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ANALYSIS OF THERMOGRAVIMETRIC TRACES AS AN APPROACH TO DETERMINE THE MECHANISM OF DISSOCIATION OF COPPER(II)-α-ARYLAZOACETOACETYLAMINOPYRIDINE CHELATES

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ABSTRACT

Mechanisms for the thermal decomposition of copper(II)-α-arylazoacetoacetylaminopyridine chelates (I–V) are proposed, on the basis of calculated kinetic and activation parameters. The kinetic and activation parameters of such pyrolysis reactions can be conveniently determined through mathematical interpretation of thermogravimetric traces. The slope and the intercept of a straight line of a function of the mass fraction left vs. temperature gives the activation energy and order of pyrolysis. The relative stabilities of the chelates were found to be in the order **I** > **II** > **V** > **III** > **IV**, depending upon the withdrawing or repelling ability of the azo group substitutent given its share in the formation of the various complexes. The most suitable out of several proposed structural formulae for each chelate is also indicated.

INTRODUCTION

Thermogravimetric analysis (TG or DTG) has come into wide use in the last decade for rapid assessment of the thermal stability of various substances. A number of workers have demonstrated its usefulness [1–10]. Often the pyrolysis occurs 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. Equations derived by Freeman and Carroll [7] for non-reversing reactions can be used to calculate energy of activation and order of reaction from TG and volumetric curves. In this case the shape of the curve is determined by 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 [4,6,7,9,11]. Some of the methods described involve either graphic or

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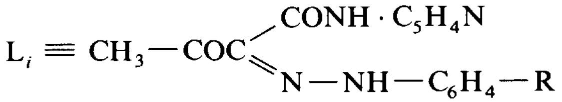
numerical differentiation of the thermograph. These procedures can, however, be cumbersome and subject to large errors when the curves are highly precipitous, as they usually are, so that determination of the parameters requires successive approximations or curve-fitting. Horowitz and Metzger [12] have described an approximate integral method similar to, but even simpler than, that of van Krevelen et al. [11], by which pyrolysis rate parameters can easily be determined through inspection of the raw data.

The present work applies the techniques devised by Horowitz and Metzger [12] and Freeman and Carroll [7], with the help of computer programs published by Ravindran [13], to the study of the mechanisms of pyrolysis of complexes (**I**–**V**) of copper(II) with α-arylazoacetoacetylaminopyridine (L_i, $i = 1$–5). The approach is based on the calculation of activation and kinetic parameters for the complexes under investigation via inspection of their TG and DTG curves. A number of possible structures for these copper(II) complexes have already been established by Zayed et al. [14], using various physico-chemical methods of analysis.

EXPERIMENTAL

In order to prepare the copper(II)–L_i complexes (**I**–**V**)



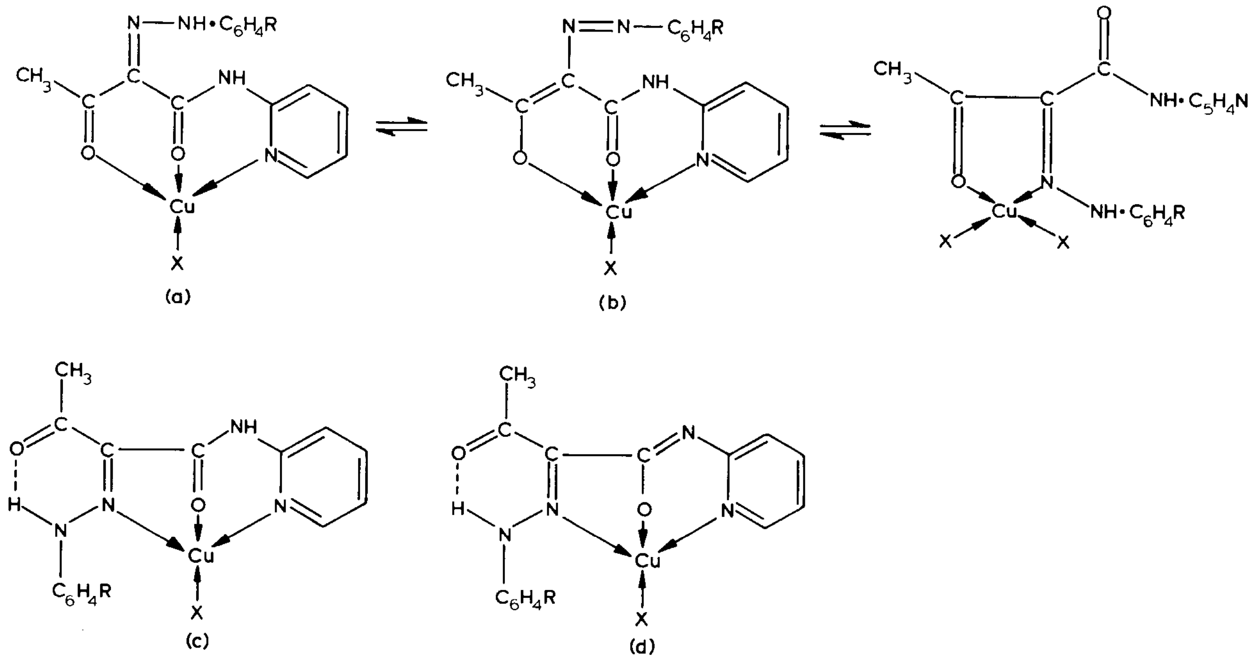
$$L_i \equiv CH_3-COC\begin{cases} CONH\cdot C_5H_4N \\ N-NH-C_6H_4-R \end{cases}$$

($R \equiv CH_3$, p-Cl, m-Cl, p-OCH_3 or o-NO_2)

solutions of the ligand L_i (0.2 g/20 ml 2,4-dioxane) and of copper acetate (0.2 g/20 ml water) were mixed thoroughly, stirred, diluted with water up to 100 ml and left overnight. The products formed were: **I**, green (m.p. 139 ° C); **II**, brownish green (m.p. > 250 ° C); **III**, brownish yellow (m.p. > 250 ° C); **IV**, yellowish green (m.p. > 250 ° C); and **V**, greenish yellow (m.p. 200 ° C). Each was recrystallized from absolute ethanol.

The structures of these complexes were investigated by Zayed et al. in a previous work [14]. Their general formulae, obtained from microanalysis data are: **I**, $Cu(C_{18}H_{19}N_4O_4)$; **II**, $Cu(C_{17}H_{16}O_4N_4Cl)$; **III**, $Cu(C_{17}H_{18}O_5N_4Cl)$; **IV**, $Cu(C_{19}H_{19}O_8N_5)$; and **V**, $Cu(C_{18}H_{18}N_4O_5)$. Their proposed structural formulae are given by the equilibria in Scheme 1.

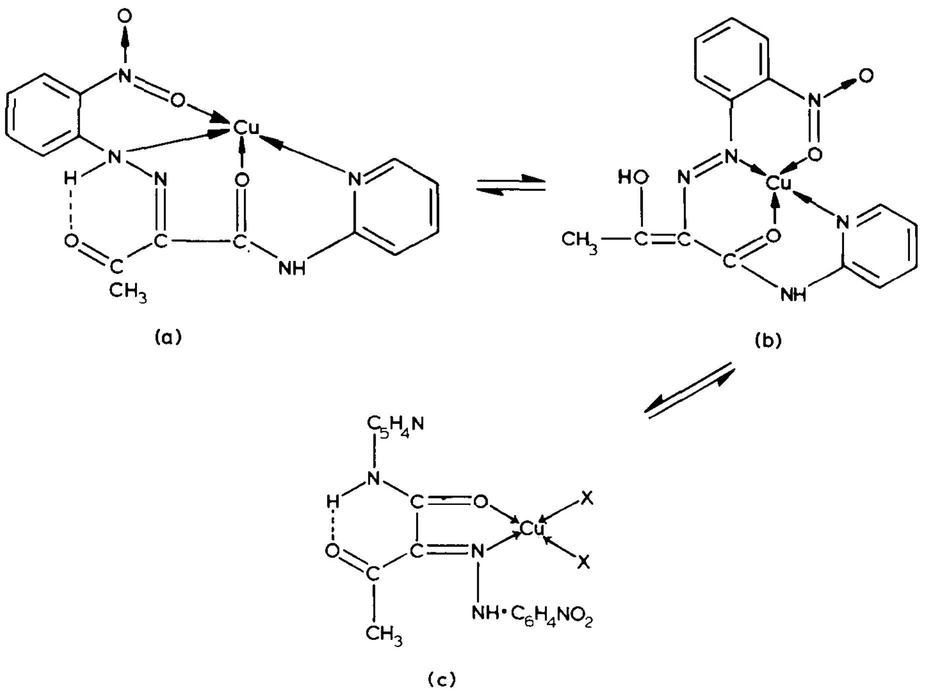
Thermal analysis (TG and DTG) of complexes **I**–**V** (Fig. 1 and Table 1) was performed using a conventional thermal analyser (Shimadzu system, Shimadzu 30 series thermal analysis instrument), with 125 mg samples of the various complexes. The pyrolysis was carried out under N_2 atmosphere at a heating rate of $5\,°C\ min^{-1}$.



I−IV

($X \equiv H_2O$ or Ac)

Scheme 1 (continued overleaf).



V

Scheme 1 (continued).

TABLE 1

Kinetic and activation parameters for steps in the decomposition of substituted phenylhydrazoneacetoacetylaminopyridine copper(II) chelates **I**–**V**

Compound	Decomposition step	Temperature range (° C)	Activation energy $E^\star$ (kJ mol^{-1})		Order n·	
			Stepwise	Overall	Stepwise	Overall
I	First step	88–152	2.758 [a]		1.4 [a]	
(p-Me)	Second step	152–200	3.16, 3.21 [b]	1.89	0.94, 0.94 [b]	0.95
	Third step	200–296	2.22		0.85	
			$\Sigma E^\star = 8.14$		$n_{av.} = 1.07$	
II	First step	88–136	4.62	2.98	1.25	
(p-Cl)	Second step	136–332	1.34		0.96	
			$\Sigma E^\star = 5.96$		$n_{av.} = 1.1$	
III	Confused					
(m-Cl)	Three steps	96–408	2.79	2.77	1.2	1.2
IV	One step	44–356	1.33	1.33	0.8	0.8
(p-CH_3O)						
V	First step	64–184	3.50		2.25	
(p-NO_2)	Second step	184–400	1.77		0.75	
			$\Sigma E^\star = 5.3$		$n_{av.} = 1.5$	

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[a] Data obtained by the Horowitz method, ref. 12.

[b] Data obtained by the Freeman and Carroll method, ref. 7.

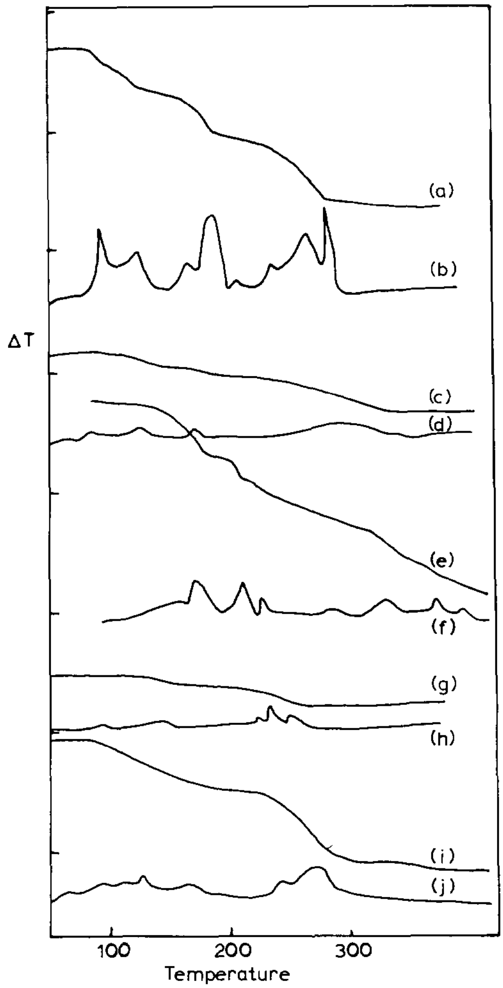


Fig. 1. TG and DTG curves for the thermal decomposition of copper(II)–α-arylhydrazoneacetoacetylaminopyridine chelates **I**–**V**.

RESULTS AND DISCUSSION

Most of the methods available for the calculation of kinetic and activation parameters from thermoanalytical data [1–11] involve preliminary trials which introduce errors, and require undesirable approximations and tedious calculations. The most important recommended method, that of Horowitz and Metzger [12], was applied in the present investigation to the pyrolysis of α-arylhydrazoneacetoacetylaminopyridine (L_i)–copper(II) complexes **I**–**V**. The equation used to calculate activation and kinetic parameters (Table 1) was

$$\ln \ln\left(W_0 - W_t^{\mathrm{f}}\right)/\left(W - W_t^{\mathrm{f}}\right) = E^{\star}\theta/RT_{\mathrm{s}}^2 + C \quad \text{or}$$

$$\ln \ln 1/C_{\mathrm{s}} = E^{\star}\theta/RT_{\mathrm{s}}^2 + C \qquad (1)$$

TABLE 2

Mass loss of arylhydrazoneacetoacetylaminopyridine (L_i)-copper(II) chelates **I**–**V**

Complex	Temperature range (° C)	Decomposition products	Mass loss (%)	
			Estim.	Calcd.
I	96–186	CH_3COO	16.0	15.5
(*p*-Me)	194–270	CO_2	12.0	11.6
II	88–136	H_2O	4.4	4.5
(*p*-Cl)	136–332	$\frac{1}{2}Cl_2$	9.11	8.86
III	68–100	H_2O of hydration	4.0	4.26
(*m*-Cl)	106–130	coord. H_2O	4.0	4.26
	130–158	CH_3COO	14.0	13.95
	168–250	$\frac{1}{2}Cl_2$	8.0	8.30
IV (*p*-CH_3O)	44–356	$CH_3O + H_2O$ of hydration	9.31	7.7
V	106–250	$2CH_3COO$	26.0	26.76
(*p*-NO_2)	or			
	106–150	CH_3–CH_3	6.0	6.76
	150–250	$2CO_2$	20.0	20.00

where W is the mass remaining at a given temperature, and W_0 and W_t^f are the initial and final masses, respectively. T_2 is defined as the temperature where $C_s = (W - W_t^f)/(W_0 - W_t^f) = 1/e = 0.368$ and $\theta = T - T_s$, and T is the temperature at each stage of pyrolysis.

Figure 1 shows TG and DTG curves for the five complexes. Table 2 shows mass losses as estimated from the curves and mass losses as calculated from microanalysis data obtained at different stages of decomposition for each of the complexes. Table 2 also lists possible fragments at each stage of pyrolysis.

From the curves in Figs. 1a and 1b it is clear that complex **I** decomposes in three steps. The first occurs within the temperature range 88–152° C, the second within the range 152–200° C, and the third within the range 200–296° C. This decomposition process can be explained by the following scheme.

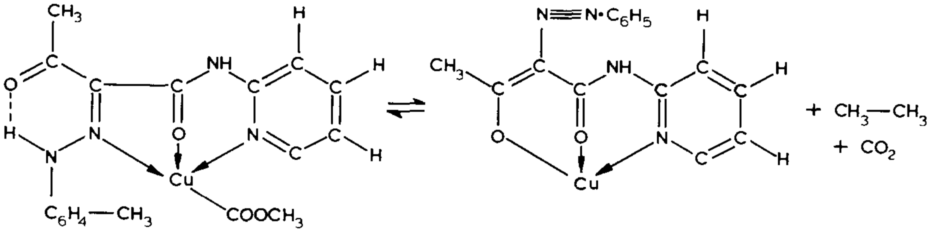
$$Cu(C_{18}H_{19}N_4O_4) \rightarrow Cu(C_{16}H_{16}N_4O_4) + CH_3COO^-$$

$$CH_3COO^- \rightarrow CH_3^{\cdot} + CO_2$$

$$Cu(C_{16}H_{16}N_4O_4) + CH_3^{\cdot} \rightarrow CH_3{-}CH_3 + Cu(C_{15}H_{13}N_4O_4)$$

Scheme 2.

This scheme involves the initial loss of an acetate group (mass loss 16% estim., 15.5% calcd.) with an approximate energy of activation of $E^\star = 2.758$ kJ mol^{-1} and $n = 1.4$ (Table 1). The second step involves the decomposition of the acetate group into $CH_3^{\bullet}$ free radicals and CO_2 gas (mass loss 12% estim., 11.6% calcd.), as indicated by many peaks in the DTG curve (Fig. 1b) within the range 88–152 °C. This decomposition has $E^\star = 3.155$ kJ mol^{-1} and $n = 0.94$ (Table 1). These active radicals tend to then interact with the moiety of the remaining part of the complex, which loses another CH_3 group to give CH_3–CH_3 gas, as indicated by the appearance of further peaks within the range 152–200 °C. The second CH_3 removed may be that of the *p*-methylphenylazo group of the complex (Scheme 3).



Scheme 3.

This vigorous loss of CH_3 from the *p*-methylarylhydrazone group through interaction with the $CH_3^{\bullet}$ free radical releases activation energy $E^\star = 2.22$ kJ mol^{-1}, with $n = 0.85$ (Table 1). The value of n is approximately 1 at each stage, which means that each of the decomposition processes depends on the concentration or activity of the decomposed part, i.e. respectively, complex I, CH_3COO^- and CH_3–N=N– for the three steps. $E^\star$ and n values were obtained from the slopes and intercepts of the straight lines in Figs. 2a–d.

Figure 2 shows the straight lines obtained from the computer plot of ln ln $1/C_s$ vs. θ by application of the least-squares method [15]. The value of $E^\star$ can be calculated from the slope of each line after choosing a T_s value. The value of C_s at T_s can be calculated from the intercept, and the order of the reaction can then be calculated using the equation

$$C_s = (n)^{1/1-n} \qquad (2)$$

and the hypothetical data given in Table 3. Jellinek [8] has shown that $E^\star$ depends on the molecular mass of the decomposed compound. The raw data used for such calculations (e.g. for complex I) are given in Table 4.

The decomposition of complex **II** involves two main steps. The first, which occurs within the range 88–136 °C (Figs. 1c and 1d), may be related to the loss of a coordinated water molecule from the moiety of complex **II** (mass loss estim. 4.4%, calcd. 4.5%). This step corresponds to $E^\star = 4.619$ kJ mol^{-1} and $n = 1.25$, calculated from the slope and intercept of the line in Fig. 2e. The second step, which occurs within the range 136–332 °C, can be attributed to the loss of Cl (mass loss estim. 9.5%, calcd. 9.86%) from the *p* position of the ligand L_2, as a free radical. The activation energy for this step, calculated from the slope of the line in Fig. 2f, is $E^\star = 1.34$ kJ mol^{-1}, and the order of the decomposition of complex **II** is $n = 0.96$. This loss of a

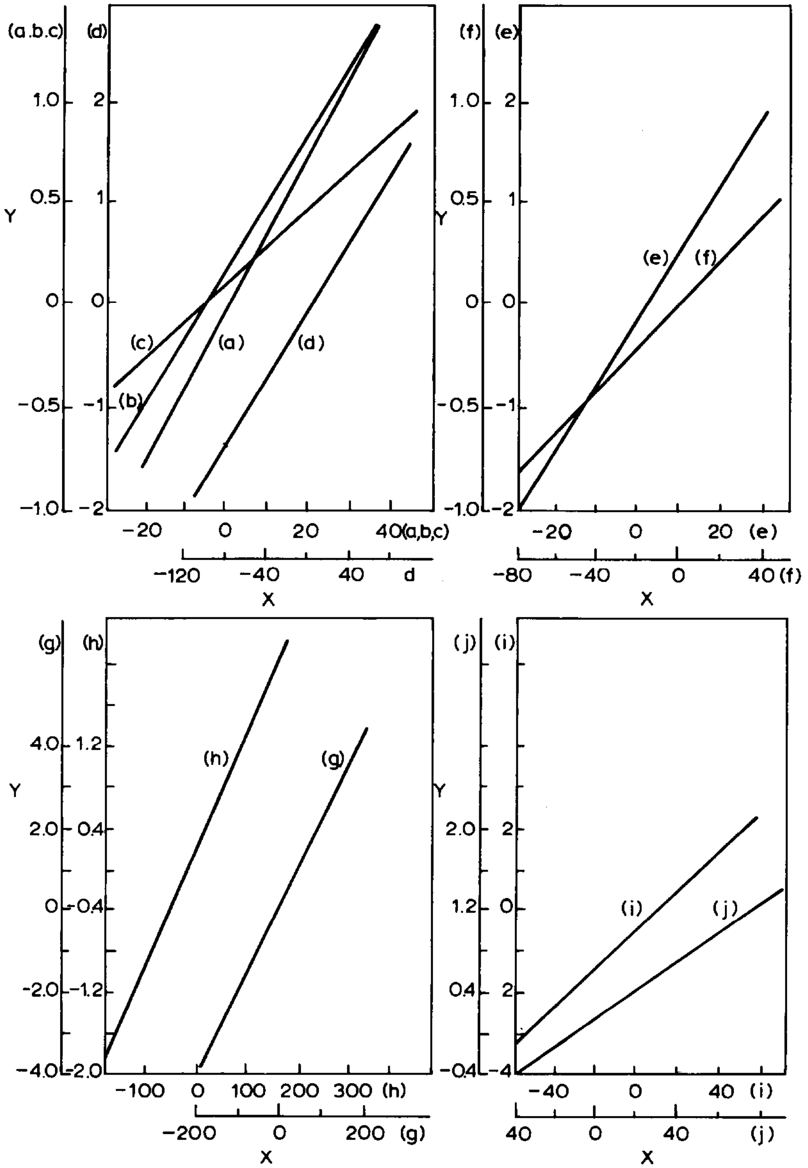


Fig. 2. Plots of ln ln $1/C_s$ vs. θ.

free radical is indicated by peaks in the DTG curve within the temperature range of the reaction (Fig. 1d). The scheme for the decomposition of complex **II** can thus be represented, tentatively, as

$Cu(C_{17}H_{16}O_4N_4Cl) \rightarrow Cu(C_{17}H_{14}O_3N_4Cl) + H_2O$

$Cu(C_{17}H_{14}O_3N_4Cl) \rightarrow Cu(C_{17}H_{14}O_3N_4) + Cl^{\cdot}$

$2Cl^{\cdot} \rightarrow Cl_2(gas)$

Scheme 4.

TABLE 3

Relation between reaction order *n* and concentration at maximum slope C_s

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

The lower stability of complex **III** (the *m*-Cl derivative, L_3) is indicated by extra successive mass losses (Table 2), including loss of water of hydration within the range 48–100 °C (mass loss estim. 4%, calcd, 4.26%), loss of coordinated water within the range 106–130 °C (mass loss estim. 4%, calcd. 4.26%), loss of an acetate group within the range 130–160 °C, which then decomposed into a CH_3 free radical and CO_2 gas (mass loss estim. 14%, calcd. 13.95%), and finally loss of *m*-Cl as a Cl free radical (mass loss estim. 8%, calcd. 8.3%). This series leads to a total estimated mass loss of 30%, and a total calculated mass loss of 31%. The scheme for the decomposition of complex **III** can thus be represented as

$$Cu(C_{17}H_{18}O_5N_4Cl) \rightarrow Cu(C_{17}H_{16}O_4N_4Cl) + H_2O$$

$$Cu(C_{17}H_{18}O_4N_4Cl) \rightarrow Cu(C_{15}H_{13}O_2N_4Cl) + CH_3COO^-$$

$$CH_3COO^- \rightarrow CH_3^{\cdot} + CO_2$$

$$2CH_3^{\cdot} \rightarrow CH_3\text{–}CH_3$$

$$Cu(C_{15}H_{13}O_2N_4Cl) \rightarrow Cu(C_{15}H_{13}O_2N_4) + Cl^{\cdot}$$

$$2Cl^{\cdot} \rightarrow Cl_2$$

Scheme 5.

The released free radicals $CH_3^{\cdot}$ and $Cl^{\cdot}$ may react to give $CH_3\text{–}Cl$

$$CH_3^{\cdot} + Cl^{\cdot} \rightarrow CH_3\text{–}Cl$$

TABLE 4

Example of raw data used for the calculation from TG curves of kinetic and activation parameters for complex **I** (by the Horowitz method)

	First step, within 88–152 °C		2nd step, within 152–200 °C		3rd step, within 200–296 °C	
	θ (°C)	$\ln \ln 1/C_s$	θ (°C)	$\ln \ln 1/C_s$	−(°C)	$\ln \ln 1/C_s$
	−20	−0.755	−20	−0.32	−29	−0.192
	−12	−0.367	−12	−0.229	−21	−0.113
	−4	−0.190	−4	−0.0529	−13	−0.061
	4	0.239	4	0.1234	−5	−0.009
	12	0.620	12	0.655	3	0.017
	20	0.834	20	1.008	11	0.146
	28	1.02	28	1.108	19	0.252
					27	0.418
					35	0.666
					43	0.814
					51	1.269
					59	1.539
Intercept	0.0475		0.194		0.118	
Slope	0.0382		0.0333		0.0184	
Correlation coefficient	0.99		0.97		0.94	
T_s (°C)	116		122		299	
$\ln \ln 1/C_s$	0.0473		0.194		0.118	
C_s	0.350		0.296		0.3245	
n	1.4		0.94		0.85	
$E^\star$ (kJ mol^{-1})	2.76		3.155		2.22	

Owing to the instability of this complex, we were not able to calculate the stepwise values of $E^\star$ and n. The overall value of activation energy $E^\star$ was found to be 2.765 kJ mol^{-1} and the overall value of n 1.2, as obtained from the slope and intercept of the straight line in Fig. 2g. The value of $E^\star$ for this complex was less than that for complex **II**, the *p*-Cl derivative ($E^\star_{\text{overall}}$ = 5.96 kJ mol^{-1}), which means that complex **II** is more stable than complex **III**.

Complex **IV** (the *p*-methoxy derivative) decomposed in one step within the temperature range 44–356 °C (Figs. 1g and 1h), with the loss of the *p*-methoxy group (mass loss estim. 9.31%, calcd, 7.7%). The difference between the estimated and calculated mass losses may be due to the loss of a trace amount of water of hydration, 1.3%. The energy of activation $E^\star$ was 1.33 kJ mol^{-1} and n was 0.8, as calculated from the slope and intercept of the straight line in Fig. 2h. The scheme for the pyrolysis of complex **IV** can thus be represented, tentatively, as

$Cu(C_{18}H_{19}O_5N_4) \rightarrow Cu(C_{17}H_{16}O_4N_4) + CH_3O^\bullet$

$2CH_3O^\bullet \rightarrow 2CH_3\text{–}CH_3 + O_2$

Scheme 6.

The last step is confirmed by the appearance of three peaks in the DTG curve (Fig. 1h) between 220 and 290 °C.

The decomposition of complex **V** passes through two distinct steps within the temperature ranges 64–184 °C and 184–400 °C, respectively (Figs. 1i and 1j). This is explained by the successive loss of two acetate groups (Table 2) leading to the formation of CH_3–CH_3 (mass loss estim. 6%, calcd. 6.76%) and CO_2 (mass loss estim. 20%, calcd. 20%) gases. The first step has activation energy $E^\star = 3.5$ kJ mol^{-1} and $n = 2.25$, and the second step has $E^\star = 1.77$ kJ mol^{-1} and $n = 0.78$. These values were obtained from the two straight lines in Figs. 2i and 2j. The value of $n = 2.25$ indicates that the first step is second order, which can be explained by its dependence on the activity of the two acetate groups released. The second step is first order, owing to its dependence on the CH_3 free radical. The decomposition of the complex can be summarized by the scheme

$$Cu(C_{19}H_{18}O_8N_5) \rightarrow Cu(C_{15}H_{13}O_4N_5) + 2CH_3COO^-$$

$$2CH_3COO^- \rightarrow 2CH_3^{\bullet} + CO_2$$

$$2CH_3^{\bullet} \rightarrow CH_3\text{–}CH_3$$

Scheme 7.

The values of $\Sigma E^\star$ for the thermal decomposition processes of complexes **I**–**V** were 8.14, 5.96, 2.8, 1.3 and 5.3 kJ mol^{-1}, respectively, which indicates that the order of stability of these complexes is **I** > **II** > **V** > **III** > **IV**. This can be related to the electron-withdrawing ability of the substituent in the phenyl hydrazone group, indicating the share of this azo group in the complex formation of these copper(II) chelates, as has been explained previously by Zayed et al. [14]. Therefore the most suitable structural formulae for the chelates are (c) and (d) for complexes **I**–**IV**, and (a) or (c) for complex **V** (cf. pp. 3, 4).

Freeman and Carroll [7] have determined both $E^\star$ and n from TG data, using the relation

$$[(E^\star/2.3\,R)(1/T)]/\log W_r = -n + (\log dW/dt)/\log W_r \qquad (4)$$

The program used for the computation of $E^\star$ and n was written in CERN FORTRAN by Ravindran [13]. We tried to apply this relation to the data obtained for the thermal decomposition of complexes **I**–**V** by very tedious calculation. The aim of this attempt was to confirm the calculations performed using the Horowitz relation [12]. Provision is made in the program for the calculation of the temperature T_s from mass loss vs. temperature data. (An example, for complex **I**, is given in Table 5). The quantity dw/dt in eqn. (4) was calculated by dividing the difference in mass loss at specific time $(t + h)$ and $(t - h)$ by $2h$, where h is the time interval. The data obtained were smoothed using the successive values of dw/dt, which should progressively increase or decrease depending on whether the data were on

TABLE 5

Example of raw data used for the calculation from TG curves of kinetic and activation parameters for complex **I** (by the Freeman and Carroll method)

First step, within 88–152°C		Second step, within 152–232°C		Third step, within 200–296°C	
X	*Y*	*X*	*Y*	*X*	*Y*
6.36×10^{-3}	363	0.0118	11.38	7.85×10^{-3}	9.038
7.50×10^{-3}	5.8	0.0107	9.87	7.29×10^{-3}	6.339
0.0100	7.61	9.76×10^{-3}	9.59	7.19×10^{-3}	6.391
9.6×10^{-3}	10.13	7.18×10^{-3}	7.96	6.53×10^{-3}	5.99
0.010	11.18	7.25×10^{-3}	7.72	6.5×10^{-3}	5.85
0.0106	11.00	7.54×10^{-3}	7.56	6.0×10^{-3}	5.41
0.01156	11.28	8.02×10^{-3}	7.406		
0.01176	11.38	8.47×10^{-3}	7.15		

the low or high temperature part of the maximum reaction rate. Our attempts were mostly unsuccessful, because of the successive approximation, except in the case of the second step of the decomposition of complex **I**, when we obtained a straight line which gave values of $E^{\star} = 3.205$ and $n = 0.94$, which are in good agreement with the values obtained using the Horowitz method. Therefore, in general, the Horowitz method can be considered as a complement to more detailed slope-plotting methods, particularly for quick analyses and as a convenient means of comparing the relative thermal stabilities of a series of substances, as in the present work.

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