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Thermochimica Acta 256 (1995) 375–380

thermochimica acta

Stages of the synthesis of indium nitride with the use of urea

Sławomir Podsiadło

Department of Chemistry, Warsaw Institute of Technology, Noakowskiego, Warsaw, Poland

Received 25 May 1994; accepted 22 July 1994

Abstract

Results of studies on the reaction of indium with urea in the temperature range 20–750°C are presented. The intermediate products of the reaction were identified and the stages of the formation of indium nitride have been suggested. During studies on formation of gallium nitride with the use of urea we have discovered that biuret ($H_2NCONHCONH_2$) plays a substantial role in this process. [S. Podsiadło, Thermochim Acta, 256 (1995) 367]. As shown in this work, biuret, formed in the course of thermal condensation of urea, is the main nitriding agent in the reaction. We decided to investigate the processes of the reactions of indium with urea to form indium nitride.

Keywords: Indium nitride; Synthesis

1. Experimental

The course of the reactions was followed by thermal analysis on a MOM derivatograph (Budapest, Hungary). The syntheses at characteristic temperatures were carried out in tube furnaces under the required atmosphere. The reaction products were studied, after freezing, by means of IR absorption of the solid and gaseous products (apparatus Specord IR, Germany), X-ray phase analysis (TUR M 62, Germany) and quantitative analysis (Microanalyser CHN 240 Perkin-Elmer).

The following substances were used in the work: urea, analytical grade, produced by POCh (Poland); indium, analytical grade, produced by SNT (Czech Republic).

SSDI 0040-6031(94)02025-6

2. Results and discussion

As shown in earlier works, urea decomposes endothermically with the formation of many compounds [1–4]:

$$H_2NCONH_2 \rightarrow HCNO + NH_3 \ (140°C) \quad (1)$$

$$H_2NCONH_2 \rightarrow H_2CN_2 + H_2O \ (140°C) \quad (2)$$

$$H_2NCONH_2 + HCNO \rightarrow H_2NCONHCONH_2 \ (180°C, \text{ biuret}) \quad (3)$$

$$H_2NCONHCONH_2 + HCNO \rightarrow H_2NCONHCONHCONH_2 \ (210°C, \text{ triuret}) \quad (4)$$

$$2H_2CN_2 \rightarrow H_4C_2N_4 \ (210°C, \text{ dicyandiamide}) \quad (5)$$

$$3H_2CN_2 \rightarrow H_6C_3N_6 \ (300°C, \text{ melamine}) \quad (6)$$

$$3HCNO \rightarrow (HCNO)_3 \ (230°C, \text{ cyanuric acid}) \quad (7)$$

Ammelide, ammeline, melame, meleme and melone formed at higher temperatures (300–450°C). In the NH_3 atmosphere, non-oxygen containing products were mostly formed:

$$H_2NCONH_2 \rightarrow H_2CN_2 + H_2O \ (140°C) \quad (8)$$

$$2H_2CN_2 \rightarrow H_4C_2N_4 \ (210°C) \quad (9)$$

$$3H_2CN_2 \rightarrow H_6C_3N_6 \ (300°C) \quad (10)$$

The formation of melame, meleme and melone was established in the temperature range 300–450°C.

Fig. 1 gives a tabulation of the decomposition temperatures of the products of urea condensation. Fig. 2 shows a thermogram of a 1:6 molar mixture of indium and urea in a nitrogen atmosphere.

The reaction proceeds in several stages and weight loss begins at 140°C. At 200°C the weight loss is 22.5%, corresponding to the formation of a mixture of cyanuric acid and melamine (or dicyandiamide) by the following reactions:

$$3H_2NCONH_2 \rightarrow 3HCNO + 3NH_3$$
$$3HCNO \rightarrow (HCNO)_3 \quad (11)$$

$$3H_2NCONH_2 \rightarrow 3H_2CN_2 + 3H_2O$$
$$3H_2CN_2 \rightarrow H_6C_3N_6 \quad (12)$$

The gaseous products of these reactions were water and ammonia, both identified by IR absorption in the gas phase. Elemental analysis of a solid product formed at 200°C gave H, 3.7%; C, 26.22%; N, 39.85%; O, 30.2% (at this temperature indium does not react with urea or with products of its thermal decomposition). These results correspond approximately to a stoichiometry of H:C:N:O = 3:2:3:1, probably corresponding to a mixture of melamine and cyanuric acid in the molar ratio 1:1. The mixture formed was amorphous.

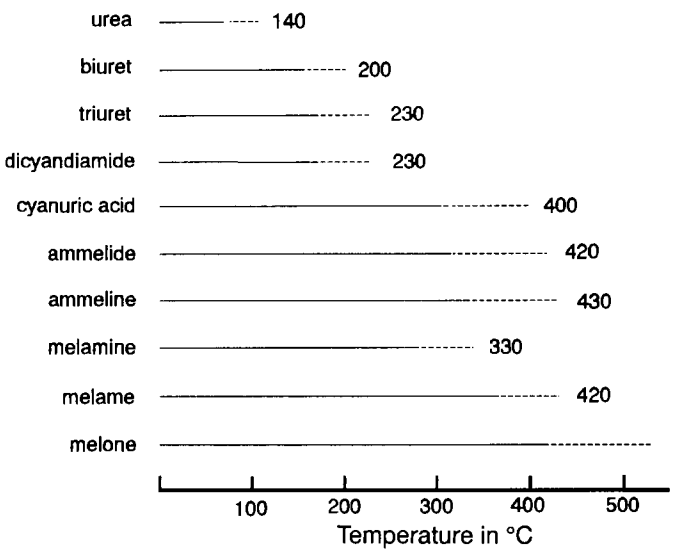

Fig. 1. Decomposition temperatures of nitriding agents (temperatures of maximum rate of decomposition are given).

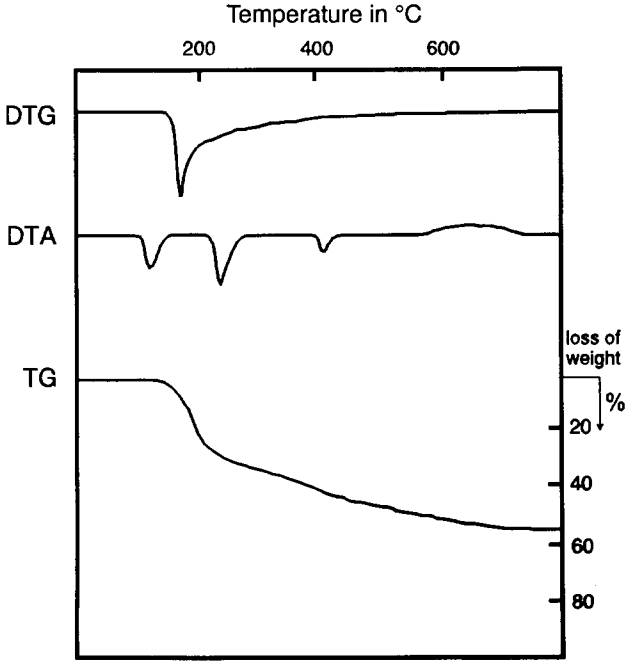

Fig. 2. Thermogravimetric analysis of a mixture of indium and urea (molar ratio 1:6); $m = 0.17$ g, $V = 2.5$ K min^{-1}, N_2 atmosphere.

Above 200°C permanent weight loss is observed, reaching the value of 31.5% at 390°C. Elemental analysis of the solid product gave: In, 17.7%; H, 2.42%; C, 24.45%; N, 36.43%; O, 19.0%. This corresponds approximately to a stoichiometry of In:H:C:N:O = 1:15:13:16:8. Some of the indium did not react and free metal was observed at the bottom of the reactor. Other products of the decomposition were the gases HCN, C_2N_2, HCNO, CO_2 and NH_3, as identified by IR spectroscopy [5]. Above 390°C continuous weight loss is observed. At 700°C a solid product is obtained with a composition corresponding to a mixture of free indium, indium nitride and indium oxide, all in crystalline form [6]. In the temperature range 390–700°C the gaseous products were mainly HCN, identified by IR spectroscopy, and a small quantity of HCNO, identified both by IR spectroscopy of the gas phase and as a crystalline condensation product — the cyanuric acid — in cool parts of the furnace. Small quantities of C_2N_2, CO_2 and NH_3 were also identified in the gas phase by IR spectroscopy.

These results lead to the conclusion that the formation of indium nitride in the reaction of indium with urea in the atmosphere of nitrogen proceeds in several stages

$$In + 6H_2NCONH_2 \rightarrow In + H_6C_3N_6 + (HCNO)_3 + 3H_2O + 3NH_3 \ (200°C) \quad (13)$$

$$In + H_6C_3N_6 + (HCNO)_3 \rightarrow InN + In_2O_3 + uHCN + wC_2N_2 + xHCNO + yCO_2 + xNH_3 \ (390–700°C) \quad (14)$$

It is impossible to explain in detail the course of the last reaction.

Similar studies of the reaction of indium with urea were carried out in an ammonia atmosphere. Fig. 3 shows a thermogram of a mixture of indium with urea (molar ratio 1:6) in an ammonia atmosphere.

A comparison of the thermograms from the reactions of indium with urea in nitrogen and ammonia atmospheres (Figs. 1 and 3 respectively) shows that their first steps are identical. Weight loss begins at 140°C, and at 200°C is 22.5% which corresponds to the formation of a mixture of melamine and cyanuric acid (molar ratio 1:1), with no reaction with indium (reaction 13).

Elemental analysis of a solid product obtained at 200°C gave the stoichiometry H:C:N:O = 3:2:3:1 which corresponds to a mixture of melamine and cyanuric acid in the molar ratio 1:1. The product of this reaction was amorphous and it was impossible to identify all its components. Indium does not react at 200°C with melamine or cyanuric acid. Above 200°C permanent weight loss is observed, reaching 31.5% at 390°C. Elemental analysis of a solid product obtained at 390°C gave: In, 34%; H, 1.4%; C, 18.65%; N, 33.29%; O, 12.4%, corresponding approximately to a stoichiometry of In:H:C:N:O = 1:5:5:8:2. This phase is amorphous and its IR spectrum is illegible. The formation of a phase of the given stoichiometry was also confirmed by the weight loss and by the analysis of gaseous products of the reaction. One of the gaseous products was HCNO, identified as a solid product of its condensation — the cyanuric acid $(HCNO)_3$ — in the cool parts of the installa-

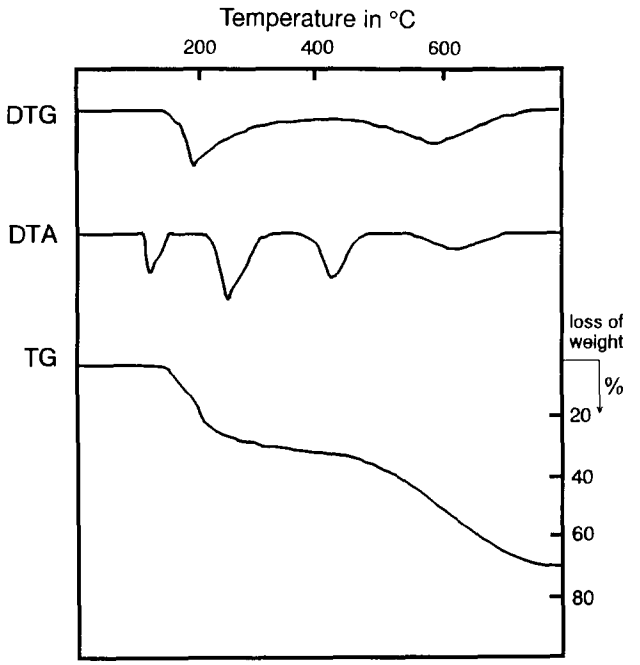

Fig. 3. Thermogravimetric analysis of a mixture of indium and urea (molar ratio 1:6); $m = 0.172$ g, $V = 2.5$ K min^{-1}, NH_3 atmosphere.

tion. The IR spectrum of gaseous ammonia is rich and it is practically impossible to detect other gaseous compounds in its atmosphere. Above 390°C continuous weight loss is observed, reaching 70% at 700°C which corresponds to the formation of indium nitride. The solid product was crystalline InN [6]. Analysis of the gaseous products of the reaction in the temperature range 390–700°C by IR spectroscopy has shown the presence of C_2N_2 and HCN. NH_4CN and $(HCNO)_3$ were found as solid products of the condensation in the cool parts of the furnace.

The solid product of this reaction at 700°C contained more than 99% InN [7]. After passing the gaseous products of the reaction through aqueous KOH, free nitrogen was also identified.

It may be concluded from the results that the synthesis of indium nitride by the reaction of indium with urea in an ammonia atmosphere proceeds as follows:

$$In + 6H_2NCONH_2 \rightarrow In + H_6C_3N_6 + (HCNO)_3 + 3H_2O + 3NH_3 \ (<200°C) \quad (15)$$

$$In + H_6C_3N_6 + (HCNO)_3 \rightarrow InH_5C_5N_8O_2 + HCNO + \tfrac{3}{2}H_2 \quad (16)$$

$$InH_5C_5N_8O_2 \rightarrow InN + 2HCN + HCNO + C_2N_2 + N_2 + H_2O \quad (17)$$

The indium nitride formed in these processes contains less than 0.06% carbon, less than 0.05% hydrogen and less than 0.15% oxygen. These impurities are smaller than in the synthesis of InN by previous reactions [8,9].

References

[1] S. Podsiadło, Thermochim Acta, 256 (1995) 367.
[2] A. Górski and S. Podsiadło, Pol. J. Chem., 58 (1984) 13.
[3] A.G. Koryakin, Zh. Org. Khim., 7 (1971) 972.
[4] N.J. Malkina, Zh. Prikl. Khim., 34 (1971) 1583.
[5] K.H. Pierson, A.N. Fletcher and E.S. Gantz, Catalog of IR Spectra for Analysis of Gases, Anal. Chem., 28 (1956) 1218.
[6] Powder Diffraction Structure Base, DHN, Wrocław, Poland, 1992.
[7] S.L. Ericson and F.J. Conrad, Talanta, 18 (1971) 1066.
[8] J. Misek and F. Srobar, Elektrotech. Cas. Czech, 30 (1979) 690.
[9] S.R. Blackburn and A.G. Jones, Patent Appl., EP 401972, 1990.