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ANALYSIS OF THERMOGRAVIMETRY CURVES TO DETERMINE THE MECHANISM OF DISSOCIATION OF 2-THIOHYDANTOIN AND ITS DERIVATIVES AND THEIR METAL CHELATES

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ABSTRACT

Mechanisms for the thermal decompositions of 2-thiohydantoin, benzal cyanothioacetamide, 5-phenylazo-2-thiohydantoin, Ni-2-thiohydantoin and Co-2-thiohydantoin are proposed, on the basis of calculated kinetic and activation parameters. The kinetic and activation parameters of such pyrolysis reactions can be conveniently determined by mathematical interpretation of the thermogravimetry curves. The slope and the intercept of the straight line produced from the plot of the mass fraction left versus temperature gives the activation energy and order of pyrolysis. The relative stabilities of the ligands and their metal chelates are compared. The most suitable of several proposed structural formulae for each compound is indicated.

INTRODUCTION

Pyrolysis often takes place via a many-stepped mechanism where the temperature ranges for each step overlap, resulting in irregular mass–temperature curves that can be difficult to analyse. The equation derived by Freeman and Carroll [1] for irreversible reactions can be used to calculate the energy of activation and order of reaction from TG and volumetric curves. In this case, the shape of the curve is determined by the kinetic parameters of the pyrolysis, such as reaction order, frequency factor and energy of activation. A number of investigators have obtained such information by the analysis of TG curves [1–5]. Some of the methods described involve either graphic or numerical differentiation of the thermograph. These procedures, however, can be cumbersome and are subject to large errors when the curves are highly precipitous, as they usually are, so that determination of the parameters requires successive approximations or curve fitting. Horowitz and Metzger [6] have described an approximate integral method similar to but even simpler than that of Van Krevelen et al. [5], by which the pyrolysis rate parameters can be easily determined by inspection of the raw data.

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TABLE 1

Elemental analyses of nickel and cobalt 2-thiohydantoin complexes, **IV** and **V**

Complex [a]		C	H	N	S	M	M.Wt.
IV	Found %	21.9	4.2	16.8	19.3	17.3	315.00
	Calcd. %	22.03	3.67	17.14	19.59	17.97	326.71
V	Found %	22.6	3.2	17.6	19.0	17.5	310.00
	Calcd. %	22.02	3.67	17.13	19.58	18.02	326.93

[a] The suggested formula of M(II)-2-thiohydantoin complexes **IV** and **V** is $ML_2 \cdot 2H_2O$ [M = Ni or Co; L = $C_3H_4N_2OS$ (2-thiohydantoin)].

The present work applies the techniques devised by Horowitz and Metzger [6], with the help of a basic computer program used previously by Zayed et al. [7], to study the mechanism of pyrolysis of 2-thiohydantoin and its derivatives, and 2-thiohydantoin-nickel and -cobalt chelates. The approach is based on the calculation of the activation and kinetic parameters for these compounds by inspection of their TG curves. A number of possible structures for these compounds and their metal chelates have already been established by Nour El-Dien et al. [8] using various physico-chemical methods of analysis.

TABLE 2

Mass loss of 2-thiohydantoin (**I**), benzolcyanothioacetamide (**II**), 5-phenylazo-2-thiohydantoin (**III**), Ni-2-thiohydantoin complex (**IV**) and Co-2-thiohydantoin complex (**V**)

Compound	Temperature range (°C)	Decomposition product loss	Wt. loss (%)	
			Estim. [a]	Calcd. [b]
I	120–210	$S+N_2$	52.0	51.7
	210–350	CH_4	13.5	13.8
			Total 65. 5	65.5
II	130–270	N_2+S+C	38.7	38.3
	270–350	C+2H	7.5	7.4
			Total 45.2	45.7
III	120–270	$C_6H_6+N_2+S$	56.0	62.7
IV	80–130	$2H_2O$ coordn.	11.25	11.0
	130–180	NH	4.5	4.6
	180–280	2S+NH	23.2	24.2
			Total 38.75	39.8
V	86–144	$2H_2O$ coordn.	11.0	11.0
	144–282	2S+2NH	29.0	28.7
			Total 40.0	39.7

[a] Estimated practical mass loss.

[b] Theoretically calculated mass loss from the general formulae of compounds **I**–**V**.

EXPERIMENTAL

Organic synthesis

2-Thiohydantoin (**I**) was formed by refluxing a mixture of glycine and ammonium thiocyanate in acetic anhydride to give 1-acetyl-2-thiohydantoin which was heated with hydrochloric acid to give **I** [9]. The other compounds, benzalcyanothioacetamide (**II**) and 5-phenylazo-2-thiohydantoin (**III**), were also prepared and investigated in this laboratory [8].

Preparation of metal chelates

In order to prepare Ni-2-thiohydantoin (**IV**) and Co-2-thiohydantoin (**V**), solutions of the ligand (**I**) (0.5 g/25 ml ethanol) and of nickel chloride or cobalt acetate (0.5 g/25 ml water) were mixed thoroughly in an ethanol: water mixture (1 : 1), adjusting the pH to 9 using 1 : 1 aqueous ammonia solution. After leaving the mixture for 48 hours, a violet nickel complex (**IV**) and a black cobalt complex (**V**) (m.p. > 300 ° C) were formed. They were recrystallised from absolute ethanol. Elemental (Table 1) and spectral (IR and NMR) analyses were performed in order to elucidate their structures [9]. Analysis of the metal content was made using a Varian Techtron (Model 1100) atomic absorption spectrophotometer [10].

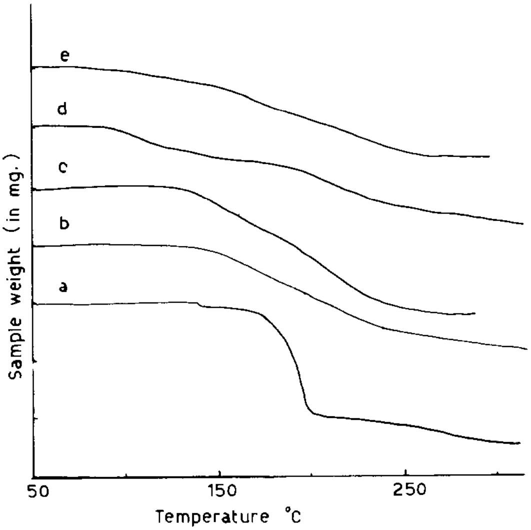


Fig. 1. Thermogravimetric analysis of: a, 2-thiohydantoin; b, benzalcyanoacetamide; c, 5-phenylazo-2-thiohydantoin; d, nickel-2-thiohydantoin complex; and e, cobalt-2-thiohydantoin complex.

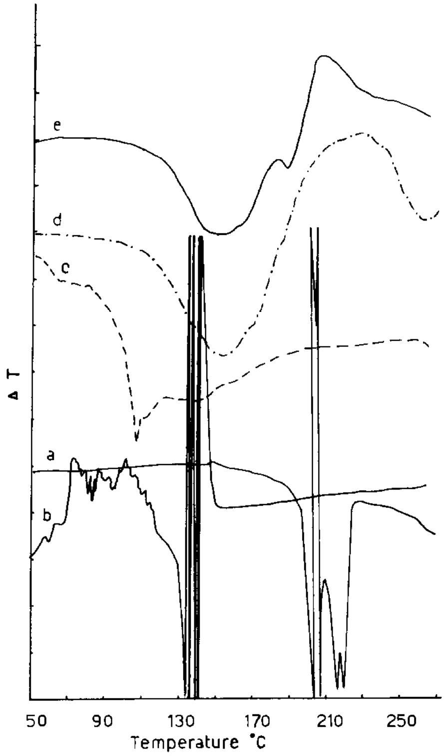


Fig. 2. Differential thermal analysis of: a, 2-thiohydantoin; b, benzalcyanoacetamide; c, 5-phenylazo-2-thiohydantoin; d, nickel-2-thiohydantoin complex; and e, cobalt-2-thiohydantoin complex.

Thermogravimetry and differential thermal analysis (TG and DTA) were performed on these compounds using a Shimadzu TG system thermal analyser (Shimadzu 30 series) (Table 2). The mass loss and DTA of 4 mg samples were measured in the temperature range 50–400 ° C, using a heating rate of 10 ° C min^{-1} (Figs. 1 and 2).

RESULTS

In the pyrolysis of compounds **I**–**V**, the rate expression includes concentrations expressed as mole fractions with the total number of moles being constant. Such expressions may be valid where only a fraction of the total weight is lost (Table 2). In this case, the weights are converted into mole fractions by

$$C = \frac{W - W_t^f}{W_0 - W_t^f} \qquad (1)$$

where W is the weight remaining at a given temperature and W_0 and W_t^f are the initial and final weights, respectively. The equation used for calculation of activation energy for the pyrolysis of these materials is

$$\ln \ln \frac{W_0 - W_t^f}{W - W_t^f} = \frac{E^* \theta}{R T_s^2} \tag{2}$$

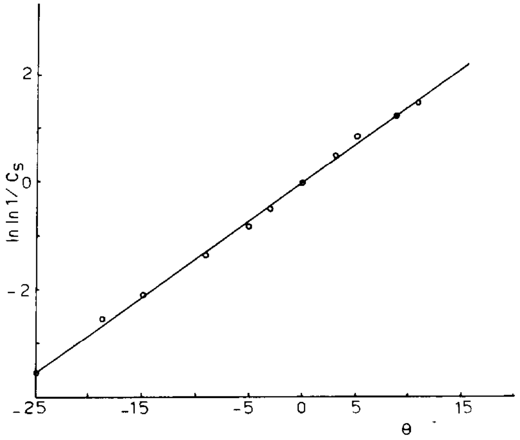


Fig. 3. The plot of $\ln \ln 1/C_s$ vs. θ.

TABLE 3

Kinetic and activation parameters calculated by the Horowitz and Metzger method [6] for pyrolysis of compounds **I**–**V**

Compound	Decomposition step	Temperature range (°C)	Activation energy E^* (kJ mol^{-1})	Order n
I	First step	120–210	255.3	1.0
	Second step	210–350	65.7	1.5
	Overall	120–350	56.8	6.0
II	First step	130–270	72.8	1.5
	Second step	270–350	137.0	1.0
	Overall	130–350	44.7	2.5
III	Overall	120–270	70.3	1.5
IV	First step	80–130	94.5	0.5
	Second step	130–180	77.5	0.5
	Third step	180–280	80.8	2.0
	2nd and 3rd	130–280	60.3	1.0
	Overall	80–280	35.8	1.0
V	First step	86–144	81.7	1.0
	Second step	144–282	67.2	1.5
	Overall	86–282	49.3	1.0

TABLE 4

Relation between reaction order (n) and concentration at maximum slope (C_s)

n	C_s
0	0.000
1/2	0.250
1	0.368 (1/e)
3/2	0.444
2	0.500
2 1/2	0.543
3	0.577
3 1/2	0.606
4	0.630
4 1/2	0.651
5	0.669
5 1/2	0.685
6	0.699
6 1/2	0.711
7	0.732
7 1/2	0.733
8	0.743
∞	1.000

or

$$\ln \ln \frac{1}{C} = \frac{E^*\theta}{RT_s^2} \tag{3}$$

The plot of $\ln \ln 1/C$ against θ should give straight lines (Fig. 3) whose slopes are related to the activation energy, E^* (Table 3). θ is given by

$$T = T_s + \theta \tag{4}$$

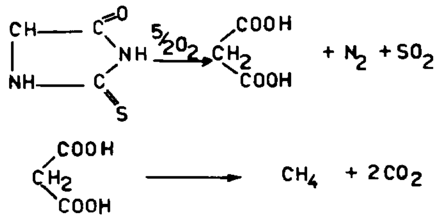
and $C = C_s$ when $\theta = 0$ and C_s is related to the order of the pyrolysis process, n, by

$$C_s = n^{1/1-n} \tag{5}$$

With an unknown n, a generally applicable method is to choose T_s where dC/dT is maximum or $d^2C/dT^2 = 0$. Thus if the inflection point of the TG curve occurs at $C = 1/e$, the reaction is known to be first-order, but at any C_s the order of the pyrolysis can be calculated from eqn. (5) or selected from the hypothetical Table 4.

DISCUSSION

The TG curve (Fig. 1a) of ligand **I** shows two consecutive decomposition stages in the temperature range 120–350 °C. The first stage at 120–210 °C

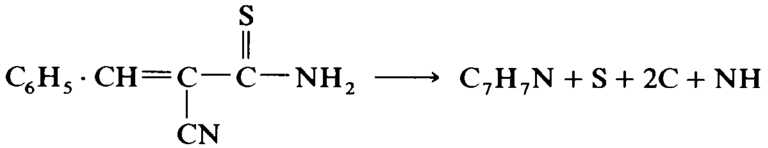


Scheme 1

refers to the loss of sulphur and nitrogen atoms (estimated mass loss, 52.0%; calculated, 51.7%). The evolved sulphur is oxidised to SO_2 and the nitrogen is evolved as N_2 gas. These reactions are confirmed by the appearance of sharp exothermic peaks in the DTA curve (Fig. 2a) of ligand **I** in the same temperature range. This stage requires an activation energy, E^*, of 255 kJ mol^{-1} and it is a first-order process ($n = 1$), see Table 3, which means that it depends only on the concentration of the ligand. The second stage at 210–350 °C involves the decomposition of the remaining active malonic acid fragment into CH_4 and CO_2 gases which requires less activation energy, $E^* = 65.8$ kJ mol^{-1}. This process has a fractional order, $n = 1.5$. The pyrolysis of **I** can only be explained by Scheme 1.

The thermal decomposition of ligand **II** (Fig. 1b) involves two main steps: the first at 130–270 °C is attributed to partial fragmentation of **II** into C, S and NH, followed by their oxidation into CO_2, SO_2, H_2O and N_2. In the second step the remaining part of the ligand decomposes into C and 2H which are oxidised to CO_2 and H_2O at 270–350 °C due to interaction with air in the furnace. These results can be explained by the proposed Scheme 2. The fractional reaction order of the first step is explained by the partial fragmentation of **II** which requires a small E^*(73 kJ mol^{-1}) in comparison with the decomposition of the remaining part in the second step which requires a high energy of 137 kJ mol^{-1}. Scheme 2 is confirmed by a series of endotherms and exotherms in the DTA of **II** over the same temperature range. The overall activation, E^*, is 45 kJ mol^{-1} and the overall order of this pyrolysis is 2.5 which means that it depends on the concentration of all possible decomposed fragments.

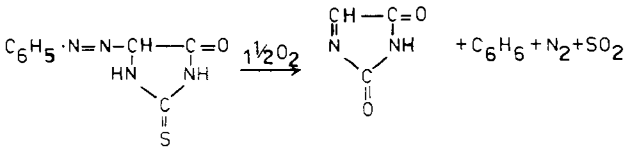
The thermal decomposition of ligand **III** involves only one step at 120–270 °C due to the partial loss of S, N_2 and C_6H_6 (estimated, 56%;



$$C_6H_5\cdot CH{=}\underset{\displaystyle CN}{\underset{|}{C}}-\overset{\displaystyle S}{\overset{\|}{C}}-NH_2 \longrightarrow C_7H_7N + S + 2C + NH$$

$$C_7H_7N \longrightarrow C_6H_5N + C + H_2$$

Scheme 2

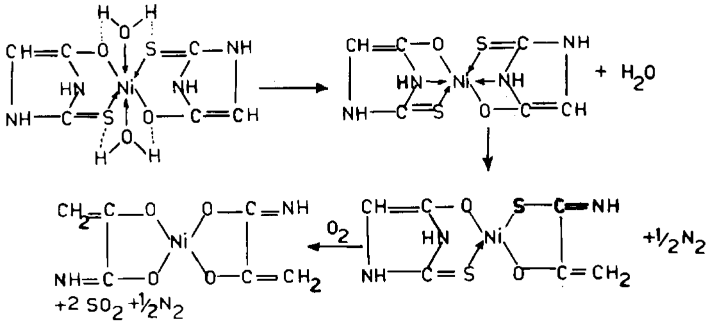


Scheme 3

calculated, 62%) as given by TG (Fig. 1c). The experimentally estimated mass loss is less than the calculated mass loss which suggests that ligand **III** is partially decomposed; this is confirmed by the fractional order $n = 1.5$, of this process. This decomposition required an activation energy of 70.37 kJ mol^{-1} and may be represented by Scheme 3.

The thermal decomposition of 2-thiohydantoin metal chelates were investigated in order to check the effect of complex formation on the thermal stability of this ligand.

Nickel 2-thiohydantoin chelate, **IV**, thermally decomposed in three steps (Fig. 1d) requiring a lower overall activation energy of 35.86 kJ mol^{-1} than that of ligand **I** itself, $E^* = 56.86$ kJ mol^{-1}. This means that complex formation makes the ligand thermally less stable. The first step involves the loss of two coordinated water molecules. This water loss occurs in the temperature range 80–130 °C (estimated mass loss, 11.25%; calculated, 11.0%). The second mass loss occurs within the temperature range 130–180 °C (estimated, 4.5%; calculated, 4.6%) and is due mainly to the loss of NH from the entity of one ligand molecule in complex **IV**. The third mass loss in the range 180–280 °C is due to the loss of two S atoms and another NH group (estimated, 23.2%; calculated, 24.2%) followed by oxidation of S to SO_2 gas. The DTA curve of this complex (Fig. 2d) shows a broad endotherm centred at 155 °C due to the first loss of coordinated water molecules. It also shows a broad exotherm at 170–270 °C which explains the steps of the above decomposition and the subsequent chemical reactions. These three stages required activation energies of 94.56, 77.59, and 80.80 kJ mol^{-1}, respectively. The first and the second steps, which refer to the partial



Scheme 4

loss of H_2O and NH_2 molecules, are of fractional order, $n = 0.5$ in both cases. The third step is second order, $n = 2$, which involves the loss of two S atoms together with half an N_2 molecule. The overall activation energy of these three steps is 35.86 kJ mol^{-1} with an overall n of 1. Therefore the thermal decomposition of complex **IV** may be explained by scheme 4.

The thermal decomposition of the cobalt 2-thiohydantoin complex, **V**, involves two main steps (Fig. 1e). The first step is the loss of two moles of coordinated water in the temperature range 86–144 ° C (estimated mass loss, 11%; calculated, 11.0%); it requires an activation energy of 81.71 kJ mol^{-1} and is first-order, which means that it depends only on the complex activity. The second step involves the fragmentation of the remaining part (estimated, 35%; calculated, 35.5%) in the temperature range 144–282 ° C; this has a fractional order ($n = 1.5$) and an activation energy of 67.21 kJ mol^{-1}. Overall, the pyrolysis of complex **V** is first order with $E^* = 49.35$ kJ mol^{-1}, i.e. greater than that of the nickel complex. This means that the cobalt complex may be more stable.

The DTA curve of the cobalt complex, **V**, (Fig. 2e) begins with an endothermic shift of the baseline starting at 90 ° C, followed by a broad endothermic peak centred at 155 ° C; then a small exothermic peak centred at 180 ° C is followed by a broad exothermic peak at 180–235 ° C. The first endothermic peaks may be explained by the loss of decomposed molecules and the final exothermic peaks represent the chemical reactions of the decomposed fragments as given by a scheme similar to that for the nickel complex **IV**, except that the last two decomposition steps of the nickel complex appear as one step in the cobalt complex, **V**. This is confirmed by the similarity of their DTA curves.

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