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THERMAL STUDIES ON ANISALDEHYDE CARBOHYDRAZONE METHYL TRIMETHYLAMMONIUM CHLORIDE COMPLEXES OF ZINC, CADMIUM AND MERCURY

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The kinetic parameters of the thermal decomposition of Zn, Cd and Hg(II) hydrazone complexes of the general formula $[MCl_2(AGT)_2]Cl_2$, where AGT = anisaldehyde carbohydrazone methyl trimethylammonium cation,

$$CH_3O{-}C_6H_4{-}CH{=}N{-}NH{-}CO{-}CH_2{-}\overset{+}{N}(CH_3)_3,$$

and M = Zn, Cd and Hg(II), have been determined from the corresponding thermal curves. The order of the reaction (n) and the activation energy (E_a) have been derived. The kinetic data are discussed in terms of the effect of the metal ion on the activation energy. A thermal decomposition mechanism is suggested.

A method for the preparation and characterization of the studied complexes was mentioned previously [1]. That work describes the calculations of the orders of the decomposition reactions and the activation energies of the studied metal hydrazone complexes. Such values are determined through TG and DTA curves, using the Coats and Redfern method [2]. The object of the present work was to examine the effect of the central metal ion on the activation energies of the thermal decomposition of the studied complexes, and also to find a suitable mechanism for the thermal decomposition process.

Experimental

Determination of the kinetic parameters

Coats and Redfern [2] proposed a method for determination of the order of reaction on the basis of thermogravimetric data, based on a plot of $-\log\left[\frac{1-(1-\alpha)^{1-n}}{T^3(1-n)}\right] = A$ against $\frac{1}{T}\times 10^3$, where α is the degree of thermal

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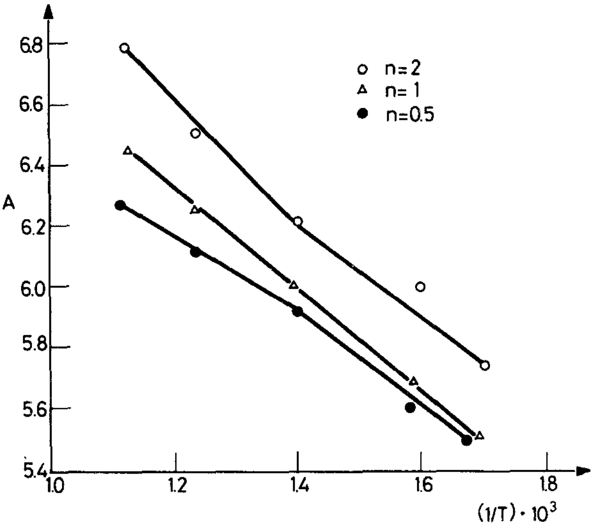


Fig. 1 Graphical determination of the order of reaction. For $n=1$: $A = -\log[-\log(1-\alpha)/T^2]$; for $n=0.5, 2$: $A = -\log[1-(1-\alpha)^{1-n}/T^3(1-n)]$

decomposition of the sample, calculated from the TG curve by means of the formula $\alpha = \frac{W_0 - W}{W_0 - W_k}$, in which W_0, W_k and W are the initial weight, the final weight and the weight of the sample at temperature T K, and n is the reaction order. A number of such relationship are plotted for a number of assumed values of n. The correct value of n for a given thermal decomposition reaction gives a straight line. Figure 1 shows the plots of the above relationship. The activation energy is calculated from the equation:

$$E = 2.303\ Rt_g\beta$$

where $t_g\beta$ is the slope of the straight line found in the previous plot, and R is the gas constant. The samples obtained were crystalline products which gave satisfactory analytical results, as mentioned earlier [1]. A heating rate of 5.5 deg/min was maintained.

The amount of sample taken varied from 14.0 to 20.0 mg. The TG and DTA curves were recorded on a TGA–DTG–DTA (1600°) GDTA 16 Thermo-analyzer, Setaram, Lyon, France, at the same heating rate, with alumina as reference.

Results and discussion

The investigations prove that the order of the decomposition reaction is one for all the examined complexes. This means that the mechanisms of the decomposition reactions are the same for all the studied complexes.

The activation energies are 179.5, 203.25 and 229.82 kJ mol^{-1} for the Zn, Cd and Hg complex, respectively; this variation of the activation energy increases with increase of the temperature of the first endothermic peak [3]. This temperature is

Table 1 Results of kinetic study of the examined metal complexes

Compound	Order of reaction (n) by		$t_{50\%,\mathrm{min}}$	E_a, kJ/mol
	graphically	Coats method		
$[ZnCl_2(C_{13}H_{20}N_3O_2)_2]Cl_2$ stable to 90°	1.05	1.00	68.4	179.53
$[CdCl_2(C_{13}H_{20}N_3O_2)_2]Cl_2$ stable to 114°	0.96	1.00	70.3	203.25
$[HgCl_2(C_{13}H_{20}N_3O_2)_2]Cl_2$ stable to 140°	0.88	1.00	56.6	229.82

Table 2 Analysis of TG curves of the studied metal complexes

Compound	Temperature range, °C	Loss %		Probable composition of expelled group
		found	(calc.)	
$[CdCl_2(C_{13}H_{20}N_3O_2)_2]Cl_2$	140–186	12.5	(12.7)	$N(CH_3)_3 + HCl$
	190–328	12.5	(12.7)	$N(CH_3)_3 + HCl$
M.wt. = 754.86	331–434	25.0	(25.5)	anisaldehyde + 2 N_2
	550–600	25.0	(25.5)	anisaldehyde + CO + C_2
	610–647	11.2	(11.2)	0.66 CdO
$[ZnCl_2(C_{13}H_{20}N_3O_2)_2]Cl_2$	90–145	9.3	(9.4)	$N(CH_3)_3 + 0.2$ HCl
	160–250	8.2	(8.4)	$N(CH_3)_3$
M.w. = 707.83	260–340	26.9	(27.1)	anisaldehyde + N_2 + CO
	353–500	19.8	(19.2)	anisaldehyde
	515–563	8.7	(8.6)	0.75 ZnO
$[HgCl_2(C_{13}H_{20}N_3O_2)_2]Cl_2$	140–250	14.9	(15.6)	$N(CH_3)_3 + 2$ HCl
	262–273	7.2	(7.0)	$N(CH_3)_3$
M.w. = 843.05	275–303	22.3	(22.8)	anisaldehyde + 2 N_2
	316–380	22.3	(22.8)	anisaldehyde + CO + C_2H
	431–552	29.8	(29.8)	HgO + $^1/_2$ Cl_2

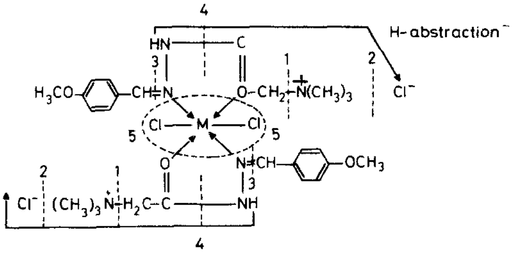
389.3, 395.6 and 430.7° for the Zn, Cd and Hg complex, respectively. The value of the activation energy depends on the strength of the $(O \rightarrow M \leftarrow N)$ bond and increases with increase in the cation radius, which leads to a stronger attraction between the central metal ion and the heteroatoms of the bidentate ligand.

This means that the distance $(N \rightarrow M \leftarrow O)$ decreases in the following sequence: $Hg < Cd < Zn$. This leads to the conclusion that the thermal stability increases in the sequence:

$$\text{Hg complex} > \text{Cd complex} > \text{Zn complex}$$

From the above analysis data, it is clear that the decomposition process takes place through five steps. The first two steps correspond to the decomposition of the tertiary amine salt $\overset{+}{N}(CH_3)_3Cl^-$, and to the formation of the volatile amine $N(CH_3)_3$ and HCl through H-migration from the NH group [4]; this step is related to the first exothermic peak in the DTA curve. The third step accounts for the decomposition of $—CH=N$ and the formation of volatile anisaldehyde (the second exothermic peak). The fourth decomposition step is due to the breaking of the N—C bond and to the formation of N_2 and CO (indicated by the first endothermic peak). The last step corresponds to the rupture of the bonds between the metal ion and the heteroatoms of the bidentate ligand (this gives the characteristic endothermic peak in the DTA curves); as a result of this decomposition, volatile metal oxide is formed. The breaking of the last bond is responsible for the difference in activation energy of the various metal complexes studied.

The suggested decomposition mechanism is:



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