Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 173–180

THERMAL STUDIES OF COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES OF 4-(SULFONYLAZIDO PHENYLAZO) PYRAZOLONES

S. S. Kandil, F. I. Abdel-Hay and R. M. Issa

Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

(Received December 22, 1999; in revised form May 22, 2000)

Abstract

The thermal decompositions of cobalt(II), nickel(II) and copper(II) complexes of 4-(3'-sulfonylazido-6'-methoxyphenylazo)-1-phenyl-3-methyl-2-pyrazolin-5-one $H(D^1–SO_2N_3)$ and 4-(4'-sulfonylazido phenylazo)-3-phenyl-3-methyl-2-pyrazolin-5-one $H(D^2–SO_2N_3)$ were studied by thermogravimetry. The decomposition in all cases takes place along two stages. The first stage is due to the elimination of water and nitrogen molecules with the formation of tetracoordinate complexes containing nitrene reactive species $[M(DSO_2N:)_2]$. The second stage represents the decomposition of the material to the metal oxide. The kinetics of the decomposition were examined by using Coats–Redfern, the decomposition in all complexes was found to be first order for the first and second stages. The activation energies and other activation parameters (ΔH^* and ΔS^* and ΔG^*) were computed and related to the bonding and stereochemistry of the complexes.

Keywords: azopyrazolones, decomposition, kinetics, metal complexes, TG-DTG

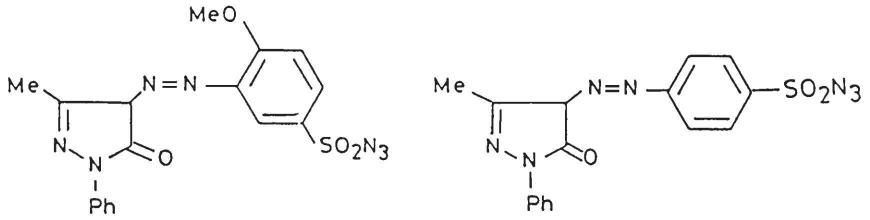
Introduction

Azopyrazolones have attracted attention of many investigators because of their potential uses in different areas of chemistry such as in medicinal chemistry as antimicrobial and therapeutic agents [1, 2], in analytical chemistry as complexing agents for the determination of some metal ions spectrophotometrically [3, 4], and in industrial chemistry as dyestuffs [1, 5–7]. Metal complexes of these compounds have shown improved dyeing properties [8, 9] and are anticipated to show increased biological activity in comparison to the unmetallized forms [10, 11].

In continuation to a recent publication [12] on the magnetic and spectral properties of Co(II), Ni(II) and Cu(II) complexes of sulphonylazido arylazopyrazolones $H(D^1–SO_2N_3)$ and $H(D^2–SO_2N_3)$, the present investigation aims to study the thermal decomposition of these complexes in order to throw more light on the influence of the structural properties of such ligands on the decomposition mechanism as well as on the values of the activation parameters.

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht



$H(D^1–SO_2N_3)$ $H(D^2–SO_2N_3)$

Scheme 1

Experimental

All reagents used for the preparation of the complexes were of analytical grade. The free ligands and their cobalt(II), nickel(II) and copper(II) complexes were prepared according to the published procedure [12, 13]. Thermoanalytical curves of the complexes were recorded by using a Shimadzu DT-50 at a heating rate of 10°C min^{-1}, using 3–6 mg of powdered samples in a nitrogen atmosphere.

Methods of calculations

The orders n and the activation energies E^* of the different stages of the thermal decomposition reactions have been evaluated from TG curves by using Coats–Redfern method [14]. The equation is used in the form:

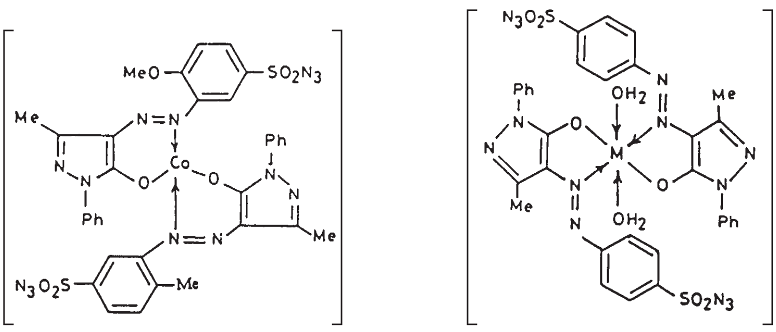
$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\log\frac{AR}{aE^*}\left(1-\frac{2RT}{E^*}\right)-\frac{E^*}{2.303RT}$$

where α is the fraction of the material decomposed at a given temperature T/K, A is the frequency factor, R is the gas constant, a is the rate of heating 10°C min^{-1} and E^* is the activation energy of the reaction.

Plots of $\log\{[1-(1-\alpha)^{1-n}]/[T^2(1-n)]\}$ *vs.* $1/T$ for different values of n have been tested, except for $n=1$, where $\log\{[-\ln(1-\alpha)]/T^2\}$ *vs.* $1/T$ has been tested. The correct value of n for the thermal reaction is the one which gives the best straight line, assuming that the term $\log AR/(aE^*)(1-2RT/E^*)$ would be constant within the temperature range, over which the thermal reaction occurs. From the slope of the straight line the activation energy E^* could be calculated, where the slope= $-E^*/(2.303R)$. The change in the activation enthalpy ΔH^* is calculated from the relation $\Delta H=E^*-RT$ and the change in the activation entropy from $\Delta S^*=R\{\ln[Ah/(KT)-1]\}$, where K is Boltzmann's constant and h is Planck's constant; the transmission coefficient is assumed to be equal unity [15–17]. The change in the free energy of activation ΔG^* is calculated from the relation $\Delta G^*=\Delta H^*-T\Delta S^*$.

Results and discussion

The complexes [M(D^1–SO$_2$N$_3$)$_2$(H$_2$O)$_n$] where n=0, 1 and 2 for M=Co(II), Cu(II) and Ni(II), respectively, and [M(D^2–SO$_2$N$_3$)$_2$(H$_2$O)$_2$] were precipitated from the reaction media as brown microcrystalline solids. Based on the elemental analyses, molar conductances, magnetic susceptibilities, infrared and electronic spectral measurements [12], the structures of these complexes were proposed as follows:



[Co(D^1–SO$_2$N$_3$)$_2$] [M(D^2–SO$_2$N$_3$)(H$_2$O)$_2$] M=Co(II), Ni(II) and Cu(II)

Scheme 2

The thermal behaviour of the complexes can be summarized as follows: Figure 1 shows the tracing of the TG curve obtained for [Co(D^1–SO$_2$N$_3$)$_2$] under conditions of N$_2$ flow and a heating rate of 10°C min^{-1}. It could be seen that, under these conditions, two major thermal processes exist. The first of them, lying in the region 175–240°C, has a mass loss of 6.5% corresponding to the loss of 2N$_2$ moles per mole of [Co(D^1–SO$_2$N$_3$)$_2$] (mass of mole=883) which is consistent with the reported decomposition of azo sulphonylazido compounds into nitrene species (D–SO$_2$N:) and N$_2$

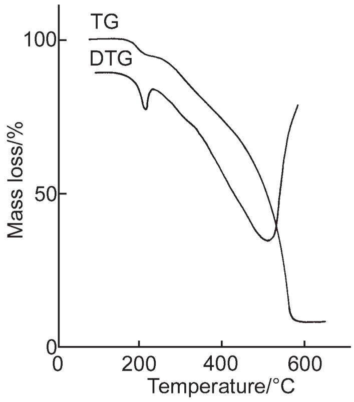


Fig. 1 TG and DTG curves of [Co(D^1–SO$_2$N$_3$)$_2$]

gas above 130°C in air [13]. The onset of decomposition of such sulphonylazido group at 175°C and not somewhat above 130°C is due to the fact that the process was performed under N_2 flow, rather than in air. This suppresses the decomposition of (D–SO_2N_3) into (D–SO_2N:) species and N_2 gas. The second thermal process is in the region 280–590°C and corresponds to the formation of CoO as revealed by the mass percentage of the end product. The thermal decomposition stages can be represented as follows:

$$[\mathrm{Co}(\mathrm{D}^1\text{–}\mathrm{SO_2N_3})_2] \xrightarrow{240\,^\circ\mathrm{C}} [\mathrm{Co}(\mathrm{D}^1\text{–}\mathrm{SO_2N}\!:)_2]+2\mathrm{N_2}$$

$$[\mathrm{Co}(\mathrm{D}^1\text{–}\mathrm{SO_2N}\!:)_2] \xrightarrow{585\,^\circ\mathrm{C}} \text{decomposition products}+\mathrm{CoO}$$

The TG curves for the aqua complexes $[\mathrm{Ni}(\mathrm{D}^1\text{–}\mathrm{SO_2N_3})(\mathrm{H_2O})_2]$ and $[\mathrm{Cu}(\mathrm{D}^1\text{–}\mathrm{SO_2N_3})(\mathrm{H_2O})]$ (Figs 2 and 3) also show two distinct thermal stages. The first of them has a mass loss corresponding to the elimination of $2H_2O+2N_2$ and $1H_2O+N_2$ moles per one mole of the complex, respectively. The second stage of the thermal de-

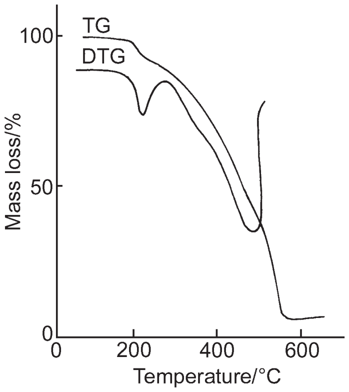


Fig. 2 TG and DTG curves of $[\mathrm{Ni}(\mathrm{D}^1\text{–}\mathrm{SO_2N_3})_2(\mathrm{H_2O})_2]$

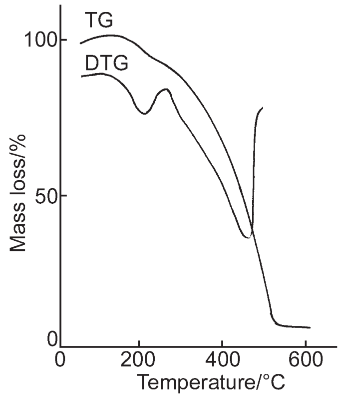


Fig. 3 TG and DTG curves of $[\mathrm{Cu}(\mathrm{D}^1\text{–}\mathrm{SO_2N_3})_2(\mathrm{H_2O})]$

Table 1 Temperatures of decomposition and activation parameters (kJ mol^{-1}) of decomposition for the complexes

Complex	T_s/°C (DTG peak) stage		E^* stage		First stage			Second stage		
	(1)	(2)	(1)	(2)	ΔS^*	ΔH^*	ΔG^*	ΔS^*	ΔH^*	ΔG^*
$[Co(D^1–SO_2N_3)_2]$	220	486	76.55	89.51	–0.14	72.45	141.47	–0.21	83.21	242.60
$[Ni(D^1–SO_2N_3)_2(H_2O)_2]$	217	448	95.69	94.49	–0.16	91.62	170.02	–0.20	88.50	232.49
$[Cu(D^1–SO_2N_3)_2(H_2O)]$	222	438	108.45	90.91	–0.14	104.34	173.64	–0.20	85.00	227.20
$[Co(D^2–SO_2N_3)_2(H_2O)_2]$	212	439	57.41	105.26	–0.11	53.38	106.73	–0.20	99.34	241.74
$[Ni(D^2–SO_2N_3)_2(H_2O)_2]$	205	445	88.32	107.17	–0.13	84.35	146.49	–0.19	101.20	237.62
$[Cu(D^2–SO_2N_3)_2(H_2O)_2]$	211	395	68.89	99.52	–0.11	64.87	118.11	–0.19	93.97	220.89

composition for all complexes gives MO as final product. The following equations for $[Ni(D^1–SO_2N_3)_2(H_2O)_2]$, as a representative example, illustrate the two stages of the thermal decompositions of these aqua complexes:

$$[Ni(D^1–SO_2N_3)_2(H_2O)_2] \xrightarrow{225°C} [Ni(D^1–SO_2N:)_2]+2H_2O+2N_2$$

$$[Ni(D^1–SO_2N:)_2] \xrightarrow{575°C} \text{decomposition products}+NiO$$

It was found that the first and second stages of the thermal decompositions for all complexes obey the equations of first-order decomposition reactions, on applying Coats–Redfern method as shown in Fig. 4. The activation parameters E^*, ΔH^*, ΔS^* and ΔG^* for the decomposition steps of the complexes are given in Table 1. The negative value of ΔS^* means that the activated complex is more ordered than that of the reactants and that the reactions are slow [18]. The values of ΔH^* and ΔG^* of the complexes refer to the effect of changing the structure of the ligand and the metal ion on the thermal stability of the complexes.

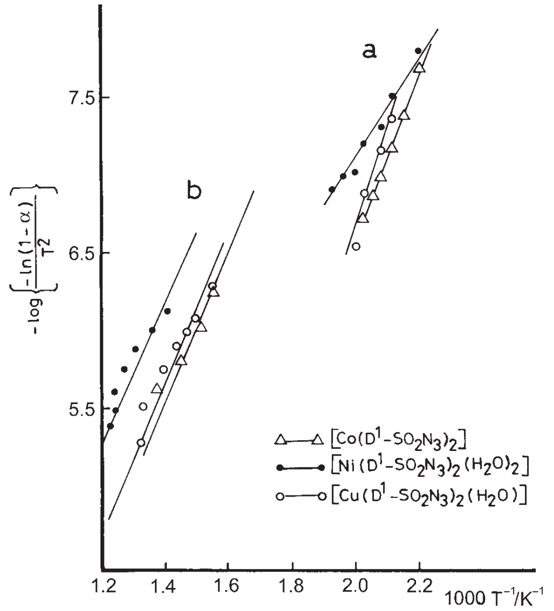


Fig. 4 Coats–Redfern plots for thermal decompositions of $H(D^1–SO_2N_3)$ complexes; a – first stage; b – second stage

For cobalt(II) complexes, the difference between ΔG_1^* values is quite obvious (for $[Co(D^1–SO_2N_3)_2]$; ΔG_1^*=141.47 kJ mol^{-1} and for $[Co(D^2–SO_2N_3)_2(H_2O)_2]$; ΔG_1^*= 106.73 kJ mol^{-1}). This variation in ΔG_1^* for the two complexes may be due to the differences in the nature of their organic ligands and the stereochemical arrangements. They influence the bonding between water molecules and metal cations. Since volatilisation of water molecules precedes the decomposition of sulphonylazido group as revealed by DTA curves of the aqua complexes [12]. It is apparent that volatilisation of these water molecules would destruct the crystal packing of the aqua complex [19], thereby assists the decomposition of SO_2N_3 as shown by lowering of its ΔG_1^* value. For copper(II) complexes, the same arguments can be given for the difference between ΔG_1^* for $[Cu(D^1–SO_2N_3)_2(H_2O)]$; ΔG_1^*=173.64 kJ mol^{-1} and for $[Cu(D^2–SO_2N_3)_2(H_2O)_2]$; ΔG_1^*=118.11 kJ mol^{-1}. In nickel(II) complexes, the difference between ΔG_1^* values for $[Ni(D^1–SO_2N_3)_2(H_2O)_2]$; ΔG_1^*=170.02 kJ mol^{-1} and for $[Ni(D^2–SO_2N_3)_2(H_2O)_2]$; ΔG_1^*=146.94 kJ mol^{-1} is pronounced, though it is smaller than in the cases of copper(II) and cobalt(II) complexes. Since the ΔH_1^* values are reasonably similar as consequences of each having the same kinds and number of donors, the difference in ΔG_1^* for the two complexes should be attributed to the difference in the ΔS_1^* values or more strictly $T\Delta S_1^*$. The former complex which has *o*-OCH_3 substituent needs more energy to be ordered in structure than that needed for the latter one which has no *o*-substituents, in the activated state with respect to the reactants and/or the reaction of *o*-CH_3 substituted complex is relatively slow. The close values of ΔG_2^* of the complexes of the two ligands with the same cation e.g. for $[Co(D^1–SO_2N_3)_2]$; ΔG_2^*=242.60 kJ mol^{-1} and for $[Co(D^2–SO_2N_3)_2(H_2O)_2]$; ΔG_2^*= 241.74 kJ mol^{-1} suggest that the tetracoordinate complexes $[M(D–SO_2N:)_2]$ produced from the first stage would have the same electronic and geometric structures so that thermal activation in this stage involves mostly similar groups. On the other hand, the difference in ΔG_2^* from one cation to the other for the same ligand is not pronounced. This suggests that the effect of the ligand is more than the cation on the second stage decomposition of the complexes.

References

1 R. H. Wiley and P. Wiley, Pyrazolones, Pyrazolidones and Derivatives, Wiley, New York 1964.
2 S. A. Ibrahim, M. A. El-Gahami, Z. A. Khafagi and S. A. El-Gyar, J. Inorg. Biochem., 43 (1991) 1.
3 A. Abdel-Razik, International J. Chem., 3 (1992) 35.
4 N. G. Smaglyuk, S. T. Talipov, Z. A. Pivenko, R. K. Dzhiyanbaeva and A. A. Khodzhaev, Zh. Anal. Khim., 30 (1975) 1680; 84 (1976) 68981.
5 A. A. Saafan, M. A. El-Borai, M. A. Sakran and I. S. El-Kamary, Melliand Textilber., 71 (1990) 25.
6 A. A. Saafan, M. A. El-Borai, M. A. Sakran and I. S. El-Kamary, Melliand Textilber., 70 (1989) 254.
7 K. I. Zamaraev, Zh. Strukt. Khim., 10 (1969) 32; C. A., 70 (1969) 110424.
8 G. B. El-Hefnawy, M. A. El-Borai, E. A. Aly and A. A. Gaber, Indian J. Fibre and Text. Res., 17 (1992) 87.
9 G. Back, (Ger. Offen. DE 351 2253); C. A., 105 (1986) 7938.
10 D. R. Williams, Chem. Rev., 72 (1972) 203.
11 A. Furst and R. T. Haro, Prog. Exp. Tumor Res., 12 (1969) 102.

12 S. S. Kandil, Transition Met. Chem., 23 (1998) 461.
13 J. Griffiths and R. I. McDarmaid, J. Soc. Dyer and Colourists, 94 (1978) 65.
14 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
15 S. Glasstone, Textbook of Physical Chemistry, 2nd ed., McMillan, Bombay, India 1974.
16 H. G. Widemann, Thermal Analysis, Vol. 2, Birkhäuser Verlag, Basel 1972.
17 A. I. El-Said, A. A. M. Aly and A. S. A. Zidan, J. Thermal Anal., 37 (1991) 2473.
18 A. A. Frost and R. G. Pearson, Kinetics and Mechanism, Wiley, New York 1961.
19 P. Roman, A. Luque, J. I. Beitie and C. G. Miralles, Thermochim. Acta, 231 (1994) 231.