the absorption is due to a radical ion[31] and Klemm[5] has shown that radical species do not exist in ammonia solutions of polyselenides. These low-energy bands are, therefore, assumed to be due to transitions arising from the polyselenide ions.

A typical Beer's law plot is presented in Figure 7 for Na_2Se_4. The absorbance values are taken from resolved spectra. Examination of this plot indicated that Beer's law is obeyed, within experimental error, for the concentration range investigated. This is strong evidence that in this concentration range no new species are being formed either from polyselenide dissociation or from a solvolysis reaction to produce amide ion. The absence of the intense amide ion absorption further supports the conclusion that no solvolysis occurs.

The spectra of Na_2Se_3, Na_2Se_4, and Na_2Se_6 do not vary as a function of temperature except in a way attributable to density changes. This supports the conclusion that there are no detectable equilibria in the temperature range studied.

Na_2Se_3 + Na_2Se_6. A 2:1 mole ratio of Na_2Se_3 and Na_2Se_6 was mixed in the optical cell and the spectrum recorded. The concentrations of the components were 0.0042 M for Na_2Se_3 and 0.0021 M for Na_2Se_6. A 0.0021 M calculated spectrum of Na_2Se_6 and a 0.0042 M calculated spectrum of Na_2Se_3 were numerically added. Band parameter data for these spectra and for a 0.0063 M solution of Na_2Se_4 were compared. The spectrum of a 2:1 molar ratio of Na_2Se_3 to Na_2Se_6 mixed together in ammonia is identical with the calculated spectrum of the 0.0063 M Na_2Se_4 solution. Furthermore, the additive sum of the spectrum of Na_2Se_3 with the spectrum of Na_2Se_6 results in a spectral profile which is considerably different from the other two.

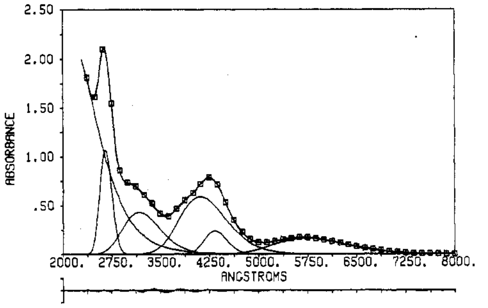

Figure 8. Na_2Se_5 (3.97 mM) at −58 °C.

The absence of detectable quantities of Na_2Se_3 or Na_2Se_6 in a solution containing sodium and selenium in a 2:4 ratio indicates that Na_2Se_4 is the only product. The oxidation–reduction between Na_2Se_3 and Na_2Se_6 is apparently heavily favored over any disproportionation of Na_2Se_4. No equilibrium is suggested and if an equilibrium should exist it is well below the detection limits of the spectrometer.

Na_2Se_5 and Na_2Se_4 + Na_2Se_6. A 2:5 mole ratio of Na:Se in ammonia was reacted to form a dark red solution. Several authors have questioned the formation of Na_2Se_5 from such a reaction.[4,28] The reaction proceeded in a manner similar to the other polyselenides. Analysis of the product isolated from the dark red solution gave a selenium content of 88.6%. This value compares to a theoretical value of 89.6% for Na_2Se_5.

Spectra were recorded at several concentrations and temperatures.[29] A typical, resolved spectrum appears in Figure 8, and the resolved band parameters are given in Table II.

In an attempt to elucidate the existence of Na_2Se_5, an equimolar ratio of Na_2Se_4 and Na_2Se_6 was mixed in the optical cell and the spectrum recorded. The concentration of the components was 0.002 M, respectively. In addition, a 0.004 M spectrum of Na_2Se_5 was resolved; the data are presented in Table II. A calculated spectrum of Na_2Se_4 (0.002 M) and a calculated spectrum of Na_2Se_6 (0.002 M) were numerically added. Band resolution data for these spectra are included in Table II.

The data reveal that the species in a solution of product analyzed to be Na_2Se_5 and in a solution of Na_2Se_4 + Na_2Se_6 are the same. That is, the reaction of a 2:5 mole ratio of Na:Se yields the same product as does the reaction of Na_2Se_4 with Na_2Se_6. This is substantiated by the fact that the addition of a calculated spectrum of Na_2Se_4 to a calculated spectrum of Na_2Se_6 yields a spectrum that is the same as Na_2Se_5. One must therefore conclude that Na_2Se_5 cannot be prepared by reacting a 2:5 mole ratio of Na:Se.

Na_2Se_2, Na + Se, Na_2Se_3 + Na_2Se. Na_2Se_2. A 1:1 mole ratio of sodium to selenium was reacted in ammonia to give a bright red solution. The reaction proceeded normally via the formation of a white solid and multicolored solution. Initially, the red solution was assumed to be Na_2Se_2; however, unlike the other polyselenide preparations, the white solid was never consumed. Even after several hours, the reaction mixture consisted of a white solid dispersed in a red solution. The solid was filtered off and a product was isolated from the solution. The analysis indicated a selenium content of 81.8% compared to theoretical values of 77.5% for Na_2Se_2 (and 83.7% for

Table II. Band Parameters for the Na_2Se_5 System

	Position, Å	Absorbance (Abs)	Half-width, Å
Obsd spectrum of Na_2Se_5[a]	2661	1.073	211
	3185	0.432	667
	4117	0.589	837
	4339	0.239	403
	5728	0.167	1270
Obsd spectrum of Na_2Se_5[b]	2661	1.167	218
	3065	0.475	543
	3480	0.262	602
	3829	0.239	328
	4260	0.767	623
	5959	0.173	1345
Obsd spectrum of Na_2Se_4 + Na_2Se_6	2661	1.048	220
	3079	0.490	512
	3460	0.244	489
	3838	0.252	346
	4256	0.701	608
	5627	0.153	1332
Additive spectrum of Na_2Se_4 + Na_2Se_6	2646	1.049	303
	3056	0.811	434
	3399	0.282	314
	3759	0.327	543
	4282	0.596	678
	5668	0.139	1347

[a] The spectrum of Na_2Se_5, prepared from the elements, resolved into five bands. [b] The spectrum of Na_2Se_5 resolved into six bands.

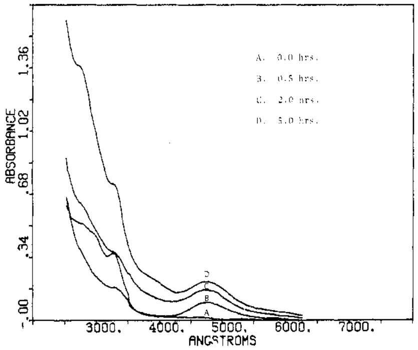

Figure 9. Spectrum of Na + Se at various time intervals.

Na_2Se_3). The selenium analysis and the persistence of the white solid suggested a mixture of Na_2Se, Na_2Se_2, and Na_2Se_3.

In subsequent preparations of Na_2Se_2 using 1:1 mole ratio of Na:Se, the solution, after transfer to the collection flask via the filtration train, was dark red. As the ammonia was evaporated, the solution took on a greenish cast; the formation of a white solid accompanied this color change. The product in the collection flask was redissolved and the solid filtered off. This procedure was repeated until no precipitate formation was observed as the ammonia was evaporated. The color of the resulting homogeneous solution was bright green. Analysis of the solid which remained in the reaction flask indicated a selenium content of 66.9%. Analysis of the solid retained by the frit, during one of the dissolution/filtration/evaporation cycles, indicated a selenium content of 64.6%. These values compare to a theoretical value of 63.2% for Na_2Se. Analysis of the product isolated from the (homogeneous) green solution indicated a selenium content of 83.5%; this compares to a theoretical value of 83.7% for Na_2Se_3.

A comparison of the resolved spectrum of the product from the green solution with the spectrum of Na_2Se_3 leads to the conclusion that the green solution formed is Na_2Se_3.

Na + Se. To follow the course of the reaction spectroscopically, a solution containing an equimolar ratio of sodium metal and selenium metal was prepared in the optical Dewar. Spectra were recorded at various time intervals. Figure 9 shows several spectra recorded within 5 h of the addition of the reactants. Figure 10 shows spectra of the same solution, after repeated boiling and addition of ammonia, many hours later.

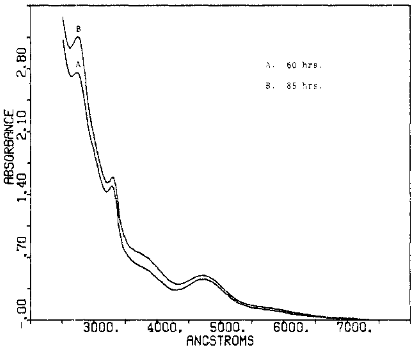

Figure 10. Spectrum of Na + Se after 60 and 85 h.

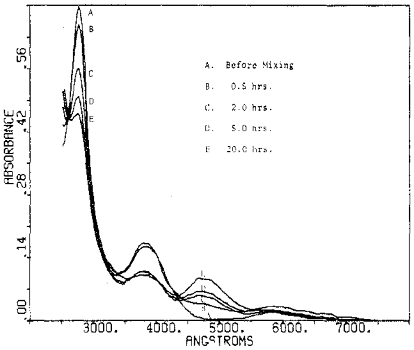

Figure 11. Spectrum of Na_2Se_3 before mixing and Na_2Se_3 + Na_2Se at several time intervals.

Na_2Se_3 + Na_2Se. A solution of Na_2Se_3 was prepared in the optical Dewar and the spectrum recorded. An amount of Na_2Se sufficient to saturate the solution was added to the Na_2Se_3 solution. Spectra were recorded at various times during a 20-h period. These spectra appear in Figure 11. An additional solution was prepared which was equimolar in Na_2Se_3 and Na_2Se and the spectrum recorded as a function of time. The results are identical with those determined using a saturated solution.

Several authors have reported the existence of Na_2Se_2;[4,32] the data presented here do not refute the existence of Na_2Se_2. However, the results of the present study indicate that the reaction of a 1:1 mole ratio of sodium and selenium in liquid ammonia does not proceed to the single product, Na_2Se_2. The existence of Na_2Se_3 and Na_2Se in the final products of the reaction suggests a disproportionation of the type illustrated below.

$$2Na + 2Se \rightarrow Na_2Se_2 \qquad (2a)$$

$$2Na_2Se_2 \rightarrow Na_2Se + Na_2Se_3 \qquad (2b)$$

Spectroscopic evidence, however, suggests that the Na_2Se_2 does not disproportionate entirely to Na_2Se_3 and Na_2Se. The spectra in Figures 9 and 10 show that the intensity around 3850 Å, a band attributed to Na_2Se_3, increases with time. This is consistent with the reaction presented in eq 2. In addition, the spectra in Figure 10 indicate that the band around 4775 Å, assigned to Na_2Se_2, does not completely disappear even after 80 h. Thus, in a closed system, the products of the reaction between equimolar ratios of sodium and selenium are Na_2Se_2, Na_2Se, and Na_2Se_3.

Further evidence was supplied from the spectra of the mixture of Na_2Se_3 and Na_2Se. Figures 11 and 12 show the spectrum of Na_2Se_3 prior to the addition of Na_2Se as well as

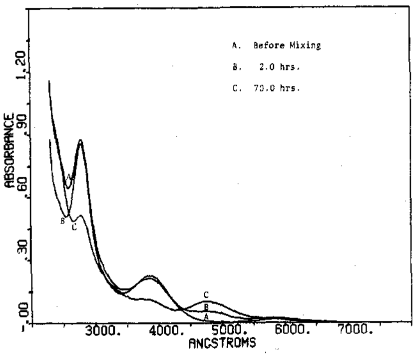

Figure 12. Spectrum of Na_2Se_3 before mixing and $Na_2Se_3 + Na_2Se$ at several time intervals.

the spectrum of the mixture at various times. Since the absorbance around 3870 Å is decreasing as the absorbance around 4775 Å is increasing, Na_2Se_3 and Na_2Se react to form Na_2Se_2. That the reaction has gone to completion is evidenced by the constant absorbances at 3870 and 4775 Å after about 20 h. The absorbances at 4775 and 3870 Å suggest that Na_2Se_3 and Na_2Se react (partially) to form Na_2Se_2. The disproportionation in eq 2b should be written as an equilibrium (eq 3).

$$\begin{array}{l} 2Na_2Se_2 \rightleftharpoons (Na_2Se) + Na_2Se_3 \\ \qquad\qquad\quad \downarrow\uparrow \\ \qquad\quad 2Na^+ + Se^{2-} \end{array} \tag{3}$$

The equilibrium expression for eq 3 in ionic form is given in eq 4a–c.

$$K_{eq} = \frac{[Na^+]^2[Se^{2-}]\,[Na^+]^2[Se_3^{2-}]}{[Na^+]^4[Se_2^{2-}]^2} \tag{4a}$$

$$K_{eq} = \frac{K_{sp}[Na^+]^2[Se_3^{2-}]}{[Na^+]^4[Se_2^{2-}]^2} \tag{4b}$$

$$K' = K_{eq}/K_{sp} = \frac{[Se_3^{2-}]}{[Na^+]^2[Se_2^{2-}]^2} \tag{4c}$$

The equilibrium concentrations of the species in eq 4c can be calculated from the initial and final concentrations of Na_2Se_3. The final concentration of Na_2Se_3 can be calculated from absorbances according to the following

$$[Se_3^{2-}]_{final} = C_f = [Se_3^{2-}]_{initial}\frac{Abs(3850)_f}{Abs(3850)_i} \tag{5}$$

The expressions for $[Se_2^{2-}]_f$ and $[Na^+]_f$ are then

$$[Se_2^{2-}]_f = 2(C_i - C_f) \tag{6}$$

where C_i is the initial concentration of Se_3^{2-}, and

$$\begin{aligned} [Na^+]_f &= 4(C_i - C_f) + 2C_f \\ &= 4C_i - 4C_f + 2C_f = 2(2C_i - C_f) \end{aligned} \tag{7}$$

Thus, K', in terms of C_i and C_f, becomes

$$K' = \frac{C_f}{4(2C_i - C_f)^2(4(C_i - C_f)^2)} \tag{8}$$

The initial concentration (C_i) of Na_2Se_3 in the spectra of Figure 11 was 0.002 13 M and the final concentration (C_f) was calculated to be 0.001 26 M. Substitution of these values into eq 8 yields a value for K' of 1.16×10^7 M^{-3}.

The initial concentration (C_i) of Na_2Se_3 in the spectra of Figure 12 was 0.002 14 M and the final concentration (C_f) was calculated to be 0.001 07 M. Substitution of these values into eq 8 yields a value for K' of 5.67×10^6 M^{-3}. This value of K' after 70 h, compared to the value of K' after 20 h (Figure 11), indicates that perhaps after 20 h the equilibrium had not been established.

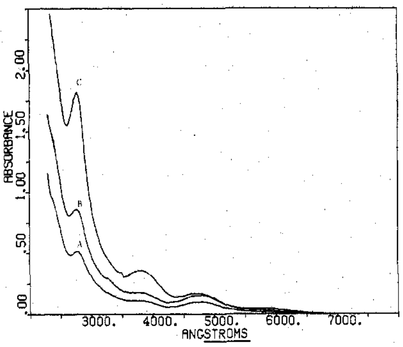

Figure 13. Spectrum of $Na_2Se_3 + Na_2Se$ at several concentrations (concentration increasing A through C).

Table III. Band Parameters for Na_2Se and H_2Se

	Position, A	Absorbance (Abs)	Half-width, A
Na_2Se (satd) at			
−72 °C	2892	0.112	308
−53 °C	2921	0.109	300
−32.5 °C	2945	0.100	294
H_2Se (3.5 mM) at			
−66.5 °C	2873	0.271	316
−51.5 °C	2881	0.268	313
−40.5 °C	2909	0.253	309

Examination of the spectra of Figure 13 shows that the ratio of the intensities of the 3850-Å band and the 4750-Å band changes with concentration. In particular, as the volume of the solution decreases, the intensity at 3850 Å increases with respect to the intensity at 4750 Å (i.e., the concentration of Se_3^{2-} increases with respect to Se_2^{2-}). This behavior is in agreement with the equilibrium expression given in eq 4.

Some discrepancy exists between the spectra arising from solutions of Na + Se and the spectra arising from solutions of $Na_2Se_3 + Na_2Se$. The anomaly centers around the intensity of the 3200-Å region. The spectra of Na + Se solutions show a definite shoulder near 3200 Å, whereas the spectra of $Na_2Se_3 + Na_2Se$ do not show a peak near 3200 Å, although there may be some broadening in this region.

The two solutions, Na + Se and $Na_2Se_3 + Na_2Se$, present a situation in which a point of equilibrium is being approached from opposite extremes. From eq 3, the Na + Se solution is an approach from the left (reactants) and the $Na_2Se_3 + Na_2Se$ solution is an approach from the right (products). The difference in the spectra of the two solutions may be due to a kinetically controlled approach to equilibrium vs. thermodynamic control. In particular, the left-side approach may have a higher activation energy than the right-side approach. Thus, the solutions of Na + Se may not be at equilibrium.

In summary, Na_2Se_2 was found to exist; however, it is apparently present only as a component in an equilibrium involving Na_2Se_3 and Na_2Se.

Na_2Se and H_2Se. The spectrum of a saturated solution of Na_2Se was recorded as a function of temperature. The resolved band parameters for Na_2Se are given in Table III.

The spectrum, as a function of temperature, was also recorded for a solution approximately 0.0035 M in H_2Se. The resolved band parameters for H_2Se are also given in Table III.

Both spectra exhibit characteristics similar to the iodide ion absorption in liquid ammonia,[33] which is associated with a charge-transfer-to-solvent transition.[34,35] Furthermore, a band in the spectra of K_2S and H_2S in liquid ammonia has also been assigned to a CTTS transition.[36] One prominent feature of any CTTS band is the decrease in energy of the absorption maxima with increasing temperature. This behavior is observed in the spectra of Na_2Se and H_2Se. A plot of E_{max} vs. temperature yields $dE_{max}/dT = -40$ cal/deg for Na_2Se and $dE_{max}/dT = -45$ cal/deg for H_2Se; this is typical for CTTS transitions.[35] CTTS transitions are usually quite intense; the molar absorptivity values are in the range 10^3 to 10^4. The value of E_{max} for Na_2Se and H_2Se is ca. 4×10^3 compared to 6×10^3 for K_2S and H_2S.[36]

One of the important features of the spectrum of Na_2Se in ammonia is the absence of the CTTS band (ca. 3250 Å) associated with the amide ion.[37] This establishes that the selenide ion is not involved in the ammonolysis reaction given by eq 9. The absence of the amide band makes possible the

$$Se^{2-} + NH_3 \rightarrow HSe^- + NH_2^- \tag{9}$$

assignment of the band at ca. 2900 Å to the selenide ion, Se^{2-}, either free or associated with Na^+ as ion pairs, rather than the hydroselenide ion (HSe^-).

Based on the behavior of H_2S,[36] the first ionization of H_2Se in liquid ammonia is assumed to occur to an appreciable extent according to the expression

$$H_2Se + NH_3 \rightarrow HSe^- + NH_4^+ \tag{10}$$

The p*K*'s for H_2Se in water are 3.9 for the first proton and 11.0 for the second.[38] In addition, the p*K* values of weak acids in ammonia decrease considerably compared to the values in aqueous solution.[36] Therefore, the removal of the first proton from H_2Se should be virtually complete in ammonia.

The sulfide species in solutions of H_2S assumed to be responsible for the absorption at ca. 2700 Å is the solvated HS^- ion which can be represented as $^-SH\cdots NH_3$ or $S^{2-}\cdots NH_4^+$.[36] The analogous selenide species, in a H_2Se solution, would be $^-SeH\cdots NH_3$ or $Se^{2-}\cdots NH_4^+$.

The selenide species in solutions of Na_2Se can only be hydrogen bonded to solvent molecules. Thus, the species giving rise to the 2900-Å band would most likely be $Se^{2-}\cdots NH_3$, which should exhibit spectral characteristics similar to $Se^{2-}\cdots NH_4^+$. This conclusion finds support in the similar spectroscopic characteristics (e.g., half-width, position) of solutions of Na_2Se and H_2Se (Table III).

The temperature effect found in the Na_2Se spectrum is not observed in the spectra of the various polyselenides. If, in fact, any band, in any of the polyselenides, has a temperature dependence, the effect is very slight and, in the UV region, could be masked by the overlap of the ammonia wing. This indicates that no CTTS transitions are occurring in the polyselenide series.

The energy of a CTTS transition in a homologous series such as the polyselenides would be expected to decrease with decreasing charge density. Thus, as the polyselenide ions become larger, maintaining a double negative charge, the charge density decreases and the energy of the CTTS transition would be expected to shift to lower energy. The positions of the intense ultraviolet bands of the polyselenides are ca. 2780 Å (Na_2Se_3), ca. 2550 Å (Na_2Se_4), and ca. 2660 Å (Na_2Se_6). Obviously, these bands are not shifted to lower energy relative to the 2900-Å band of Na_2Se. This fact, coupled with the absence of any temperature dependence, leads to the conclusion that the ultraviolet bands in the polyselenide spectra are due to intramolecular electronic transitions.

Conclusions

Isolation, analysis, and spectroscopic investigations indicate that Na_2Se, Na_2Se_3, Na_2Se_4, and Na_2Se_6 are stable in ammonia solution. Na_2Se_5 could not be prepared. All evidence indicates that Na_2Se_5 is a mixture of Na_2Se_4 and Na_2Se_6. Similarly, Na_2Se_2 could not be prepared and isolated in a pure state; instead, the solutions with Na_2Se_2 stoichiometry always had equilibrium amounts of Na_2Se and Na_2Se_3 present.

Acknowledgment. We wish to acknowledge the financial support of The Robert A. Welch Foundation and the Texas Christian University Research Foundation.

Appendix. Estimation of σ^2_{int}

The reliability of the *F* test is dependent on the estimate of the unit variance from the adjustment of the observations to the function (σ^2_{ext}) and the estimate of the unit variance obtained from repeated observations of a given value of the variable (σ^2_{int}). The estimate of σ^2_{ext} is calculated as part of the curve fitting procedure. Variations in absorbance of replicate runs were used to estimate σ^2_{int}.

Standard alkaline chromate solutions were used for the estimation of σ^2_{int} and for calibration of the cell path length (vide infra). Four standard solutions of chromate were prepared with the concentration varying such that absorbance readings were obtained between 0 and 1, 1 and 2, 2 and 3, and 3 and 4 absorbance units. Ten replicate absorbances were determined for each solution. The optical cell was rinsed and a water baseline determined between each absorbance measurement.

The unit variance for each absorbance reading was computed according to the following expression

$$\sigma^2_{int} = \frac{\Sigma(Y_i - \bar{Y})^2}{n}$$

where Y_i is the absorbance of the *i*th replicate, $\bar{Y}$ is the average value, and *n* is the number of observations. Estimates of unit variance for absorbance intervals were as follows: 0–1, 0.0004; 1–2, 0.0004; 2–3, 0.0025; 3–4, 0.004. The estimate of σ^2_{int} for a spectrum was calculated by multiplying each of the range values by a frequency factor which is simply the number of data points in the absorbance range. For example, if a data set had 100 points with 50 points between 0 and 1, 40 points between 1 and 2, and 10 points between 2 and 3, then the value for σ^2_{int} would be

$$\sigma^2_{int} = (50 \times 0.0004 + 40 \times 0.0004 + 10 \times 0.0025)/100$$
$$= 0.0061$$

Registry No. Na_2Se_3, 63104-41-6; Na_2Se_4, 39438-69-2; Na_2Se_6, 1313-86-6; Na_2Se_5, 12439-18-8; Na_2Se, 1313-85-5; H_2Se, 7783-07-5; Na_2Se_2, 12505-03-2.

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High-Pressure Reactions of Small Covalent Molecules. 9. Reaction of Methylsilanes with Covalent Oxides[1]

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Received January 18, 1977 AIC70038+

The siloxane linkage forms when silicon compounds having an alkyl group are combined with covalent oxides at increased pressure. Tetramethylsilane forms hexamethyldisiloxane when combined with CO_2 (200 °C), H_2O (250 °C), and N_2O (360 °C) at 4000 atm. Methylfluorosilanes of the type $(CH_3)_xSiF_y$ ($x + y = 4$) also react with nitrous oxide with the reactivity declining in the order $(CH_3)_2SiF_2 > (CH_3)_3SiF > (CH_3)_4Si \gg CH_3SiF_3$. When dimethyldifluorosilane is combined with nitrous oxide at 3800 atm (230 °C), a 90% yield of the previously unreported substance $(CH_3SiF_2)_2O$ is obtained.

The silicon–carbon linkage in alkylsilanes is considered to be nonreactive at conditions which do not lead to thermal decomposition. The cleavage of this linkage followed by the subsequent formation of a silicon–oxygen bond is thermodynamically permitted at 25 °C (1 atm); however, the rate of reaction is exceedingly slow when nitrous oxide, carbon dioxide, or water provides the oxygen at moderate temperatures and at normal pressures. The cleavage reaction does not take place at moderate temperatures when the pressure is increased to at least 500 atm with the best yields occurring at pressures in excess of 1500 atm. This reaction also provides a general synthetic route for the formation of a silicon–oxygen linkage without the use of a hydrolysis reaction of a difficultly prepared precursor.

Results and Discussion

Reactions of Tetramethylsilane. The experimental results for the reaction of tetramethylsilane with carbon dioxide, nitrous oxide, and water are summarized in Table I. The reaction in each case leads to the formation of hexamethyldisiloxane and appropriate other materials representative of the oxygen source

$$CO_2 + 4(CH_3)_4Si \rightarrow 2[(CH_3)_3Si]_2O + C + 2C_2H_6 \qquad (1)$$

$$N_2O + 2(CH_3)_4Si \rightarrow [(CH_3)_3Si]_2O + N_2 + C_2H_6 \qquad (2)$$

$$H_2O + 2(CH_3)_4Si \rightarrow [(CH_3)_3Si]_2O + 2CH_4 \qquad (3)$$

Table I. Tetramethylsilane Reactions[a]

Pressure, atm	Temp, °C	Conversion, %	Pressure, atm	Temp, °C	Conversion, %
		Carbon Dioxide			
4000	200	83	4000	150	0
3000	250	62	3000	200	0
1900	290	48	1700	250	0
1000	290	11	1000	250	0
			500	300	0
		Water			
4000	250	55	4000	200	0
3000	300	52	3000	270	0
2000	300	52	2300	270	0
1000	325	48	1500	270	0
500	300	10	400	300	0
			200	400	0
		Nitrous Oxide			
4000	360	55	4000	260	0
2900	360	55	2900	280	0
2500	400	52	2000	280	0
900	400	21	900	320	0
			300	400	0

[a] Conversion based on recovered methylfluorosilane. All reactions were for 18 h.

The reaction with carbon dioxide below 400 °C takes place exactly as given by eq 1 with a 83% conversion at 200 °C (4000 atm). When the temperature is above 400 °C, nonvolatile siloxanes and methane are also obtained.

The reaction with N_2O does not take place below 360 °C (2000 atm). The reaction does not form any other products, and a 63% conversion is obtained at 3700 atm. However, when the temperature is increased to 400 °C, a greater variety of products is obtained which includes CH_4, C_2H_6, CO_2, and nonvolatile siloxanes.

The reaction with water continues beyond the first cleavage. At 325 °C (1000 atm), reaction 3 takes place with a 48% conversion, but when the pressure reaches 2000 atm, the hexamethyldisiloxane undergoes further reaction to form a mixture of nonvolatile silicone oils. At 400 °C (4000 atm) 95% of the tetramethylsilane reacts forming a complex mixture of volatile and nonvolatile siloxanes.

It is reasonable to propose that, of the reactions described in this report, some take place via the same general mechanism since the reaction conditions and products are similar. The initial reaction is postulated as the formation of a silyl radical, viz.

$$(CH_3)_4Si \rightarrow CH_3\cdot + (CH_3)_3Si\cdot$$

which then attacks the oxygen source. This hypothesis is supported by the isolation of simple substances which are reasonable reaction products of the methyl radicals. When elemental sulfur is added to the reaction tube containing one of the oxygen sources and tetramethylsilane, a mixture of sulfides is obtained and no hexamethyldisiloxane is isolated.