Journal of Thermal Analysis, Vol. 48 (1997) 367-371

KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA XXX. Thermal decomposition of some Reinecke salt like complexes

J. Zsakó[*], I. Gănescu*[**], Cs. Várhelyi*[*] and L. Chirigiu*[**]*

[*]Chemistry Department, Babeş-Bolyai University, 3400 Cluj
[**]Chemistry Department, Craiova University, 1100 Craiova, Romania

(Received March 13, 1996)

Abstract

Thermal decomposition of 6 complexes of the type $AH[Cr(NCS)_4\,(am)_2]\cdot nH_2O$ is studied with derivatograph. The formation of $Cr(NCS)_3$ as a labile intermediate is presumed. For some decomposition stages kinetic parameters are derived. The kinetic compensation effect is discussed.

Keywords: chrom(III)-complexes, isokinetic relations, non-isothermal kinetics, thermal decomposition

Introduction

The $AH[Cr(NCS)_4\,(am)_2]\cdot nH_2O$ type complexes, (where *A* and *am* stand for NH_3 and/or different aliphatic, aromatic, heterocyclic amines) may be considered to be Reinecke salt like compounds, since with the Reinecke salt one has $A=am=NH_3$ and $n=1$. Thermogravimetric (TG) study of the decomposition of both Reinecke salt [1, 2] and some Reinecke salt like complexes [3, 4] suggested the formation of $Cr(NCS)_3$ as a labile intermediate, Cr_2O_3 being the final product of the pyrolysis.

In the present paper the following $AH[Cr(NCS)_4\,(am)_2]\cdot nH_2O$ type complexes have been studied:

Complex	*A*	*am*	*n*
I	benztriazole	benztriazole	3
II	NH_4	tripropylamine	–
III	NH_4	butylamine	1
IV	NH_4	hexylamine	–
V	NH_4	heptylamine	2
VI	NH_4	octylamine	2

0368–4466/97/ $ 5.00

John Wiley & Sons, Limited
Chichester

Results and discussions

TG curves indicate 3 and 2 distinct decomposition stages in the case of crystalohydrates and anhydrous complexes, respectively. With hydrates the first stage consists in the elimination of the water molecules, i.e. it is a dehydration process, marked by an endothermal peak situated between 96 and 120°C on the DTA curves and leading to the formation of the anhydrous complex as a relatively stable intermediate.

The first pyrolysis stage of the anhydrous complex will be referred to as deamination. During this decomposition on the DTA curves appear one or two endothermal peaks. The final decomposition stage is accompanied by two marked exothermal peaks, and in some cases also by several smaller ones, which suggests the idea that in this stage combustion reactions occur with the participation of atmospheric oxygen. At about 650–700°C the sample attains its final weight corresponding to Cr_2O_3.

In Table 1 the weight losses during the dehydration and deamination stages are given, expressed in moles of H_2O and of *am* respectively.

In the case of dehydration, it is compete with V and VI, but the values for I and III show that presumably up to the weight loss stop the water vapours, eliminated from the deeper layers did not succeed to leave completely the sample.

As far as the deamination is concerned, the general picture is not so clear. In most cases the number of *am* molecules evolved depasses 2. This means that besides the real deamination reaction, i.e. the elimination of the 2 *am* molecules from the internal co-ordination sphere, also other decomposition processes occur, presumably mainly the volatilization of one mole of AHNCS. These two reactions would entail the formation of $Cr(NCS)_3$ as intermediate. In order to obtain a more clear picture in this respect, in the last column of Table 1 the weight loss corresponding to the transformation of $AH[Cr(NCS)_4(am)_2]$ into $Cr(NCS)_3$ is given, expressed in moles of *am*. By comparing these data with the weight losses in the 'deamination' process, one can see that in the case of III, IV and V the formation of a labile $Cr(NCS)_3$ intermediate seems to be very likely, although the transformation is not complete up to the beginning of the next decomposition stage. The values for I and VI are not inconsistent with the formation of $Cr(NCS)_3$ either. In the case

Table 1 Weight losses during the first decomposition stages expressed in moles of H_2O and of *am*, respectively

Compound	Dehydration	Deamination	$Cr(NCS)_3$
I	2.75	1.52	2.41
II	–	3.36	2.53
III	0.725	2.73	3.04
IV	–	2.50	2.75
V	2.02	2.47	2.66
VI	2.12	1.37	2.59

of compound II, according to the TG curve and to Table 1, the $Cr(NCS)_3$ intermediate must be completely unstable.

With respect to the thermal effects, Table 2 is relevant, showing one or two endothermal peaks in the temperature interval in which the 'deamination' process occurs, including the volatilisation of AHNCS. Both important exothermal peaks given in Table 2 are situated in the temperature interval of the last decomposition stage. The highest exothermal peak appears at about 500°C. Presumably, these exothermal reactions consist in the combustion of the NCS ligands with the participation of atmospheric oxygen. It is worth mentioning that the shape of the DTA curves and the position of the 4 peaks are very near to those reported earlier for analogous complex salts [4].

Table 2 DTA peak temperatures in °C

Compound	Endothermal		Exothermal	
I	250	280	442	510
II	270	310	370	505
III	255	330	438	512
IV	280	322	435	512
V	–	325	430	490
VI	240	–	470	520

In the case of dehydration of I and deamination of all the complexes studied, the shape of the TG curves allowed us to perform a kinetic analysis. For deriving kinetic parameters, our nomogram method [5–7] has been used. The apparent kinetic parameters, i.e. the reaction order n, the activation energy E and the pre-exponential factor A, together with the characteristic temperature $T_{0.1}$ at which the conversion in the decomposition stage becomes equal to 0.1, are given in Table 3. By inspecting this table, the variation in parallel of E and $\lg A$ values is the only clear trend which can be observed.

Table 3 Apparent kinetic parameters derived for different decomposition stages

Stage	n	E/kJ mol^{-1}	$\lg A$ (A in s^{-1})	$T_{0.1}$/K
Dehydration of I	0.57	61.6	6.2	352
Deamination of I	4.40	341.8	33.0	501
Deamination of II	0.51	171.3	13.1	557
Deamination of III	0.95	86.1	5.5	518
Deamination of IV	2.29	224.6	18.6	543
Deamination of V	–0.19	93.3	5.8	543
Deamination of VI	1.26	533.7	51.9	513

The above mentioned parallelism is the manifestation of the so called kinetic compensation effect which can be expressed by means of the following linear isokinetic relation

$$\lg A = aE + b = (RT_i \ln 10)^{-1}E + \lg k_i \tag{1}$$

This effect may be considered to be an apparent one, due to the use of the Arrhenius equation in heterogeneous non isothermal kinetics. The isokinetic temperature T_i corresponding to the slope of the lg$A$ *vs.* E straight line accordingly to (1), is thought to be a certain decomposition temperature [8]. In the case of a set of pyrolysis processes, occurring approximately in the same temperature interval, we proposed to take the mean value of the characteristic temperatures $T_{0.1}$ for this decomposition temperature [6]. Irrespective of the nature of the thermal decomposition reaction, a rather good agreement has been observed between the T_i calculated from the slope of the straight line and the mean value $T_{0.1}$. The b parameter, i.e. lgk_i in (1), has been found to be near to –3, irrespective of the temperature interval of the pyrolysis [9].

In order to verify the compensation effect in the case of kinetic parameters presented in Table 3, first the validity of Eq. (1) has been tested for all deamination reactions. Further, the reactions have been divided into two sets with $T_{0.1}$ values more close to each other. The compensation parameters a and b, the correlation coefficients r, the mean values of $T_{0.1}$ and the isokinetic temperatures derived from a are presented in Table 4. Obviously, by dividing the deamination processes into two sets, the agreement between $\overline{T_{0.1}}$ and T_i becomes much better, r has a higher value and b is nearer to –3. This means that the slope a of the lg$A$ *vs.* E straight lines is indeed determined by the decomposition temperature and that for this temperature $T_{0.1}$ is a good approach.

Table 4 Kinetic compensation effect in the case of the deamination processes

Compounds	a/mol kJ^{-1}	b	r	$\overline{T_{0.1}}$/K	T_i/K
I–VI	0.10553	–4.201	0.9990	529	495
I, III, VI	0.10387	-3.162	0.9997	511	503
II, IV, V	0.09720	-3.350	0.9996	548	538

Processes occurring in different temperature intervals may be compared with each other from the point of view of the compensation effect by calculating a 'theoretical' pre-exponential factor A^* defined as

$$\lg A^* = \frac{E}{RT_{0.1} \ln 10} - 3 \tag{2}$$

i.e. by taking in (1) $T_i \approx T_{0.1}$ and $\lg k_i \approx -3$. In Table 5 lg$A$ values determined directly by means of the nomogram method are compared with the lgA^* values calculated by means of Eq. (2).

Table 5 'Experimental' pre-exponential factors from Table 3 and 'theoretical' ones given by Eq. (2)

Process	$\lg A$	$\lg A^*$
Dehydration of I	6.2	6.2
Deamynation of I	33.0	32.7
Deamynation of II	13.1	13.1
Deamynation of III	5.5	5.7
Deamynation of IV	18.6	18.6
Deamynation of V	5.8	6.0
Deamynation of VI	51.9	51.4

As seen from Table 5 the agreement between A and A^* values is rather good. The relation between them may be expressed as

$$\lg A = 1.014 \lg A^* - 0.216$$

The above expression has been established by means of linear regression, the correlation coefficient being equal to 0.99999. Obviously, the slope of the straight line does not differ essentially from unity and the ordinate intercept is almost zero. This means that Eq. (2) is a good approximation. Consequently, in the case of our experimental data the linear isokinetic relation (1) is valid and this compensation effect presents the same features as with all kinetic parameters derived from TG curves, viz. $T_i \approx T_{0.1}$ and $\lg k_i \approx -3$.

Experimental

The Reinecke salt like complexes studied in this paper have been obtained as described earlier [10].

Thermal decomposition of the complexes has been followed by means of a Derivatograph MOM. Measurements have been performed with a constant heating rate of 10 K min^{-1}, in air atmosphere, by using Pt crucibles and samples of 100 mg.

References

1 B. T. Aykock, J. Amer. Chem. Soc., 73 (1951) 1351.

2 P. J. Krausz and J. Kovács, Ann. Univ. Sci. Budapestiensis de L. Eötvös nom. sect. Chim., 4 (1962) 37.

3 G. Boda, Cs. Várhelyi and A. Mostis, Studia Univ. Babeş-Bolyai, Ser. Chem., 10 (2) (1965) 63.

4 J. Zsakó, G. Liptay, Cs. Várhelyi and E. Brandt-Petrik, J. Thermal Anal., 23 (1982) 123.

5 J. Zsakó, J. Thermal Anal., 15 (1979) 369.

6 J. Zsakó, M. Várhelyi and Cs. Várhelyi, J. Thermal Anal., 17 (1979) 123.

7 J. Zsakó, Gh. Marcu and M. Várhelyi, Rev. Roumaine Chim., 27 (1982) 815.

8 P. D. Garn, J. Thermal Anal., 7 (1975) 475; 10 (1976) 99.

9 J. Zsakó, J. Thermal Anal., in press.

10 I. Gănescu, L. Chirigiu and M. Mureşanu, J. Indian Chem. Soc., 72 (1996) 1237.