

FORMATION AND THERMAL DECOMPOSITION OF SILICON OXYNITRIDE COMPOUNDS, IV

A. Kraśnicka and S. Podsiadlo

DEPARTMENT OF INORGANIC CHEMISTRY, FACULTY OF CHEMISTRY,
TECHNICAL UNIVERSITY OF WARSAW, 00-664, POLAND

(Received May 7, 1987)

The hypothetical salts $\text{Li}_4\text{SiN}_2\text{O}$ and $\text{Li}_7\text{SiN}_3\text{O}$ were sought in the course of studies on the reactions of Li_2SiN_2 and Li_5SiN_3 with lithium oxide, and of LiSiNO with lithium nitride.

Earlier studies on silicon oxynitride salts led to the formation of lithium and sodium salts containing SiNO_2^- [1, 2], SiNO_3^- [3] and SiN_2O_2^- [4] anions. The possibility of formation of other salts with a mixed coordination shell round silicon was predicted on the basis of the morphological classification of the simple species [5]. A classificatory analysis has been carried out processes occurring within the whole region of silicon oxynitride compounds described in [1–4].

Experimental

Materials and apparatus

The following compounds were used in our studies: Li_2SiN_2 , Li_5SiN_3 , LiSiNO , Li_3N (all prepared in our laboratory) and Li_2O (Research Org. Inorg. Corp.).

Initial studies of the reaction course were performed with a derivatograph. Processes on a larger scale were carried out in a tube furnace under an inert atmosphere. The products obtained in consecutive reactions were studied after cooling, by means of X-ray phase analysis and classical quantitative analysis.

Results

The thermal curves of the Li_2SiN_2 and lithium oxide mixture at a 1:1 reactant mole ratio are presented in Fig. 1. A very weak exothermic effect is observed at 560° in the DTA curve, and a broad exothermic effect within the range $850\text{--}1200^\circ$, with

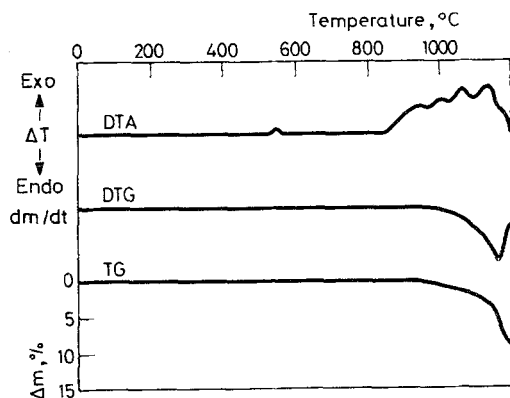


Fig. 1 TG, DTG and DTA curves of $\text{Li}_2\text{SiN}_2 + \text{Li}_2\text{O}$ ($m = 285$ mg, $6 \text{ deg} \cdot \text{min}^{-1}$ N_2 atmosphere)

regional exo effects at 930, 990, 1040 and 1130°. The process is accompanied by a slow mass loss of 3% within 900–1150°. The rate of this loss increases near 1200°, where it reaches 7%. This process is accompanied by the evaporation of lithium nitride. At 600 and 700°, only the substrates were identified in the reaction products by means of X-ray phase analysis. Above 750° the formation of Li_3SiNO_2 [1, 2] was found, and from 925° $\text{Li}_6\text{SiN}_2\text{O}_2$ too [4]. At 1200° the presence of Li_5SiNO_3 [3] and Li_2SiN_2 was detected and an amorphous silicate was also probably formed. LiSiN_2 and Li_4SiO_4 were identified in the thermal decomposition products at 1300°. No previously unknown crystalline phases were found within the whole temperature range studied.

The thermal curves of the 1 : 1 $\text{LiSiNO} + \text{Li}_3\text{N}$ mixture are presented in Fig. 2. A weak exothermic effect is observed at 640° in the DTA curve, and then a number of

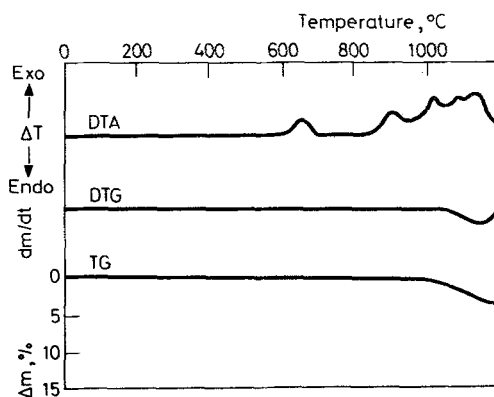


Fig. 2 TG, DTG and DTA curves of $\text{LiSiNO} + \text{Li}_3\text{N}$ ($m = 261$ mg, $6 \text{ deg} \cdot \text{min}^{-1}$, N_2 atmosphere)

exothermic effects occur within the range 850–1100 °C. From 900° a slow mass loss starts. The X-ray phase analysis shows the presence of Li_3SiNO_2 at 900°, Li_2SiN_2 at 1100° and Li_2SiN_2 and Li_4SiO_4 at 1300°. No new crystalline phases were obtained in either of the processes described, which were hoped would lead to a new salt, Li_4SiNO_2 .

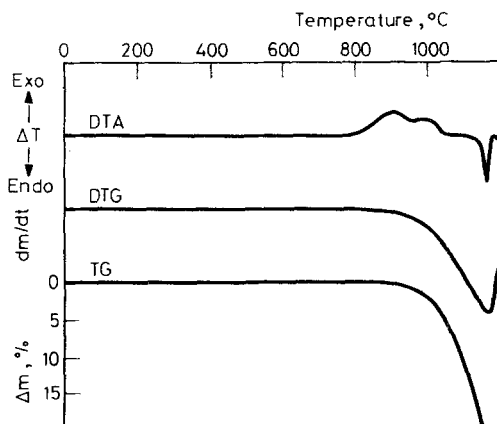


Fig. 3 TG, DTG and DTA curves of $\text{Li}_5\text{SiN}_3 + \text{Li}_2\text{O}$ ($m = 255$ mg, 6 deg \cdot min $^{-1}$, N_2 atmosphere)

The curves of the 1 : 1 $\text{Li}_5\text{SiN}_3 + \text{Li}_2\text{O}$ mixture are presented in Fig. 3. Two broad exothermic effects are observed within the range 800–1050° in the DTA curve and a sharp endothermic effect at 1160°. From 800° a slow mass loss begins, the rate of which increases from 1000°. The X-ray phase analysis up to 850° shows the presence of only the substrates, and from 950° of Li_2SiN_2 . The presence of Li_2SiN_2 and of $\text{Li}_5\text{SiN}_3 \cdot 2\text{Li}_2\text{O}$, described earlier in the literature [6], was found in the reaction mixture at 1050°. Li_4SiO_4 was the only crystalline product identified at 1300°.

The thermal curves of the 1 : 2 $\text{LiSiNO} + \text{Li}_3\text{N}$ mixture are presented in Fig. 4.

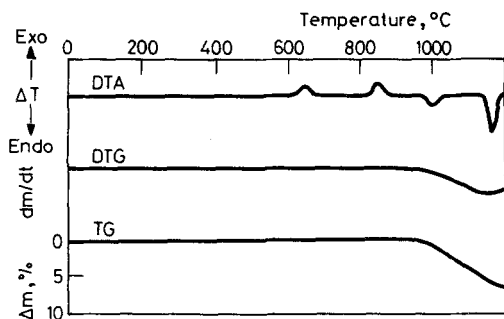


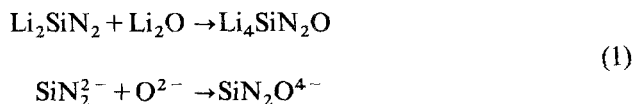
Fig. 4 TG, DTG and DTA curves of $\text{LiSiNO} + 2\text{Li}_3\text{N}$ ($m = 246$ mg, 6 deg \cdot min $^{-1}$, N_2 atmosphere)

Weak exothermic effects appear at 640° and 850°. A weak endothermic effect is observed at 1000° and a strong one at 1150°. From 900° a slow mass loss occurs. X-ray phase analysis permitted identification of the following compounds in the products; Li_3SiNO_2 and Li_2SiN_2 at 900°, exclusively Li_2SiN_2 at 1100°, and Li_2SiN_2 and Li_4SiO_4 at 1300°. Thus, the hypothetical crystalline compound $\text{Li}_7\text{SiN}_3\text{O}$ was not isolated in this case either.

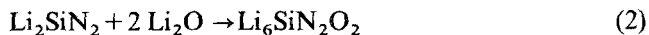
Discussion

The courses of the reactions of Li_2SiN_2 and Li_5SiN_3 with lithium oxide, and of LiSiNO with lithium nitride, have been studied. No previously unknown crystalline salts were obtained in any of the processes. Thus, no crystalline salts with $\text{SiN}_2\text{O}^{4-}$ and $\text{SiN}_3\text{O}^{7-}$ anions were obtained, as had been expected from earlier studies. It was found, however, that at the corresponding temperatures other oxynitride salts, described previously [1–4], are formed instead of the hypothetical species. The classificatory table, in which oxide, nitride and oxynitride species of silicon are included within the $e_2(\text{O}^{2-}) - e_2(\text{N}^{3-})$ coordinate system, is presented in Fig. 5. The $e_2(\text{O}^{2-})$ and $e_2(\text{N}^{3-})$ values denote the number of elementary charges formally introduced by oxide or nitride ligands, respectively, to the coordination center.

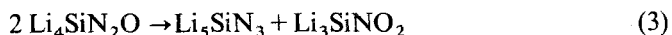
The reaction of Li_2SiN_2 and Li_2O was hoped to lead $\text{Li}_4\text{SiN}_2\text{O}$:



In reality, Li_3SiNO_2 and $\text{Li}_6\text{SiN}_2\text{O}_2$, identified by X-ray phase analysis, were found in the reaction products at comparatively low temperatures [1, 2, 4]. The phase $\text{Li}_6\text{SiN}_2\text{O}_2$ is probably formed in the following reaction:



The phase Li_3SiNO_2 on the other hand, probably results from decomposition of the unstable species $\text{Li}_4\text{SiN}_2\text{O}$:



However, Li_5SiN_3 was not identified among the products. The thermal decomposition course of a multicomponent mixture, in which crystalline Li_5SiNO_3 also appears at 1200° [3], is very difficult to interpret. In the pure state, the consecutive products undergo decomposition according to the following reactions [2–4]:



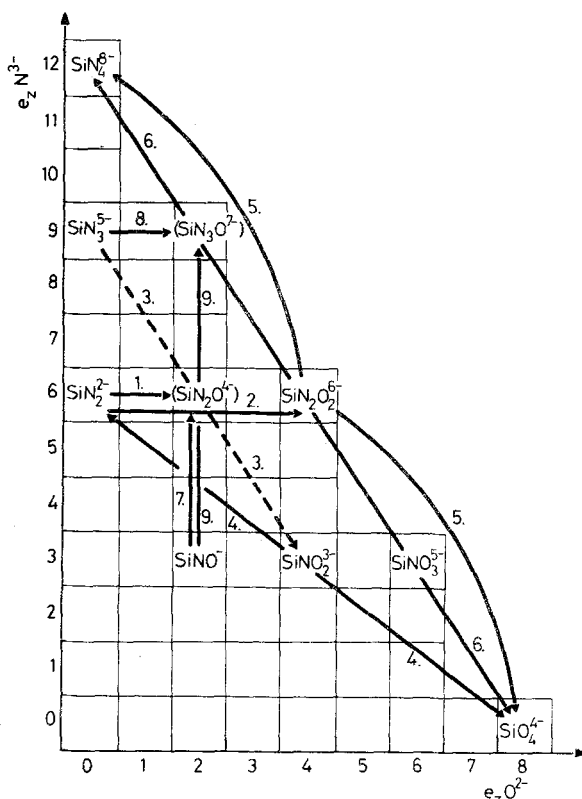
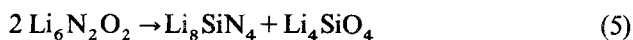
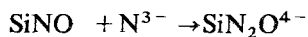
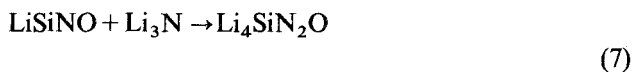


Fig. 5 Classification table of silicon oxynitride compounds



On the other hand, the reaction of $LiSiNO$ and Li_3N may also lead to Li_4SiN_2O :

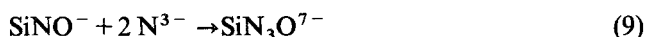


However, only Li_3SiNO_2 and Li_2SiN_2 were identified in the reaction products, and Li_4SiO_4 and Li_2SiN_2 in those of the thermal decomposition. The unstable Li_4SiN_2O is probably transformed directly, as in reaction (3):



Li_2SiN_2 and Li_4SiO_4 were the final thermal decomposition products.

The products of reactions in which $\text{Li}_7\text{SiN}_3\text{O}$ was expected are also in contrast with the productions:



In the first case, the phase $\text{Li}_5\text{SiN}_3 \cdot 2\text{Li}_2\text{O}$ known earlier [6], was obtained, and in the second one, only Li_3SiNO_2 . The thermal decompositions of these species proceed similarly as the earlier described ones for purely oxide or purely nitride compounds. It seems that the preparation of $\text{Li}_4\text{SiN}_2\text{O}$ and $\text{Li}_7\text{SiN}_3\text{O}$ in a crystalline form is not possible by the route described.

References

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Zusammenfassung — In einer Reihe von Studien der Reaktionen von Li_2SiN_2 und Li_5SiN_3 mit Lithiumoxid bzw. LiSiNO mit Lithiumnitrid wurde nach den hypothetischen Salzen $\text{Li}_4\text{SiN}_2\text{O}$ und $\text{Li}_7\text{SiN}_3\text{O}$ gesucht.

Резюме — В процессе изучения реакций взаимодействия Li_2SiN_2 и Li_5SiN_3 с окисью лития и LiSiNO с нитридом лития были обнаружены гипотетические соли состава $\text{Li}_4\text{SiN}_2\text{O}$ и $\text{Li}_7\text{SiN}_3\text{O}$.