Asian Journal of Chemistry Vol. 6, No. 1 (1994), 130–134

Kinetic Parameters of Thermolysis of Complexes of Rhodium(III), Palladium(II) and Platinum(II) with Substituted Morpholines from their Non-Isothermal Thermogravimetric Data

H.L. AGRAWAL†, A. MISHRA, R.K. AMBASTA, L. VERMA, R.K. VERMA*
and B.P. VERMA
Department of Chemistry
Magadh University
Bodh-Gaya-824 234, India

The non-isothermal decomposition of complexes of Rh(III), Pd(II) and Pt(II) with N-substituted methyl and ethyl morpholines has been studied in static air. The TG data have been analysed for the kinetic parameters of decomposition using the graphical Freeman-Carroll method and the trial and error method of Zsako.

INTRODUCTION

The complexes of rhodium, palladium and platinum are usually very much particular in furnishing the metal relatively earlier when heated[1]. This aspect is also used in the estimation of the metals in their complexes[2]. In contrast, the N–substituted methyl and ethyl morpholino complexes of Rh(III), the N-methyl morpholino complex of Pt(II) prepared from their respective chlorides show horizontals for brief periods due to stability of complexes having non-stoichiometric compositions formed during heating. This delays occurrence of metallic residues and generates curiosity. An attempt has been made in the present paper for assigning reasons of occurrence of such horizontals, on the basis of kinetic analysis of the TG data of the complexes. The non-isothermal decompostion of $RhCl_3L_3$, $RhCl_3L_3^*$ and $PtCl_2L_4$ has been studied in static air (L = N-methyl morpholine; L* = N-ethyl morpholine). Studies have also been undertaken on thermolysis of $PtCl_2L_2^*$ and $PdCl_2L_2^*$ which do not form non-stoichiometric intermediate residues, for the sake of comparison. A comparative kinetic and thermodynamic study of their thermal decomposition has been made for observed percentage mass losses by using the graphical method of Freeman-Carroll[3] and the trial and error method of Zsako[4], which is a modification of the curve fitting method of Doyle[5].

EXPERIMENTAL

The thermal measurements (TGA) on samples of 5.5 to 8.5 mg in size were

---

†Dept. of Chemistry, G.L.A. College, Daltonganj-822 101, India.

carried out (Fig. 1) in static air atmosphere on a Stanton Redcroft Thermobalance

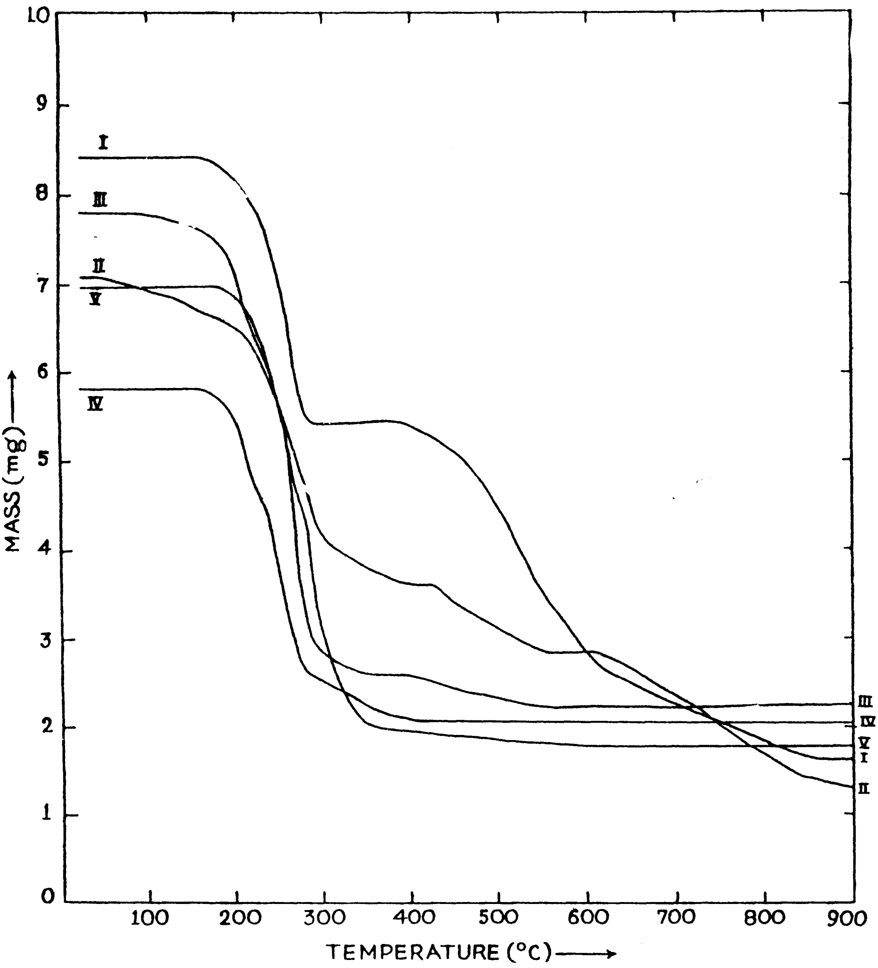

Fig. 1 TGA traces of (I) $RhCl_3L_3$, (II) $RhCl_3L^*_3$, (III) $PtCl_2L_4$, (IV) $PtCl_2L^*_2$, and (V) $PdCl_2L^*_2$ [L = N-methyl morpholine and L* = N-ethyl morpholine].

TG-750 upto 900°C with heating rate programmed at 10°C min^{-1}. Residues of non-stoichiometric compositions formed in the first step of decomposition. As such the thermodynamic and kinetic parameters for observed % mass losses were evaluated for the first step decomposition of all the five complexes. Values of order of reaction (b), energy of activation (E_a), frequency factor (A) of Arrhenius equation and activation entropy (ΔS^*) were approximated using the Freeman- Carroll equation (1), the Zsako equations (2) and (3) and the thermodynamic relation (4).

$$\frac{-\frac{E_a}{2.3R}\Delta T^{-1}}{\Delta \log W_r} = b + \frac{\Delta \log \frac{dw}{dt}}{\Delta \log W_r} \qquad (1)$$

$$\log \frac{AE_a}{Rq} = \log g(\alpha) - \log p(x) = B \tag{2}$$

$$\log A = \overline{B} + \log Rq - \log E_a \tag{3}$$

$$\Delta S^* = R \ln \frac{Ah}{kT_{1/2}} \tag{4}$$

where $W_r = W_c - W$

W_c = weight loss at completion of reaction

w = total weight loss upto time t

q = heating rate

$g(\alpha) = \int \frac{d\alpha}{(1-\alpha)^b}$

α = degree of completion of reaction

p(x) = function of x (x depends upon T and E_a)

$\overline{B}$ = mean (A.M.) of most consistent series of B values

$T_{1/2}$ = temp. at which half of the transformation under consideration is complete

k = Boltzman constant

R = gas constant

h = Planck's constant

The straight line Freeman-Carroll plot furnished the value of order of reaction from the intercept on the $\Delta \log (dw/dt)/\Delta \log W_r$ axis and the value of energy of activation from the slope, which amounted to $E_{a/2.303R}$.

In the Zsako calculations, the most consistent series of B was found out by standard deviation method, [–log p(x)] values were taken from the Zsako chart and the order of reaction and activation energy values which corresponded to the most consistent series of B values were accepted.

RESULTS AND DISCUSSION

The decompositions of rhodium complexes furnish residues of non-stoichiometric compositions. In case of platinum only, the *tetrakis* (N-methyl morpholino) platinum(II) chloride gives non-stoichiometric chloride which is stable for a brief period of 30°C from 350°C. The horizontal disappears at 380°C after which the curve slowly descends to a horizontal corresponding to metallic platinum at 600°C. The bis-(N-ethyl morpholino) complex of platinum loses weight somewhat precipitously after 170°C and the metal is obtained at 400°C. In case of the corresponding palladium complex, the initial weight loss is almost identically precipitous, but there is a horizontal corresponding to PdO in the region 360–420°C. Palladium appears above 600°C. In contrast, rhodium metal appears at 860°C and 900°C in the above mentioned first two cases respectively. Values of % mass loss have been given in Table 1 for the five complexes, and the values of order of reaction, energy of activation, frequency factor and activation entropy as obtained by the Freeman-Carroll and Zsako methods for the first steps of decomposition in Table 2. The magnitude of activation entropy values for the two rhodium and the one platinum complexes, which furnish residues of non-

TABLE 1
DIFFERENT STEPS OF THERMAL DECOMPOSITION OF THE COMPLEXES

Complex	Step	% Mass loss	
		Obs.	Calcd.
$RhCl_3L_3$	$RhCl_3L_3 \xrightarrow{170\text{–}280°C} RhCl_3L_{1.23}$	34.52	35.00
	$RhCl_3L_{1.23} \xrightarrow{400\text{–}860°C} Rh$	45.71	44.92
$RhCl_3L^*_3$	$RhCl_3L^*_3 \xrightarrow{50\text{–}410°C} RhCl_3L^*_{0.63}$	49.15	48.87
	$RhCl_3L^*_{0.53} \xrightarrow{430\text{–}560°C} RhCl_3L^*_{0.15}$	10.16	10.31
	$RhCl_3L^*_{0.15} \xrightarrow{610\text{–}900°C} Rh$	22.31	22.27
$PtCl_2L_4$	$PtCl_2L_4 \xrightarrow{80\text{–}350°C} PtCl_{0.85}$	66.19	66.53
	$PtCl_{0.85} \xrightarrow{380\text{–}600°C} Pt$	5.08	4.35
$PtCl_2L^*_2$	$PtCl_2L^*_2 \xrightarrow{170\text{–}400°C} Pt$	62.39	61.53
$PdCl_2L^*_2$	$PdCl_2L^*_2 \xrightarrow{180\text{–}360°C} PdO$	71.22	70.35
	$PdO \xrightarrow{420\text{–}600°C} Pd$	3.16	3.74

L = N-methyl morpholine
L^* = N-ethyl morpholine

TABLE 2
KINETIC PARAMETERS OF FIRST STEP DECOMPOSITION OF THE COMPLEXES

Complex	E_a (KJ mol^{-1})		b		A (S^{-1})	ΔS^* (KJ mol^{-1})
	F–C	Zsako	F–C	Zsako		
$RhCl_3L_3$	110.7923	75.312	0.55	0	1.4862×10^5	–150.6867
$RhCl_3L^*_3$	51.4422	50.208	0.86	0	2.9460×10^2	–199.7441
$PtCl_2L_4$	70.3748	83.680	1.25	1	3.0084×10^6	–125.4279
$PtCl_2L^*_2$	134.8712	167.360	2.17	2	3.5220×10^{15}	48.1996
$PdCl_2L^*_2$	167.4980	167.430	1.75	2	1.1038×10^{15}	38.3254

stoichiometric composition, clearly suggests that appreciable rearrangement is taking place among various degrees of freedom. It can also be suggested that the ligand might be acting as bridging component to give extra stability to lattices having composition ML_{1-x}. The activation entropy value of the other platinum complex and the single palladium complex do not give such evidence. The lower stability of the N-ethyl morpholino complex of rhodium and the N-methyl morpholino complex of platinum may be attributed to relatively more steric crowding at the co-ordination sites. The activation energy values for the two complexes suggest that the ligands are relatively more loosely held than in other cases.

REFERENCES

1. C. Duval, Inorganic Thermogravimetric Analysis, 2nd Ed., Elsevier, New York, pp. 472–481, 591–594 (1963).
2. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 3rd Ed. (1962).
3. E.S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).
4. J. Zsako, *J. Phys. Chem.*, **72**, 2406 (1968).
5. C.D. Doyle, *J. Appl. Polym. Science*, **15**, 285 (1961).

(*Received*: 28 December 1992; *Accepted*: 1 May 1993) AJC–611