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KINETIC PARAMETERS OF THERMAL DECOMPOSITION OF ANISALDEHYDE-GIRARD T COMPLEXES OF COBALT AND COPPER BROMIDES FROM TG AND DSC DATA

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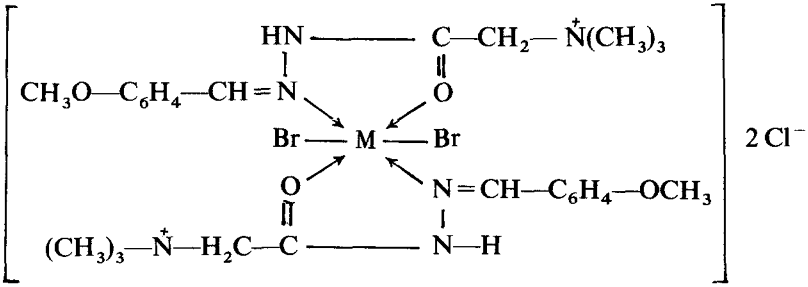
The kinetic parameters relating to the thermal decompositions of the Co(II) and Cu(II) hydrazone complexes of general formula $[ML_2Br_2]Cl_2$, where L = anisaldehyde-Girard T cation: $CH_3OC_6H_4CH=N\text{-}NHCOCH_2=\overset{+}{N}(CH_3)_3$, and M = Co(II) or Cu(II), were evaluated from TG and DSC data. The thermal stabilities of the cobalt and copper complexes are discussed.

In a continuation of studies [1–3] on the hydrazone complexes of Girard T (carbohydrazide methyl trimethyl-ammonium chloride), the present work is concerned with the anisaldehyde-Girard T complexes of cobalt and copper bromides. It has been shown that these hydrazone ligands undergo bidentate coordination, in keto or enol form, via azomethine and carbonyl groups. The structures of these complexes can be represented as follows:



The present paper describes the calculation of the kinetic parameters of thermal decomposition of these complexes: the order of the reaction (n), the preexponential factor (A) and the activation energy (E_a). Such values are determined from

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corresponding TG and DSC data by using the methods of Coats and Redfern [4], Chatterjee [5], Kissinger [6] and Ozawa [7]. The object of this work was to examine the effect of the central metal ion on the thermal stability of the complex.

Experimental

The anisaldehyde-Girard T ligand was prepared with the general method [8]. The complexes were prepared by addition of the metal bromide solution in absolute ethanol to twice its equivalent of the ligand (in the same solvent) and the mixture was refluxed on a water bath for half an hour. The complexes formed were filtered off, washed several times with ethanol and vacuum-dried over anhydrous calcium chloride. The solid complexes obtained gave satisfactory analytical results. The TG/DTG/DTA data were obtained with a Setaram (1600 °C) GDTA 16 system. Sample masses were in the range 16.5±0.2 mg and the heating rate was 5.5 deg/min. Decompositions were carried out in a platinum crucible. Alumina was used as a reference standard under identical conditions. The DSC data were

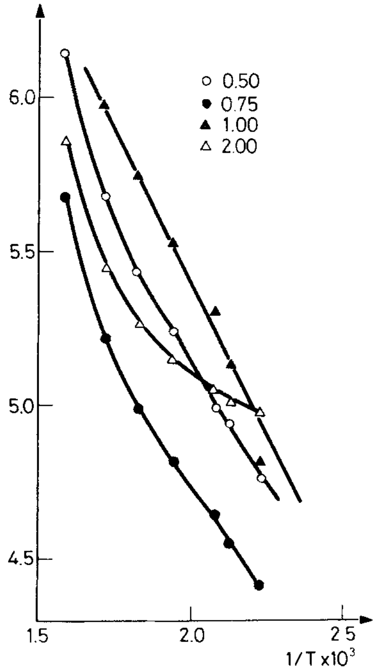

Fig. 1 Determination of the reaction order for the thermal decomposition of [CoL_2Br_2] by the Coats–Redfern method using TG data.

obtained with a Seteram DSC 777 system. Conditions: sample masses in the range 43.2 ± 0.2 mg, under vacuum in a platinum crucible, the same reference material, and cooling under liquid nitrogen.

Results and discussion

Analysis of thermogravimetric (TG) data

Table 1 lists the mass loss, the time required for this loss to occur (t), the corresponding decomposition temperature (T, K) and the degree of thermal decomposition of the sample (α). From these data it is clear that the mass loss of the cobalt complex on thermal decomposition is less than that of the copper complex for the same step, and the decomposition occurs at a higher temperature for the cobalt complex than for the copper complex. This means that the cobalt complex is more thermally stable than the copper complex under these experimental

Table 1 Analysis of TG curves of anisaldehyde-Girard T complexes of cobalt and copper bromides

Mass loss, mg		t, min		T_m, K		α		$V = -\frac{dm}{dt}$	
Co(II)	Cu(II)	Co(II)	Cu(II)	Co(II)	Cu(II)	Co(II)	Cu(II)	Co(II)	Cu(II)
0.83	1.36	36.0	24.8	495.7	391.3	0.05	0.08	0.45	0.61
1.97	3.90	45.8	54.4	553.8	486.6	0.12	0.24	0.36	0.23
4.11	6.24	66.5	62.5	579.0	533.0	0.25	0.38	0.25	0.16
6.08	7.80	82.9	77.2	668.2	577.3	0.37	0.43	0.20	0.11
8.22	9.75	113.7	91.8	703.7	619.5	0.50	0.61	0.14	0.07
10.19	11.15	143.7	97.2	755.4	684.0	0.63	0.69	0.11	0.05
12.33	13.26	172.9	108.7	817.5	728.7	0.72	0.81	0.09	0.02
14.79	16.18	192.0	117.3	928.0	803.0	0.91	0.99	0.08	0.00

Table 2 Analysis of DSC curves of anisaldehyde-Girard T complexes of cobalt and copper bromides

$\log a$		Peak temperature, K		$\log a/T_m^2$		$\frac{1}{T_m} \times 10^3$	
Co(II)	Cu(II)	Co(II)	Cu(II)	Co(II)	Cu(II)	Co(II)	Cu(II)
1.176	1.176	575	560	4.343	−4.320	1.74	1.78
1.00	1.00	568	550	−4.508	−4.480	1.76	1.82
0.778	0.698	555	535	−4.710	−4.757	1.80	1.87
0.301	0.301	535	506	−5.155	−5.107	1.87	1.97

Table 3 Kinetic parameters for thermal decompositions of cobalt and copper complexes of anisaldehyde-Girard T

Parameter	Coats–Redfern		Chatterjee		Kissinger		Ozawa	
	Co(II)	Cu(II)	Co(II)	Cu(II)	Co(II)	Cu(II)	Co(II)	Cu(II)
n	1.00	1.00	1.00	1.00	—	—	—	—
A, sec	—	—	5.0×10^6	1.0×10^5	—	—	—	—
kJ mol^{-1}	108.97	85.69	108.47	81.09	108.68	82.84	114.66	89.95

conditions. This conclusion is supported by the values of the activation energy (E_a) of the decomposition process, calculated with two different methods [4, 6] (see Table 3).

Analysis of the differential scanning calorimetric (DSC) data

Increase of the heating rate (a) (2, 5, 10 and 15 deg/min) is accompanied by a shift in the temperature of the endothermic peak (T_m) to higher values, as shown in Table 2. A plot of a/T_m^2 vs. $\frac{1}{T}$ gives a straight line with slope

$$\frac{d\log a/T_m^2}{d\log\frac{1}{T}} = -\frac{E_a}{R} \qquad \text{(Kissinger method).}$$

Figure 2 shows this plot for the examined complexes. A plot of log a *vs.* $\frac{1}{T_m}$ gives a

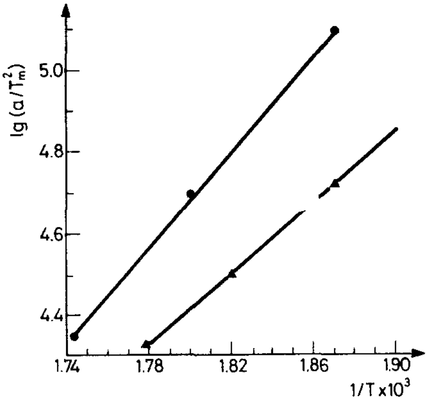

Fig. 2 Determination of the reaction order of the thermal decomposition process of $(ML_2Br_2]Cl_2$ M = Co(II) or Cu(II) by Kissinger method. ●—● Co(II);; ▲—▲ Cu(II)

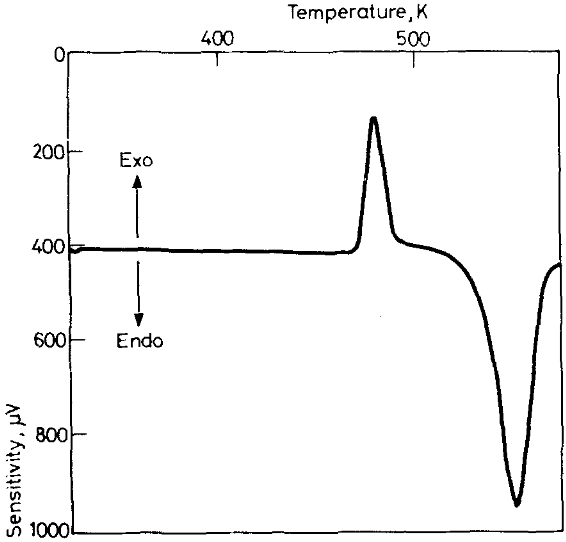

Fig. 3 Thermal decomposition of $[CoL_2Br_2]Cl_2$ complex as recorded by DSC

straight line with slope

$$\frac{d\log a}{d\left(\frac{1}{T_m}\right)} = 0.4567\frac{E_a}{R} \qquad \text{(Ozawa method).}$$

Table 3 reveals that the order of the decomposition reaction is unity for both complexes, which means that the thermal decomposition mechanism is the same for the two complexes [9]. It is also clear from Table 3 that the activation energy values calculated from the TG curves (with the Coats–Redfern and Chatterjee methods) are in good agreement with the values calculated from the DSC curves (with the Kissinger and Ozawa methods).

For each complex, the activation energy depends on various factors, but mainly on the strengths of the bonds between the central metal ion and the hetero atoms of the bidentate ligand, i.e. the carbonyl oxygen and the azomethine nitrogen. The higher activation energy (E_a) for decomposition of the cobalt complex may be due to the strengths of these bonds ($O \rightarrow Co \rightarrow N$) being higher than those in the copper complex. The strengths of the bonds between the metal ion and the hetero atoms of the ligand increase with increase in the covalent character of these bonds, i.e. with decrease in the electronegativity difference between the carbonyl oxygen—metal ion and the azomethine nitrogen—metal ion bonds.

The higher thermal stability of the cobalt complex than that of the copper complex is in good agreement with the increase in temperature of the first endothermic peak [10] (Table 2).

References

1 M. N. H. Moussa, F. I. M. Taha and M. A. K. Khattab, UAR J. Chem., 13 No. 4 (1970) 445.

2 F. I. M. Taha, M. N. H. Moussa and M. M. Moustafa, Egypt J. Chem., 16 No. 3 (1973) 209.

3 F. I. M. Taha, M. N. H. Moussa, M. A. K. Khattab and M. E. M. Emam, Mansoura Science Bulletin, 5 (1975) 151.

4 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.

5 P. V. Chatterjee, J. Polymer. Sci., 3 (1965) 4253.

6 H. E. Kissinger, Anal. Chem., 29 (1957) 702.

7 T. Ozawa, J. Thermal Anal., 2 (1970) 301.

8 A. I. Vogel "Text book of practical organic chemistry" Third Ed. London 1956, p. 976.

9 M. E. M. Emam, M. A. H. Hafez and M. N. H. Moussa, J. Thermal Anal., 32 (1987) 937.

10 K. Boguslawska and A. Cyganski, J. Thermal Anal., 9 (1976) 337.

Zusammenfassung — Auf der Grundlage von TG- und DSC-Messungen wurden die kinetischen Parameter der thermischen Zersetzung von Co(II)- und Cu(II)-hydrazonkomplexen der allgemeinen Formel $[ML_2Br_2]Cl_2$ mit L = Anisaldehyd-Girard T-Kation:

$$CH_3OC_6H_4CH=N\text{—}NHCOCH_2=\overset{+}{N}(CH_3)_3,$$

und M = Co(II) oder Cu(II), bestimmt. Es wurde weiterhin die thermische Stabilität dieser Komplexe beschrieben.

Резюме — Из кривых ТГ и ДСК были определены кинетические параметры термического разложения гидразонов двухвалентных меди и кобальта общей формулы $[ML_2Br_2]Cl_2$, где L = анисовый альдегид-Жирард Т катион:

$$CH_3OC_6H_4CH=N\text{—}NHCOCH_2=\overset{+}{N}(CH_3)_3,$$

а M = медь или кобальт. Обсуждена термическая устойчивость данных комплексов.