Thermal decomposition of sodium tetrazolate monohydrate and its mixture with tetrazole

A.I. Lesnikovich, G.V. Printsev, O.A. Ivashkevich, P.N. Gaponik and V.A. Shandakov

Research Institute of Physico-Chemical Problems, Byelorussian State University, 220080 Minsk (USSR)

Abstract

The thermal decomposition of sodium tetrazolate monohydrate and its mixture with tetrazole (64% tetrazole) was investigated by differential scanning calorimetry and complex thermal analysis at different heating rates. It was found that the exothermal single-stage decomposition of sodium tetrazolate proceeding at a high rate within the range 596–610 K is preceded by the processes of dehydration (393–443 K), polymorphic transformation (465 K) and melting (557 K). The activation energy of sodium tetrazolate decomposition was 98 ± 5 kJ mol^{-1}. Using the methods of IR spectroscopy, mass spectrometry and elemental analysis, it was found that the decomposition proceeds with the elimination of a nitrogen molecule and the formation of sodium acid cyanamide. Heating the mixture leads to dehydration, melting of the tetrazole and dissolution of the anhydrous salt in the tetrazole melt. During thermolysis of the solution formed, the tetrazole decomposition temperature rises and the sodium tetrazolate decomposition temperature is lowered, compared with thermolysis of the individual components. The heat of decomposition decreases significantly relative to the total heat of thermolysis of pure tetrazole and sodium tetrazolate. These features are due to the mutual influence of the components, in particular to the possible stabilization by the sodium tetrazolate molecules in the solution formed of the tetrazole 1-H form, which leads to thermolysis of the latter mainly in the melt.

INTRODUCTION

Recently, when investigating the burning of mixtures of tetrazole and sodium tetrazolate, we revealed a previously unknown type of self-organization in combustion — a liquid-flame dynamic dissipative structure [1]. To gain insight into the nature of this phenomenon, it is necessary, apart from studying its physical characteristics, to investigate the thermal decomposition of the above-mentioned mixture and its individual components, tetrazole and sodium tetrazolate. The thermolysis of tetrazole has been studied earlier [2–4]. In the present paper, we report the results of investigating the peculiarities of the thermal decomposition of sodium tetrazolate monohydrate and of its mixture with tetrazole.

EXPERIMENTAL

Tetrazole was synthesized and purified as before [2]. Sodium tetrazolate was obtained by neutralization of 1 N aqueous tetrazole solution by 0.1 N NaOH solution with the equivalence point (pH 9.11) being indicated by the potential jump measured on an EV-14 ionometer.
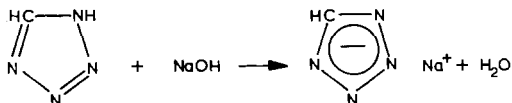
The solution obtained was evaporated to dryness in a vacuum and the residue was recrystallized from isopropanol. With slow cooling of the solution, large (up to 10 mm long) rhomb-shaped transparent crystals of sodium tetrazolate monohydrate are formed. The composition of the product was monitored using X-ray analysis (DRON-3 instrument, Cu Kα radiation) and by ^{1}H NMR data (JEOL-PS-100 instrument; the spectra were recorded on 1 mol.% solutions in dried deuteromethanol, the internal reference being hexamethyldisiloxane). The ratio of integrated intensities of the water of crystallization protons (4, 74 ppm) and the hydrogen atom on the ring carbon atom (8, 60 ppm) corresponds exactly to 2 : 1. The X-ray analysis data for the sample are identical with the data for sodium tetrazolate monohydrate [5].

The thermal decomposition of the samples was investigated by differential scanning calorimetry (DSC) on a Mettler TA-3000 thermoanalyser in a self-generated atmosphere and by complex thermal analysis (CTA) using a Paulik–Paulik–Erdey derivatograph at various heating rates from 2.5 to 20 K min^{-1}. For a correct comparison of the data obtained with the results of the investigation of the thermolysis of pure tetrazole, the DSC experiments were carried out in hermetically sealed crucibles. The details of the experiment are given in ref. 2. It was found that when sodium tetrazolate monohydrate samples of over 10 mg were used in derivatographic experiments, the samples decompose with explosion. Therefore the substances to be investigated were diluted (1 : 10) with an inert heat-transfer agent; as in the investigation of tetrazole thermolysis, silicon powder was chosen. Special investigations by DSC have shown that the thermoanalytical curves of silicon-diluted samples of sodium tetrazolate monohydrate and its mixture with tetrazole are identical with those of undiluted samples.

It should be noted that the strong (1 : 10) dilution of the sample with silicon powder required for performing the derivatographic experiments complicates the procedure used to prepare the mixture for investigation. Simply mixing the diluent powder with the powder of the mixture components prevents contact between the particles of the latter, thus impeding the interaction between the components during thermolysis which would take place is an undiluted mixture. This may lead to distortion of the nature of

the thermolysis. To avoid this disadvantage, we proposed a procedure for preparing samples of high energy mixtures for derivatographic studies [6]. According to this procedure, the particles of the original components are comminuted to fractions of less than 50 μm, mixed with one another and compressed; the pellets thus obtained are crushed, the agglomerate fraction of 0.5–0.8 mm size is isolated and diluted with the heat-transfer agent. The mixture obtained is then used in derivatographic studies. Because the volume of the agglomerates is significantly greater than the volume of particles of the original components, the content of these particles in each agglomerate is fairly high. Owing to this, the composition of the agglomerates is close to that of the original mixture. The volume of each agglomerate, however, is low, and its dilution with the heat-transfer agent prevents the sample from overheating during thermolysis.

The proposed procedure was used to prepare samples for investigating the thermolysis of a mixture of tetrazole with sodium tetrazolate monohydrate. For the investigations, we chose a mixture containing 36 wt.% of the salt, since such a composition lies within the correct ratio of components which, on burning, forms the liquid-flame dynamic dissipative structure [1].

To analyse the composition of gaseous and condensed thermolysis products, the samples (5–6 mg) were decomposed for 15 min in sealed glass ampoules, washed with argon, and then evacuated by complete immersion in Wood's alloy heated to 613 K. The composition of the gaseous products of thermolysis was investigated by mass spectrometry (Varian MAT-311). IR spectroscopy (Specord-75-IR, KBr pellets) and elemental analysis (Hewlett-Packard 1080) were used to analyse the condensed residue.

RESULTS AND DISCUSSION

Figure 1 shows the DSC curve of the thermal decomposition of sodium tetrazolate monohydrate, which contains three endo effects with minima at 423 K, 465 K and 557 K respectively and a sharp intense exo effect at 604 K. Figure 2(a) gives the DTA and TG curves of sodium tetrazolate monohydrate, and Fig. 2(b) shows analogous curves for anhydrous sodium tetrazolate obtained by drying the monohydrate in a vacuum (10^{-1} mmHg) at 393 K for 2 h. It should be noted that anhydrous sodium tetrazolate, a friable white powder, is highly hygroscopic. The DTA curve of the monohydrate has two endo effects within 390–400 and 560–670 K, as well as a sharp endo effect at 610–620 K. The mass-loss steps on the TG curve correspond to the first endo effect of the anhydrous sodium tetrazolate decomposition. Table 1 gives the thermoanalytical characteristics of the sodium tetrazolate monohydrate decomposition process.

Analysis of the data obtained leads to the conclusion that the first endo effect on the DSC and DTA curves is due to dehydration. The corresponding loss of mass is 16% (the calculated water content of the monohydrate is
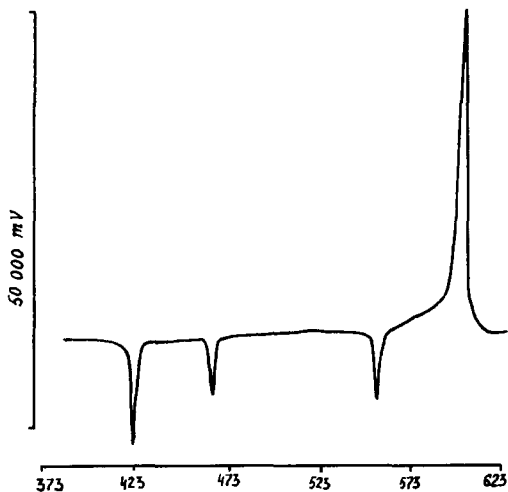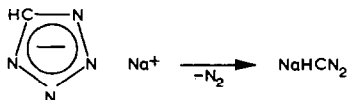
Fig. 1. DSC curve of sodium tetrazolate monohydrate (heating rate, 10 K min^{-1}).

16.36%). The shift of this endo effect minimum to higher temperatures in DSC relative to the derivatographic experiments is probably due to the fact that in the first case, decomposition took place in a sealed cell. An increase in pressure in the cell leads to the shift to higher temperature regions.

The second endo effect on the DSC curve at 466 K is probably due to the polymorphic transformation of sodium tetrazolate. The absence of this effect from the DTA curve is probably associated with the low heat of transformation and the considerable dilution of the sample. The endo effects on the DSC (557 K) and DTA (563 K) curves are caused by the melting of sodium tetrazolate followed by its explosive decomposition. This process is accompanied by loss of mass corresponding to the elimination of one nitrogen molecule (the theoretical loss of mass being 25.45%). The results obtained are in agreement with the mass spectrometric data (Fig. 3) which indicate that the single gaseous product of sodium tetrazolate thermolysis is molecular nitrogen ($m/e = 28.14$).

The IR spectrum of the condensed product of sodium tetrazolate thermolysis, which is a white solid substance with a light pink shade, is given in Fig. 4. The spectrum contains characteristic groups of bands with absorption maxima at 2149–2220 cm^{-1} ($\nu(-N=C=N-)$), 1551 cm^{-1} ($\delta(N-H)$) and 1392 cm^{-1} ($\nu(C=N)$). This suggests that during thermolysis of sodium tetrazolate, sodium acid cyanamide is formed which, according to the literature data [7], displays a carbodiimide structure, Na$^+$[N$^-$=C=N$^-$]H$^+$
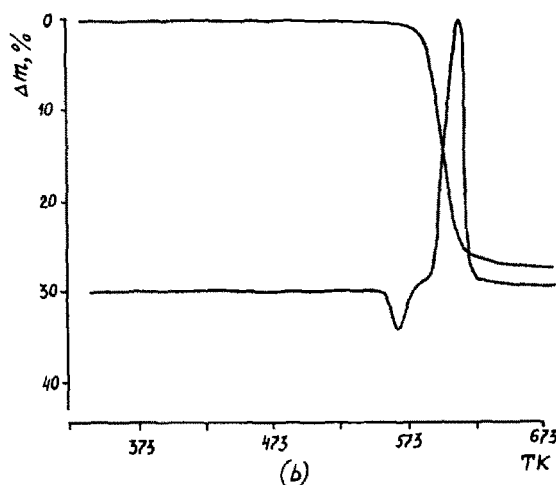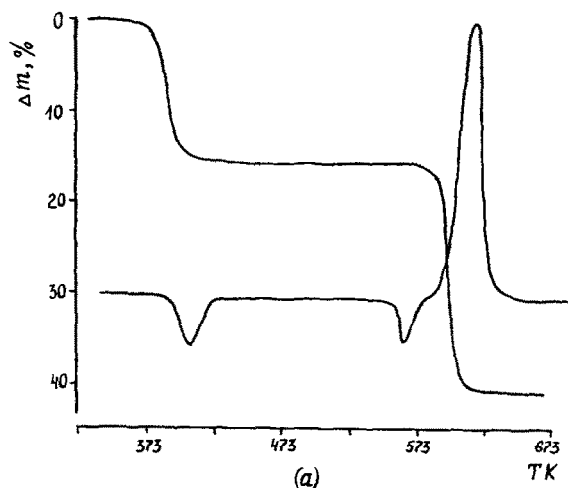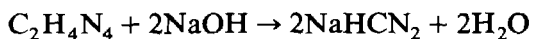
Fig. 2. Systems of matched DTA and TG curves of sodium tetrazolate monohydrate (a) and anhydrous sodium tetrazolate (b).

To confirm this, sodium acid cyanamide was synthesized by the interaction of dicyandiamide with alkali in a vacuum at 633 K according to the scheme described in ref. 8:

$$C_2H_4N_4 + 2NaOH \rightarrow 2NaHCN_2 + 2H_2O$$

A comparative spectroscopic study was made of the sample obtained and the condensed product of sodium tetrazolate thermolysis. The appearance and the IR spectra of both compounds were practically identical (Fig. 4). The only difference is some redistribution of the band intensities at 2149–2220 cm^{-1}, which is probably associated with the different preparations of the samples and of the band with a maximum at 2076 cm^{-1}, which relates to

TABLE 1

Thermoanalytical parameters of sodium tetrazolate monohydrate thermolysis (heating rate, 10 K min^{-1})

(a) DSC

T_{endo} (K)	ΔH_{endo} (kJ mol^{-1})	T_{endo} (K)	ΔH_{endo} (kJ mol^{-1})	m.p. (K)	ΔH_{melt} (kJ mol^{-1})	T_{exo} (K)	ΔH_{exo} (kJ mol^{-1})
423	27	466	11	557	21	604	112

(b) DTA

T_{endo} (K)	Δm [a] (%)	m.p. (K)	Δm [a] (%)	T_{exo} (K)	Δm [a] (%)
394	16	563	–	613	25.1

[a] Mass loss.

$\nu(C\equiv N)$ of sodium cyanide [9] formed as the result of partial decomposition of sodium acid cyanamide under the conditions of its preparation.

According to the elemental analysis, the H : C : N ratio of the solid product of thermolysis is close to 1 : 1 : 2, which also confirms the formation of NaHCN$_2$.

The activation energy of sodium tetrazolate thermolysis calculated by the Kissinger method [10] from the DSC data for the exo effect maximum shift at different heating rates, is 98 ± 5 kJ mol^{-1}.

It should be noted that unlike tetrazole, sodium tetrazolate is non-volatile, and therefore its thermal decomposition proceeds exclusively in the melt, and the thermal effect measured by the DSC method (Table 1) characterizes the process in the melt. For tetrazole thermolysis under similar conditions, simultaneous decomposition of substrate in the condensed and gas phases
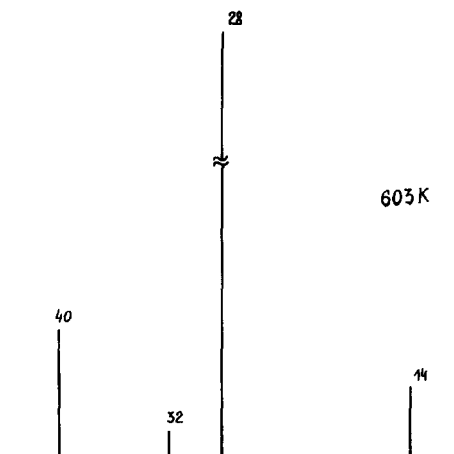

Fig. 3. Mass spectrum of gaseous products of sodium tetrazolate decomposition.
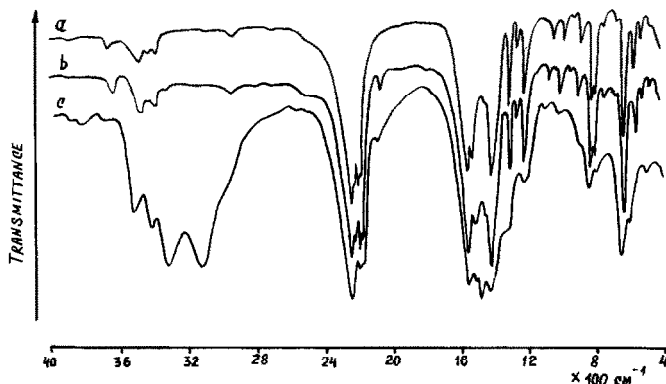
Fig. 4. IR spectra of the condensed product of sodium tetrazolate thermolysis (curve a), the sodium acid cyanamide (curve b), and the condensed product of thermal decomposition of tetrazole and sodium tetrazolate mixture (curve c).

has been detected [2,4]. In spite of the fact that in both cases the thermal effect is conditioned by the breaking of the tetrazole ring, the thermal effect of the total process for tetrazole thermolysis (158 kJ mol^{-1}) considerably exceeds the sodium tetrazolate decomposition heat. This indirectly confirms our previous conclusion [4] concerning the smaller decomposition heat for tetrazole in the melt compared with that in the gas phase.

Comparing the DSC curve of a mixture of tetrazole and sodium tetrazolate monohydrate with similar curves for the individual components [2], it can be concluded that the former cannot be obtained by a mere overlapping of the latter (Fig. 5). This suggests that the components interact during heating of the mixture. The first endo effect on the DSC curve of the
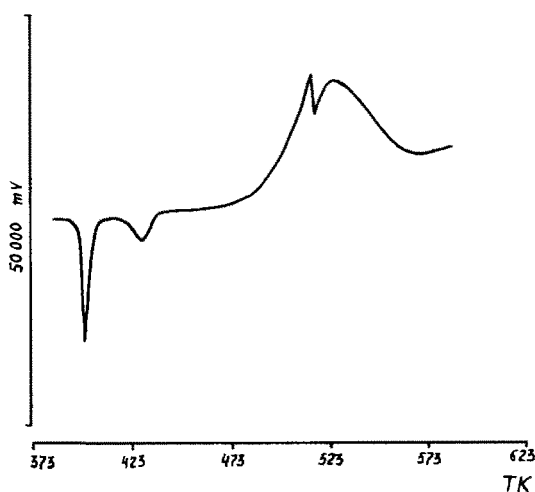

Fig. 5. DSC curve of a mixture of tetrazole and 36 wt.% sodium tetrazolate monohydrate.

TABLE 2

Thermoanalytical parameters of decomposition of the tetrazole and sodium tetrazolate mixture and of pure tetrazole according to DSC data (heating rate, 10 K min^{-1})

Sample	T_{endo} (K)	ΔH_{endo} (kJ mol^{-1})	T_{melt} (K)	ΔH_{melt} (kJ mol^{-1})	$T_{onset\ of\ decomp.}$ (K)	$T_{end\ of\ decomp.}$ (K)	$\Delta H_{decomp.}$ (kJ mol^{-1})
Mixture	398	14	429	5	475	525	71
Tetrazole	–	–	429	20	447	516	158

mixture, the sodium tetrazolate monohydrate dehydration, appears at a somewhat lower temperature (398 K, see Table 2) than the dehydration temperature of the monohydrate component alone (423 K). This is probably due to the decrease in the content of the component being dehydrated in the sealed cell and, consequently, to the decrease in the pressure inside this cell, compared with thermolysis of pure sodium tetrazolate monohydrate. The endo effect at 429 K corresponds to tetrazole melting, but it is characterized by a considerably lower heat compared with thermolysis of the tetrazole component alone and differs in peak shape. This is attributed to the fact that when tetrazole melts, there is dissolution of sodium tetrazolate in the melt, accompanied by heat release, which partially compensates for the heat absorption during tetrazole melting.

Experiments on heating mixtures of tetrazole with sodium tetrazolate (both monohydrate and anhydrous) over a wide range of component concentrations (from 1:2 to 2:1) have shown that when the melting point of tetrazole is reached (429 K), the whole mixture becomes liquid, although the melting point of sodium tetrazolate is considerably higher (557 K).

The broadened exo effect in the 470–545 K range on the DSC curve is due to decomposition of the mixture, the thermal effect of its decomposition being much smaller than the combined decomposition heats of its components:

$$H_{mix} < 0.64\ \Delta H_{tetrazole} + 0.36\ \Delta H_{tetrazolate}$$

It should be remembered that during thermolysis of the liquid mixture the tetrazole molecules are distributed among the molecules of ionic sodium tetrazolate. Equilibrium between the tautomeric forms of tetrazole in polar solvents is known to be shifted towards the formation of the 1-H form [11,12], which is characterized by a volatility lower than that of the 2-H form [13,14]. Therefore the thermolysis of the mixture proceeds to a greater extent in the melt than does the thermolysis of tetrazole alone; this must lead to a decrease in the overall effect of decomposition.

Analysis of the system of matched DTA and TG curves of the mixture (Fig. 6) reveals that the sample begins to lose mass slowly after 373 K. In the
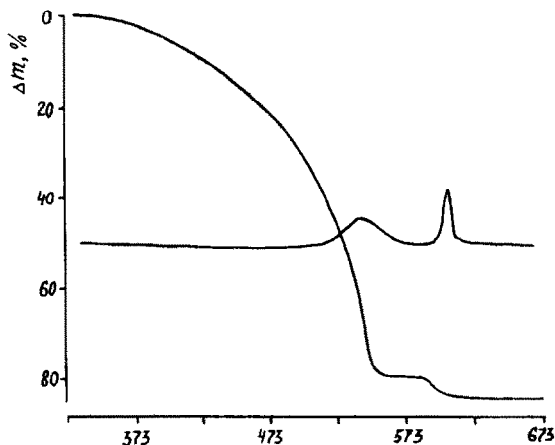
Fig. 6. System of matched DTA and TG curves of a mixture of tetrazole and 36 wt.% sodium tetrazolate.

443–553 K range, a significant (about 70%) mass loss is observed. It should be noted that there is only one weak exo effect on the DTA curve corresponding to this phenomenon. This curve shape is due to a number of concurrent processes which are accompanied by loss of mass: tetrazole evaporation, sodium monohydrate dehydration and decomposition of the mixture, of which only the last is characterized by heat release.

The loss of mass of the mixture below the tetrazole melting point is about 6%, which agrees with the water of crystallization content in the sample (5.9%) and shows that the dehydration process takes place prior to tetrazole melting and in the same temperature range as in the case of the individual sodium tetrazolate monohydrate (Fig. 2). Thus, when the tetrazole melts, anhydrous sodium tetrazolate is dissolved in it, which agrees with the DSC data.

The mass spectrum of the gaseous products of the mixture thermolysis (Fig. 7) is identical with the mass spectrum of the products of tetrazole decomposition [2]. This indicates that some tetrazole decomposes in the gas phase during mixture thermolysis, despite the fact that in the melt the equilibrium is shifted towards the formation of the less volatile 1-H form. A comparison of the IR spectrum of the condensed residue of thermal decomposition of the tetrazole and sodium tetrazolate monohydrate mixture with the IR spectra of the solid products of thermolysis of sodium tetrazolate and tetrazole [4] alone shows that sodium acid cyanamide and polycyanamide are formed as a result of the decomposition of the mixture.

The results obtained indicate that the peculiarities of the decomposition of the mixture of tetrazole and sodium tetrazolate are due to the mutual influence of the components, in particular, to the possible stabilization by the sodium tetrazolate molecules in the solution formed of the tetrazole 1-H form, which leads to the decomposition of the latter mainly in the melt.
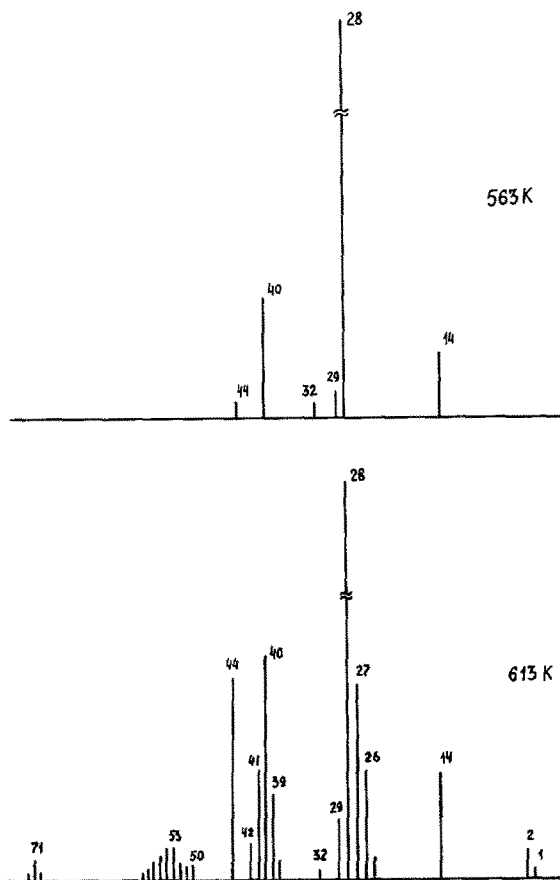
Fig. 7. Mass spectra of the gaseous products of thermal decomposition of tetrazole and sodium tetrazolate monohydrate mixture.

These results, as well as the data on the composition of the gaseous and condensed products of thermolysis of the mixture and its individual components, may be useful in the discussion of the nature of the chemical processes taking place in the liquid-flame dynamic dissipative structure formed when tetrazole and sodium tetrazolate mixture burns. These problems will be considered in our next study.

REFERENCES

1 A.I. Lesnikovich, V.V. Sviridov, G.V. Printsev, O.A. Ivashkevich, and P.N. Gaponik, Nature, 323 (1986) 706.
2 A.I. Lesnikovich, O.A. Ivashkevich, V.A. Lyutsko, G.V. Printsev, K.K. Kovalenko, P.N. Gaponik and S.V. Levchik, Thermochim. Acta, 145 (1989) 195.
3 S.V. Vyazovkin, A.I. Lesnikovich and V.A. Lyutsko, Thermochim. Acta, 115 (1990) 17.
4 A.I. Lesnikovich, O.A. Ivashkevich, G.V. Printsev, P.N. Gaponik and S.V. Levchik, Thermochim. Acta 171 (1990) 207.

5 G.J. Palenik, Acta Crystallogr., 16 (1963) 596.

6 A.I. Lesnikovich, G.F. Levchik, S.V. Levchik, V.G. Guslev and G.V. Printsev, U.S.S.R. Patent N 1350577, 1987.

7 B.I. Sukhorukov and A.I. Finkelstein, Opt. Spectrosk., 7 (1959) 653 (in Russian).

8 V.A. Shushunov and A.M. Pavlov, Zh. Prikl. Khim., 28 (1955) 98 (in Russian).

9 N. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1966, p. 108.

10 H.E. Kissinger, Anal. Chem., 29 (1957) 1702.

11 R.N. Butler, Adv. Heterocycl. Chem., 21 (1977) 323.

12 J.B. Launsbury, J. Phys. Chem., 63 (1963) 721.

13 A. Razynska, A. Tempczyk, E. Maslinski, J. Szafranek and Z. Grzonka, J. Chem. Soc., Perkin Trans., 2 (1983) 379.

14 A.P. Mazurek and R. Osman, J. Phys. Chem., 89 (1985) 460.