Journal of Thermal Analysis, Vol. 32 (1987)445–449

FORMATION AND THERMAL DECOMPOSITION OF SILICON OXYNITRIDE COMPOUNDS II

S. Podsiadło

DEPARTMENT OF INORGANIC CHEMISTRY, FACULTY OF CHEMISTRY, TECHNICAL UNIVERSITY (POLITECHNIKA), 00–664 WARSAW, POLAND

(Received March 14, 1986)

In studies on the reactions of silicon oxynitride, Si_2N_2O, with lithium oxide and of lithium metasilicate with lithium nitride, the formation of a previously unknown compound with stoichiometry Li_5SiNO_3 has been observed.

In part I of this paper, the existence of salts with the stoichiometry $Li_3(Na_3)SiNO_2$, formed in the reaction of silicon nitride or silicon oxynitride with the corresponding oxide or from silicon dioxide with the corresponding nitride, was proved. The possibility of the existence of a salt with $SiNO_3^{5-}$ anions has also been considered [1, 2]. The prediction was based on the morphological classification of simple species and on a number of analogies between the chemistry of nitroxy compounds of carbon and of silicon [3]. The results presented here are proof of the existence of the salts mentioned.

Apparatus and materials

The following compounds were used in the work: Si_2N_2O, our own product; Li_3N, our own product; Li_2O, Research Organic and Inorganic Laboratories (USA) p.a.; Li_3SiNO_2, our own product.

The reaction course was studied by thermal analysis methods on a MOM (Budapest) derivatograph. The synthesis of the new compound and its thermal decomposition were carried out in pipe furnaces under a protective atmosphere. The reaction products were studied by means of phase X-ray analysis, absorption analysis in the IR and classical (qualitative and quantitative) analysis.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Results

In the classification table in Fig. 1, the known silicon oxy compounds, silicon compounds with a nitride coordination shell, compounds with a mixed coordination shell and also the nitroxy salts under study have been placed within the $e_{zO2-} - e_{zN3-}$ coordinate system.

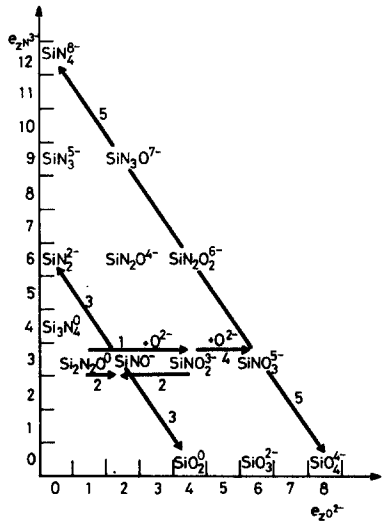

Fig. 1 Classification table of silicon oxynitride compounds

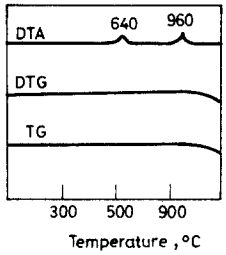

Fig. 2 Thermal curves of $Si_2N_2O + 3Li_2O$

From the reactions of silicon oxynitride, Si_2N_2O, with lithium and sodium oxides at the appropriate molar ratio, the salts $Li_3(Na_3)SiNO_2$ are obtained [2]:

$$Si_2N_2O + 3\ O^{2-} \rightarrow 2\ SiNO_2^{3-} \qquad \text{(reaction 1 in Fig. 1)}$$

The thermal curves of the mixture of reactants $Li_2O + Si_2N_2O$ is presented in Fig. 2. The weak exothermic effect at 650° corresponds to the reaction:

$$Si_2N_2O + 3\ Li_2O \rightarrow 2\ Li_3SiNO_2$$

This supposition is confirmed by the result of phase X-ray analysis, which shows the presence of Li_3SiNO_2 and unreacted Si_2N_2O after this reaction step. Only at 950° does a consecutive reaction take place, which leads to the formation of a new crystalline phase. It is probably formed via the reaction:

$$Si_2N_2O + Li_3SiNO_2 \rightarrow 3\ LiSiNO \qquad (2 \text{ in Fig. 1})$$

The X-ray identification data on this compound are presented in Table 1; they are in agreement with those given in the literature [4].

Table 1 X-ray identification data on LiSiNO

d, Å	6.24	2.714	2.362	2.327	1.778	1.519
I/I_0	60	80	100	60	40	50

The thermal decomposition of LiSiNO at 1300° leads to the formation of Li_2SiN_2 (which can be identified by X-ray analysis) and probably SiO_2 (amorphous):

$$2\ LiSiNO \rightarrow Li_2SiN_2 + SiO_2 \qquad (3 \text{ in Fig. 1})$$

Thus, the thermal decomposition would proceed analogously to the known decomposition of cyanates [3]:

$$Ca(CNO)_2 \rightarrow CaCN_2 + CO_2$$

The course of the reaction of silicon oxynitride with an excess of lithium oxide is of interest. In Fig. 3 the thermal curves of the 5 $Li_2O + Si_2N_2O$ mixture are presented. The exothermic effect at 640° corresponds (as confirmed by phase X-ray analysis) to the reaction:

$$Si_2N_2O + 3\ Li_2O \rightarrow 2\ Li_3SiNO_2 \qquad (1 \text{ in Fig. 1})$$

A new phase is then formed in a reaction with the excess of Li_2O

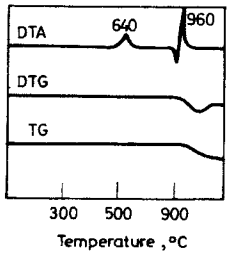

Fig. 3 Thermal curves of $Si_2N_2O + 5Li_2O$

$$Li_3SiNO_2 + Li_2O \rightarrow Li_5SiNO_3 \qquad (4 \text{ in Fig. 1})$$

The X-ray identification data on this new phase are given in Table 2.

Table 2 X-ray identification data on Li_5SiNO_3

D, Å	2.698	2.531	2.370	1.848	1.759	1.558	1.436	1.349	1.328
I/I_0	100	40	30	25	5	35	20	5	10

The reaction of lithium metasilicate with lithium nitride, the course of which is illustrated by the curves in Fig. 4, is additional confirmation of the existence of this phase.

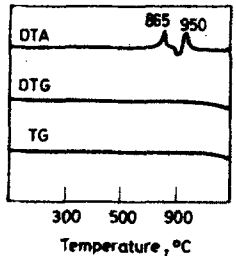

Fig. 4 Thermal curves of $Li_2SiO_3 + Li_3N$

At 865° an exothermic effect without loss of mass is observed, and Li_2O and Li_3SiNO_2 are the reaction products:

$$Li_2SiO_3 + Li_3N \rightarrow Li_3SiNO_2 + Li_2O$$

At 960° the following reaction most probably proceeds:

$$Li_3SiNO_2 + Li_2O \rightarrow Li_5SiNO_3 \qquad (4 \text{ in Fig. 1})$$

The reaction product has a diffraction pattern identical to that presented in Table 2.

At 1300° Li_5SiNO_3 undergoes thermal decomposition; Li_4SiO_4 and Li_8SiN_4 were identified among the reaction products. The decomposition most probably proceeds according to the following reaction:

$$4\ Li_5SiNO_3 \rightarrow Li_8SiN_4 + 3\ Li_4SiO_4 \qquad (5 \text{ in Fig. 1})$$

Conclusions

The reactivity of silicon nitroxide, Si_2N_2O, with lithium oxide at various stoichiometric ratios has been studied. Besides Li_3SiNO_2, obtained in earlier studies, the formation of a previously unknown phase with the stoichiometry Li_5SiNO_3, and of LiSiNO, already described in the literature [4, 5], has been observed. They are formed in the following reactions

$$SiNO_2^{3-} + Si_2N_2O \rightarrow 3\ SiNO^-$$

$$SiNO_2^{3-} + O^{2-} \rightarrow SiNO_3^{5-}$$

The thermal decompositions of these lithium salts proceed according to the scheme we have described, with the formation of products with a pure coordination shell round the silicon, i.e.

$$2\ SiNO^- \rightarrow SiN_2^{2-} + SiO_2$$

$$4\ SiNO_3^{5-} \rightarrow 3\ SiO_4^{4-} + SiN_4^{8-}$$

It should be noted that the silicon nitroxide salts, LiSiNO and Li_3SiNO_2, may be substrates for the synthesis, in reactions with Li_3N, of other hypothetical compounds, e.g. Li_4SiN_2O or $Li_6SiN_2O_2$.

References

1 S. Podsiadło, J. Thermal Anal, 32 (1987).
2 S. Podsiadło, Polish J. Chem., 58 (1984) 339.
3 S. Podsiadło, Polish J. Chem., 58 (1984) 653.
4 Y. Laurent, F. F. Grekov, J. David and J. Guyader, Ann. Chim. Fr., 5 (1980) 647.
5 Y. Laurent and J. Guyader, Acta Cryst., B37 (1981) 911.

Zusammenfassung — Eine bisher unbekannte Verbindung der Zusammensetzung Li_5SiNO_3 wurde bei Reaktionen von Siliciumoxynitrid (Si_2N_2O) mit Lithiumoxid und von Lithiummetasilikat mit Lithiumnitrid erhalten.

Резюме — При изучении реакций оксинитрида кремния (Si_2N_2O) с окисью лития и метасиликата лития с нитридом лития, наблюдали образование ранее неизвестного соединения состава Li_5SiNO_3.