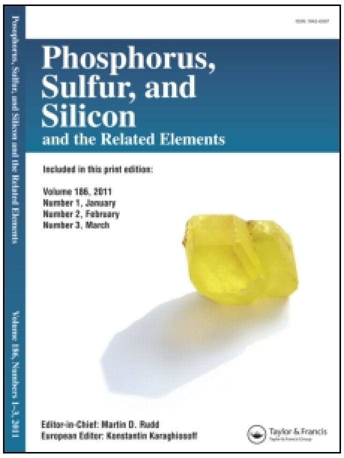

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Siivari, Jarl , Laitinen, Risto S. and Hiltunen, Yrjo(1992) 'The Quest for the Neutral Sulfur-Selenium-Nitrogen Compounds. The Reaction of Dichlorodiselane-Dichlorodisulfane Mixtures With Ammonia', Phosphorus, Sulfur, and Silicon and the Related Elements, 65: 1, 177 — 180

To link to this Article: DOI: 10.1080/10426509208055347

URL: http://dx.doi.org/10.1080/10426509208055347

Phosphorus, Sulfur, and Silicon, 1992, Vol. 65, pp. 177–180

THE QUEST FOR THE NEUTRAL SULFUR-SELENIUM-NITROGEN COMPOUNDS. THE REACTION OF DICHLORODISELANE-DICHLORODISULFANE MIXTURES WITH AMMONIA

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Abstract The reactions of dichlorodiselane and dichlorodisulfane mixtures with ammonia produce heterocyclic selenium sulfides as well as sulfur nitrides and imides. The reaction products have been identified with ^{77}Se and ^{14}N NMR spectroscopy. No evidence on the formation of sulfur-selenium nitrides and imides was observed.

INTRODUCTION

Dichlorodisulfane S_2Cl_2 reacts with ammonia at varying reaction conditions to produce sulfur nitrides S_4N_4, S_4N_2, and sulfur imides $S_n(NH)_{8-n}$.[1] Analogous reaction of Se_2Cl_2 at high pressure and temperature has been shown to yield Se_4N_4.[2] In the present work the syntheses of sulfur-selenium nitrides and imides were sought for by reacting the Se_2Cl_2/S_2Cl_2 mixtures at varying molar ratios with both aqueous and gaseous ammonia. The reaction products were identified with ^{77}Se and ^{14}N NMR spectroscopy.

EXPERIMENTAL

S_2Cl_2 (Fluka) and NH_3(aq) (Baker) were used without further purification. Se_2Cl_2 was prepared according to the method of Fehér.[3] Gaseous ammonia (AGA) was dried with Na_2CO_3 and CS_2 (E. Merck) was distilled over $CaCl_2$ and stored in molecular sieves (4Å).

The reaction of Se_2Cl_2/S_2Cl_2 (molar ratios 1:9, 3:7, 5:5, 7:3, and 9:1) mixtures with aqueous ammonia were carried out at three different temperatures (-20, 0, +20 °C) applying the previously described method for the reaction of S_2Cl_2 with NH_3(aq).[4] The second series of Se_2Cl_2/S_2Cl_2 mixtures in CS_2 were treated with gaseous ammonia for 30 minutes at -20 °C.

All NMR spectra were recorded at 300 K with a Jeol JNM-GX400 spectrometer. For ^{77}Se the spectrometer was operating at 76.312 MHz. The spectral width was 200.0 kHz and the resolution 1.5 Hz/data point. The pulse width was 5.0 μs corresponding to the nuclide tip angle of 45 °. The pulse delay was 1.3 s. The accumulations contained ca. 40,000 transients. D_2O was used as an external ^{2}H lock and the saturated solution of SeO_2 as an external reference. The chemical shifts (ppm) were reported relative to neat Me_2Se [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$].

For ^{14}N the spectrometer was operating at 28.88 Mhz. The spectral width was 70.423 kHz and the resolution 1.5 Hz/data point. The pulse width was 15.0 μs and the pulse delay 0.53 s. The accumulations contained ca. 60,000 transients. D_2O was used as an ^{2}H lock and CH_3NO_2 as an external reference.

RESULTS AND DISCUSSION

S_2Cl_2 with aqueous ammonia produces elemental sulfur, sulfur nitrides (S_4N_4, S_4N_2) and sulfur imides $S_n(NH)_{8-n}$.[4] The ^{14}N NMR spectrum of the product shows signals due to S_4N_4 (-252.1 ppm) and S_4N_2 (-111.5 ppm) based on the assignment by Chivers et al.[5] There is also a broad resonance ranging from -340 to -360 ppm which is due to sulfur imides (the ^{14}N chemical shift of S_7NH in THF is -364 ppm [6]).

The ^{14}N NMR spectra of the reaction mixtures of Se_2Cl_2/S_2Cl_2 with both aqueous and gaseous ammonia showed only signals due to S_4N_4 and S_4N_2. Their intensities quickly decreased with increasing selenium content of the reaction mixture and the resonances disappeared completely when using equimolar amounts of Se_2Cl_2 and S_2Cl_2.

^{77}Se NMR spectra of the products from the reactions of the full series of Se_2Cl_2/S_2Cl_2 mixtures with both aqueous and gaseous ammonia are very complex (see Figure 1). All signals can be assigned to heterocyclic selenium sulfides Se_nS_{8-n} based on our earlier study.[7] The assignment is shown in Table I.

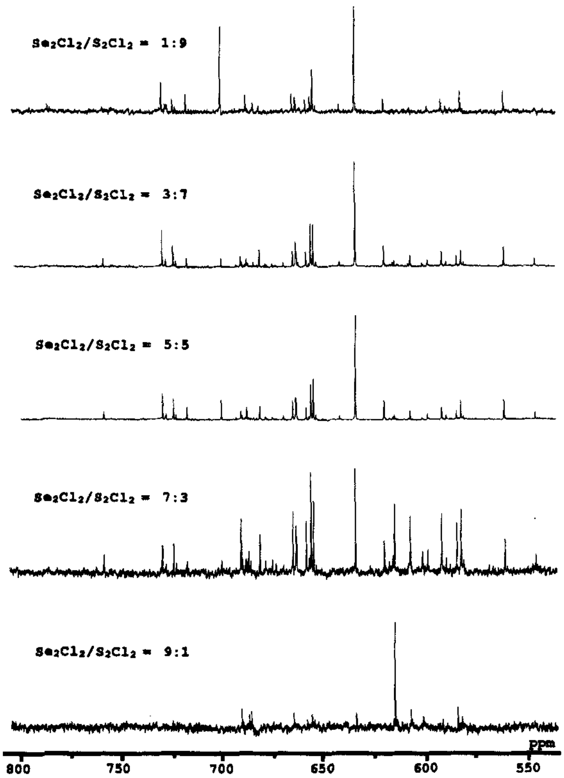

FIGURE 1. ^{77}Se NMR spectra of the

SeS_7 and 1,2-Se_2S_6 are expectedly the main selenium containing components in the sulfur-rich reaction mixtures. With increasing initial selenium content the relative abundances of more selenium-rich selenium sulfides increase. When the molar ratio of Se_2Cl_2 and S_2Cl_2 is 9:1, Se_8 and 1,2-Se_6S_2 are the main components in the reaction mixture. The product composition was not affected by the temperature of the reaction.

The reaction of Se_2Cl_2/S_2Cl_2 with ammonia seems to be rather analogous to the reaction of the dichalcogen dichlorides with potassium iodides.[8] The formation of sulfur-selenium-nitrogen species, however, is not indicated by NMR spectroscopy.

Table I The assignment and the relative abundance of the components (in mol%) of the reaction products as a function of the initial molar ratio in the Se_2Cl_2/S_2Cl_2 mixture.

Molecule	δ (ppm)	Initial Molar Ratio 1:9	3:7	5:5	7:3	9:1
SeS_7	700.4	39	7	12	5	-
1,2-Se_2S_6	634.6	19	16	24	14	-
1,3-Se_2S_6	729.8	6	13	9	5	-
1,4-Se_2S_6	688.0	4	3	4	3	15
1,5-Se_2S_6	717.6	4	3	4	2	-
1,2,3-Se_3S_5	654.9, 561.2	9	13	13	12	-
1,2,4-Se_3S_5	728.1, 663.6, 653.7	3	8	3	7	-
1,2,5-Se_3S_5	724.3, 663.6, 620.3	6	15	12	11	-
1,2,3,4-Se_4S_4	665.1, 582.3	4	5	6	10	15
1,2,3,5-Se_4S_4	723.1, 669.7, 642.3, 589.6	2	4	3	4	-
1,2,3,6-Se_4S_4	758.9, 681.5, 545.9	1	6	4	6	-
1,2,3-Se_5S_3	658.5, 598.8, 591.9	2	4	4	8	12
1,2-Se_6S_2	690.8, 607.4, 584.5	-	3	2	8	19
Se_8	615.3	-	-	-	3	24
Se_6	687.2	-	-	-	1	6

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