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# THERMAL DECOMPOSITION OF OCTAHEDRAL Ni(II) COMPLEXES WITH 1-NAPHTHYLACETIC ACID HYDRAZIDE

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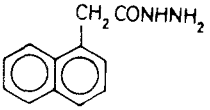
The thermal decompositions of the octahedral complexes of Ni(II) with 1-naphthylacetic acid hydrazide ($L$), of the type $NiL_nX_2 \cdot mH_2O$, where $n=2$ and 3, $m=2$ and 4, and $X=$ Cl, Br, I, NCS, OAc and 1/2 $SO_4$, were studied in both air and nitrogen atmospheres at temperatures up to 1000 °C. The most probable mechanism of the process was proposed.

In a previous paper [1] we described the syntheses and spectrophotometric and magnetic investigations of the following complexes: $NiL_2Cl_2 \cdot 2H_2O$, $NiL_2(NCS)_2$, $NiL_2(OAc)_2$, $NiL_2SO_4 \cdot 4H_2O$, $NiL_3Cl_2 \cdot 2H_2O$, $NiL_3Br_2 \cdot 2H_2O$ and $NiL_3I_2 \cdot 2H_2O$, where L is the hydrazide of 1-naphthylacetic acid:



The present paper reports the results of an investigation of the thermal decomposition of these complexes, with the aim of completing their physico-chemical characterization. The spectroscopic data on the newly synthesized complex $NiL_3SO_4 \cdot 4H_2O$ are also given.

## Experimental

Thermogravimetric investigations were carried out with a derivatograph. Each sample was heated from room temperature to 1000° at a rate of 10 deg/min. The processes were carried out in both air and nitrogen atmospheres. $Al_2O_3$ was used as the reference.

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Reflection spectra were recorded in the range 10000–45000 cm$^{-1}$ at room temperature with an SPM–2 monochromator (VEB Zeiss, Jena) with an R–45/0 reflection cell. MgO served as "white" reference.

Magnetic susceptibilities were measured by Faraday's method at room temperature, with Hg[Co(NCS)$_4$] as calibrant.

$NiL_3SO_4 \cdot 4H_2O$ was obtained by the reaction of an aqueous ethanolic solution of $NiSO_4 \cdot 7H_2O$ with a hot ethanolic solution of the ligand in the molar ratio 1 : 3. Analysis: Ni 7.00% (found), 7.09% (calcd.), $H_2O$ 8.70% (found), 8.71% (calcd.), $\mu_{eff}$ = 3.2 BM (298 K).

## Results and discussion

Figure 1 shows the DTA curves for the ligand alone, registered in air atmosphere and in nitrogen atmosphere. Figures 2 to 9 illustrate the decomposition processes of particular complexes in air atmosphere. In Fig. 5, the DTA curve obtained in nitrogen atmosphere for $NiL_2SO_4 \cdot 4H_2O$ is given for the sake of comparison. It is evident that the decomposition mechanisms of the ligand and the complexes in air are different from those in nitrogen atmosphere.

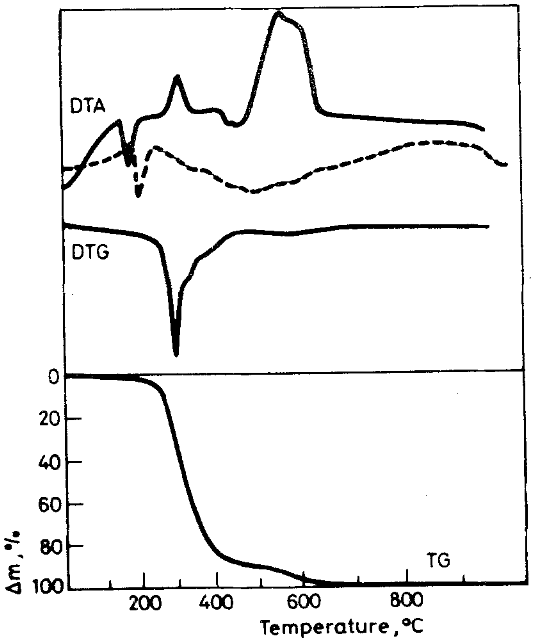

Fig. 1 TG, DTA and DTG curves of *L* (—— air, – – – nitrogen)

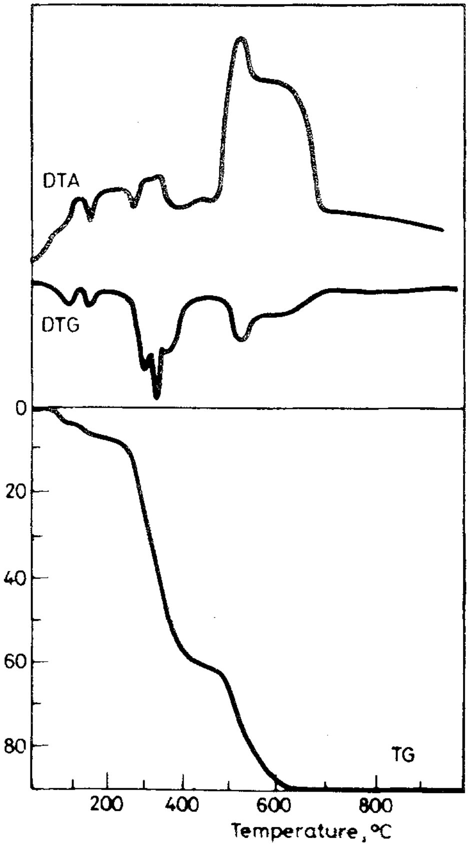

Fig. 2 TG, DTA and DTG curves of $NiL_2Cl_2 \cdot 2H_2O$ complex

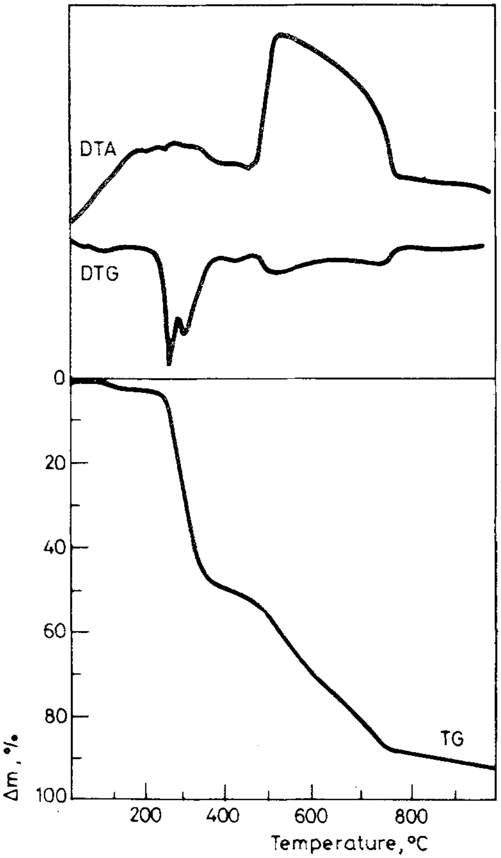

Fig. 3 TG, DTA and DTG curves of $NiL_2(NCS)_2$ complex

The investigation of the thermal decomposition of the ligand in air atmosphere indicates that the ligand is stable up to 160°, i.e. its melting point (Table 1). The exothermic peak at 325° can be ascribed to cleavage of the naphthalene ring. This was confirmed by studying the decomposition of pure naphthalene.

The broad exothermic peak corresponds to the decomposition of the second part of the ligand, which in the presence of oxygen from the air is accompanied by the liberation of ethylene and carbon dioxide. This assumption was proved by the DTA curve obtained in nitrogen atmosphere, where an analogous single endothermic peak represents the melting of the ligand, while the other endothermic peaks correspond to the exothermic peaks recorded in air atmosphere.

As concerns the bis-ligand hydrate complexes (Table 1), the first endothermic peak relates to the elimination of the corresponding number of crystalline water

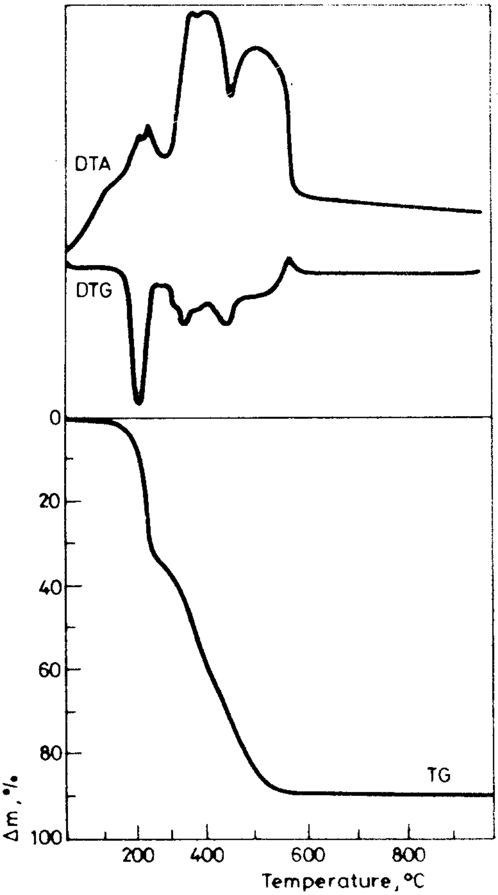

**Fig. 4** TG, DTA and DTG curves of $NiL_2(OAc)_2$ complex

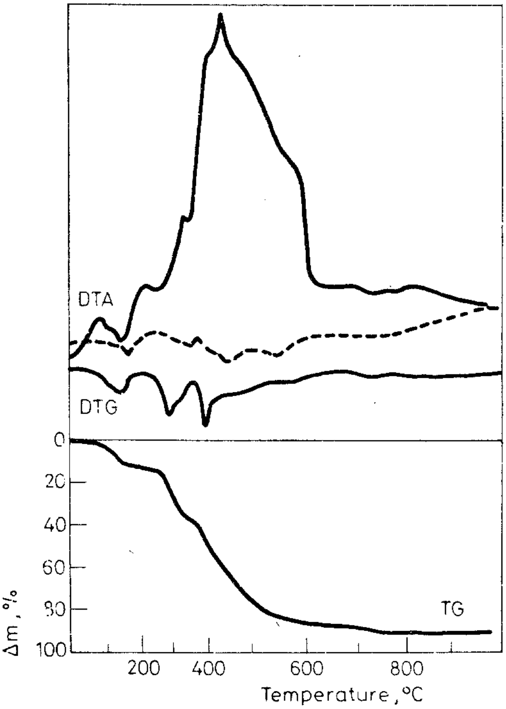

**Fig. 5** TG, DTA and DTG curves of $NiL_2SO_4 \cdot 4H_2O$ complex (—— air, – – – nitrogen)

molecules, and the second one to the melting of the complex. The only exception is $NiL_2Cl_2 \cdot 2H_2O$, for which the first and second endothermic peaks correspond to the elimination of non-coordinated and coordinated water, respectively.

In the case of $NiL_2X_2 \cdot 2H_2O$ ($X$ = Cl, Br, I), the TG analyses had shown two water molecules in the composition, and not only one as supposed on the basis of the elemental analysis [1]. Considering the temperatures at which the water molecules are eliminated from the above tris-ligand complexes, as well as the complex composition and the bidentate character of the ligand, it can be stated that the water is not coordinated. In contrast, in the case of $NiL_2Cl_2 \cdot 2H_2O$, from which one water molecule is eliminated at lower temperature (90°), it is possible to suppose

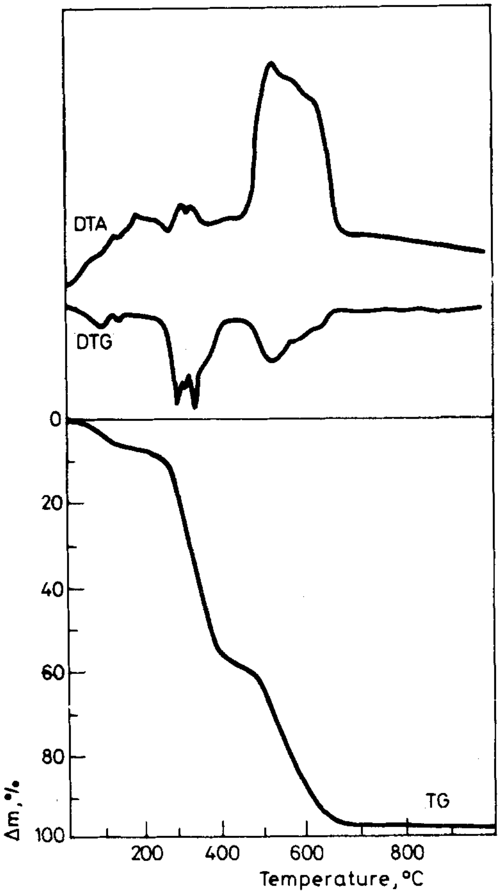

Fig. 6 TG, DTA and DTG curves of $NiL_3Br_2 \cdot 2H_2O$ complex

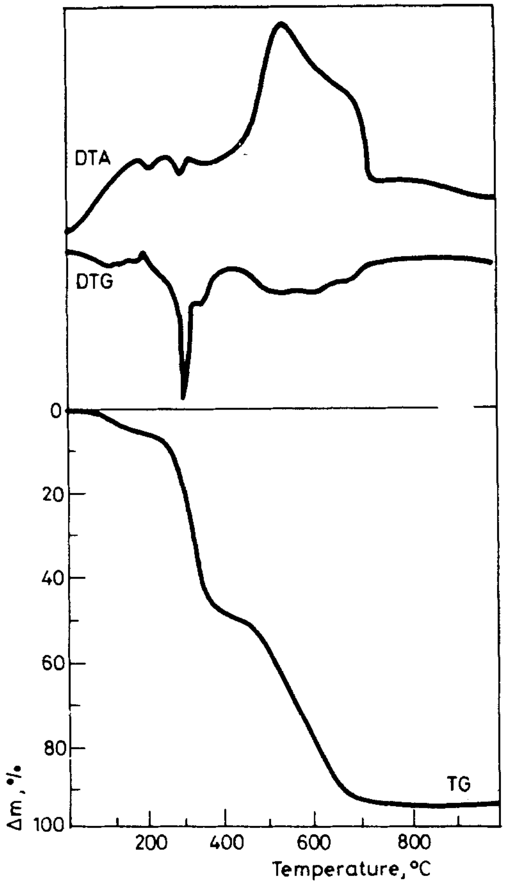

Fig. 7 TG, DTA and DTG curves of $NiL_3Cl_2 \cdot 2H_2O$ complex

that the octahedral configuration is achieved via participation (in addition to two molecules of the bidentate ligand and one water molecule) of one $Cl^-$ ion. Therefore, the coordination formula $[NiL_2(H_2O)Cl]ClH_2O$ may be ascribed to this complex.

However, in the case of the bis- and the newly synthesized tris-ligand sulphate complexes, all four water molecules are eliminated at the same temperature, which can serve as an indication that even the bis-ligand complexes contain non-coordinated water. This means that the coordination number 6 in this complex is attained by additional coordination of the $SO_4$ group, which is in agreement with the discussion presented in [1]. The position of the maxima in the electronic spectra

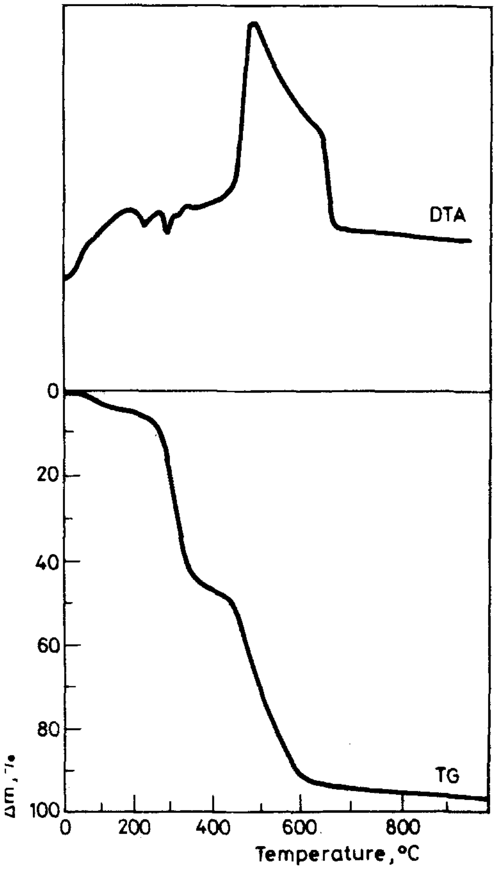

**Fig. 8** TG, DTA and DTG curves of $NiL_3I_2 \cdot 2H_2O$ complex

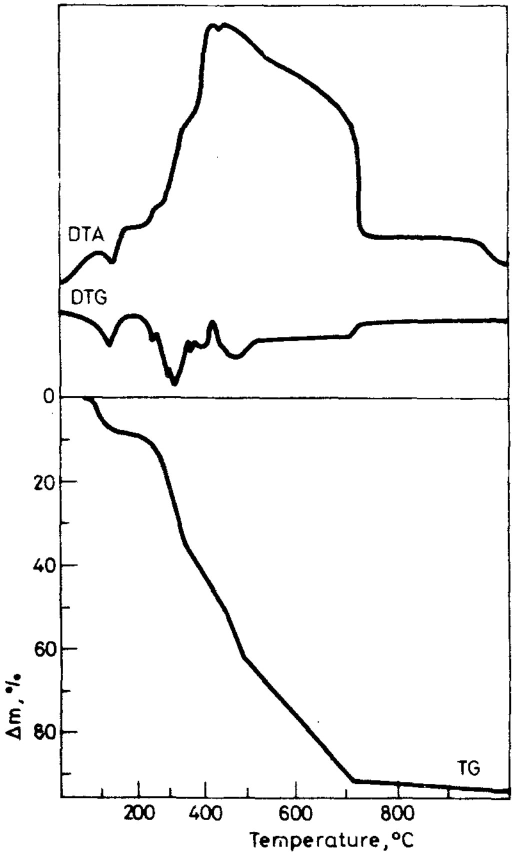

**Fig. 9** TG, DTA and DTG curves of $NiL_3SO_4 \cdot 4H_2O$ complex

and the values of the magnetic moments of $NiL_3SO_4 \cdot 4H_2O$ indicate the presence of an approximate point group of $O_h$ symmetry in this complex, i.e. and octahedral configuration of the metal ion. As the $d^8$ system is being discussed, the corresponding transitions at 12.00, 17.00 and $27.20 \cdot 10^3$ $cm^{-1}$ could be identified as $^3A_2g \rightarrow {}^3T_2g(F)$, $^3A_2g \rightarrow {}^3A_1g(F)$ and $^3A_2g \rightarrow {}^3T_1g(P)$, respectively [2]. The octahedral configuration of Ni(II) is realized as in the case of other tris-ligand complexes, by participation of three molecules of the bidentate ligand.

The other endothermic peak, characteristic of the halogen complexes and of $NiL_2(NCS)_2$, relates to elimination of the halogen or the corresponding NCS group, respectively, which is in agreement with the literature data [3–5]. The exothermic peak at 215° for $NiL_2(OAc)_2$ corresponds to elimination of the

**Table 1** TG analyses of octahedral Ni(II) complexes with *L*

| Effect | Fragment eliminated | *L* | | | $NiL_2SO_4 \cdot 4H_2O$ | | | $NiL_3SO_4 \cdot 4H_2O$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $t$, °C | $\Delta m_{exp}$, % | $\Delta m_{calc.}$, % | $t$, °C | $\Delta m_{exp}$, % | $\Delta m_{calc}$, % | $t$, °C | $\Delta m_{exp}$, % | $\Delta m_{calc}$, % |
| endo | $4H_2O$ | | | | 130 | 11.5 | 11.5 | 130 | 8.5 | 8.7 |
| endo | melting | 160 | | | 260 | | | 240 | | |
| exo | naphthalene ring | 290–340 | 63 | 63.5 | | | | | | |
| exo | acetic acid hydrazide | 340–650 | 37 | 36.5 | 270–360 | 24 | 23.2 | 250–360 | 26.5 | 26.5 |
| exo | naphthalene ring + $SO_4$ | | | | 360–740 | 55.5 | 56.1 | 360–710 | 57.5 | 57.7 |

**Table 1** (continued I)

| Effect | Fragment eliminated | $NiL_3Cl_2 \cdot 2H_2O$ | | | $NiL_3Br_2 \cdot 2H_2O$ | | | $NiL_3I_2 \cdot 2H_2O$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $T$, °C | $\Delta m_{exp}$, % | $\Delta m_{calc}$, % | $T$, °C | $\Delta m_{exp}$, % | $\Delta m_{calc}$, % | $T$, °C | $\Delta m_{exp}$, % | $\Delta m_{calc}$, % |
| endo | $2H_2O$ | 130 | 5 | 4.7 | 115 | 4.5 | 4.4 | 115 | 4 | 3.8 |
| endo | melting | 160 | | | 210 | | | 220 | | |
| endo | HX* | 290 | 10 | 9.5 | 310 | 20 | 19 | 300 | 26 | 27 |
| exo | acetic acid hydrazide | 250–360 | 30 | 27.8 | 290–380 | 25 | 25.6 | 320–440 | 21 | 21.9 |
| exo | naphthalene ring | 380–700 | 49 | 49.7 | 440–740 | 44.5 | 44.6 | 440–660 | 40.1 | 40 |

* $X$ = Cl, Br, I

**Table 1** (continued II)

| Effect | Fragment eliminated | $NiL_2Cl_2 \cdot 2H_2O$ | | | $NiL_2(CH_3COO)_2$ | | | $NiL_2(NCS)_2$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $T$, °C | $\Delta m_{exp}$, % | $\Delta m_{calc}$, % | $T$, °C | $\Delta m_{exp}$, % | $\Delta m_{calc}$, % | $T$, °C | $\Delta m_{exp}$, % | $\Delta m_{calc}$, % |
| endo | $H_2O$ | 90 | 3.3 | 3.2 | | | | | | |
| endo | $H_2O$ | 160 | 3.3 | 3.2 | | | | | | |
| exo | $CH_3COO$ | | | | 215 | 20 | 20.4 | | | |
| endo | NCS | | | | | | | 260 | 20 | 20.2 |
| endo | 2HCl | 295 | 13 | 12.9 | | | | | | |
| exo | acetic acid hydrazide | 295–380 | 25.5 | 25.3 | 240–350 | 23.8 | 25 | 280–380 | 25 | 25.3 |
| exo | naphthalene ring | 380–730 | 45 | 45.0 | 350–690 | 43.5 | 43.9 | 380–760 | 43 | 44.1 |

$CH_3COO$ group. In the case of the sulphate complexes, it should be taken into account that the $SO_4$ group and the naphthalene ring of the ligand are eliminated simultaneously, which is registered as a broad exothermic peak in the interval 360–740° [6].

From a comparison with the decomposition of the ligand itself, it can be concluded that the decomposition of the ligand moiety in the complexes in air atmosphere is accompanied by oxidation processes. This was proved by the DTA curve recorded for $NiL_2SO_4 \cdot 4H_2O$ in the presence of nitrogen, where the corresponding peak is endothermic.

An X-ray analysis of the solid residue confirmed the assumption that NiO is formed as the final product of thermal decomposition of all investigated complexes.

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**Zusammenfassung** — In dieser Arbeit wurde die thermische Zersetzung oktaedrischer Ni(II)-Komplexe mit Hydraziden der 1-Naphthylessigsäure ($L$) des Types $NiL_nX_2 \cdot mH_2O$ untersucht, wobei $n = 2$ bzw. 3, $m = 2$ bzw. 4 und $X$=Cl, Br, I, NCS, OAc bzw. 1/2 $SO_4$ ist. Die thermische Zersetzung wurde in Luft- bzw. Stickstoffatmosphäre bis zu Temperaturen von 1000 °C durchgefürt und der wahrscheinlichste Mechanismus des Prozesses gegeben.

**Резюме** — Проведено исследование термического разложения октаэдрических комплексов никеля с гидразидом 1-нафтилуксусной кислоты ($L$) типа $NiL_nX_2 \cdot mH_2O$, где $n = 2$ и 3, $m = 2$ и 4, а $X$=Cl, Br, I, NCS, OAc и 1/2 $SO_4$. Термическое разложение проведено в атмосфере воздуха и азота до температуры 1000°. Предложен наиболее вероятный механизм термического разложения.