

Studies on Thermal Decomposition Kinetics of 3-Methyl-4-nitroso-5-pyrazolone Complexes with Thorium(IV) and Dioxouranium(VI) Nitrate

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Parameters related to thermal decomposition kinetics, viz., E^* , A and ΔS^* are computed on the basis of thermal decomposition data on the complexes of 3-methyl-4-nitroso-5-pyrazolone with thorium(IV) and dioxouranium(VI) nitrate using different methods and it was inferred that the values of E^* are sufficiently high and positive while ΔS^* are negative.

INTRODUCTION

Thermogravimetric analytical studies of thorium(IV) and dioxouranium(VI) metal complexes were of great interest for many workers in the past¹⁻⁴. Thermal decomposition kinetics parameters, viz., E^* , A and ΔS^* were also computed for transition metal complexes⁵ and of thorium(IV) and dioxouranium(VI) complexes⁶⁻⁸. Continuing with the studies, the author wishes to report thermal decomposition kinetic parameters for two representative complexes, viz. $[\text{Th}(\text{MNP})_2(\text{NO}_3)_4]$ and $[\text{UO}_2(\text{MNP})_2(\text{NO}_3)_2]$ (MNP = 3-methyl-4-nitroso-5-pyrazolone).

EXPERIMENTAL

The complexes $[\text{Th}(\text{MNP})_2(\text{NO}_3)_4]$ and $[\text{UO}_2(\text{MNP})_2(\text{NO}_3)_4]$ were prepared by the reported methods^{9,10}. TGA of these complexes were recorded on Santon Red-Craft thermobalance model TG-750 at heating rate $10^\circ/\text{min}$ and these TGA curves were used to draw the rate of loss of mass vs temperature (DTG) curves for these complexes. The decomposition data for the complexes is presented in Table-1.

Three different methods, Freeman-Carroll¹¹ (F.C.), Coats-Redfern¹² (C.R.) and Horowitz-Metzger¹³ (H.M.), were used to evaluate kinetic parameters from these TGA traces mentioned in Table-1.

Freeman-Carroll Method¹¹: Freeman-Carroll had given an idea about evaluation of kinetic parameters using an equation which may be represented as

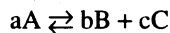
$$-\frac{dx}{dt} = A \exp \{-E^*/RT\} X^n \quad (1)$$

where the symbols have usual meanings.

TABLE-1
 THERMAL DECOMPOSITION DATA FOR 3-METHYL-4-NITROSO-5-PYRAZOLONE
 COMPLEXES WITH THORIUM(IV) AND DIOXOURANIUM(VI) NITRATE

Complex	Stage of decomposition	Reaction	Peak temperature in DTG (°C)	Temperature range in DTG (°C)
Th(MNP) ₂ (NO ₃) ₄	1st Stage	Th(MNP) ₂ (NO ₃) ₄ → Th(MNP)(NO ₃) ₄	225	180-280
	2nd Stage	Th(MNP)(NO ₃) ₄ → Th(NO ₃) ₄	335	290-390
	3rd Stage	Th(NO ₃) ₄ → ThO ₂	600	560-640
UO ₂ (MNP) ₂ (NO ₃) ₂	1st Stage	UO ₂ (MNP) ₂ (NO ₃) ₂ → UO ₂ (MNP)(NO ₃) ₂	245	220-270
	2nd Stage	UO ₂ (MNP)(NO ₃) ₂ → UO ₂ (MNP) _{0.3} (NO ₃) ₂	500	460-530
	3rd Stage	UO ₂ (MNP) _{0.3} (NO ₃) ₂ → [UO ₃] → U ₃ O ₈	645	610-670

For the general equation



they had solved equation (1) and found out the result for studying the reaction kinetics.

$$\frac{-E^*/2.3R}{\log W_r} \Delta(T^{-1}) = -n + \frac{\Delta \log (dW/dt)}{\Delta \log w_r} \quad (2)$$

where $W_r = W_c - W$,

W_c = weight loss at completion of reaction, and

W = weight loss up to time t .

From this equation (2) we may conclude that on plotting

$$\frac{\Delta \log (dW/dt)}{\Delta \log W_r} \text{ vs } \frac{\Delta(T^{-1})}{\Delta \log W_r} \quad (3)$$

For decomposition reactions we are able to find out 'n' as intercept and $-E^*/2.3R$ as slope from where E^* can be computed.

On application of this equation to our present thermal decomposition data for dioxouranium(VI) complexes, it was inferred that all the reactions mentioned in Table-1. are of order unity. E^* values for each case were calculated from slopes of Freeman-Carroll plots which are given in Table-2.

*Coats Redfern Method*¹²: For the similar type of reactions, Coats-Redfern had also derived some relation relating α , fraction of compound at time 't' and all other parameters. This relation is given as

$$\log \left\{ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right\} = \log \left\{ \frac{AR}{AE^*} \frac{(1-2RT)}{E} - \frac{E^*}{2.3RT} \right\} \text{ for } n \neq 1 \quad (4)$$

TABLE-2
KINETIC PARAMETERS OF COMPLEXES OBTAINED USING EQUATIONS
OF FREEMAN CARROLL(FC), COATS-REDFERN(CR) AND
HOROWITZ-METZGER(HM)

Complex	Decomposition stage	Equation	Parameters		
			E* KJ mol ⁻¹	A s ⁻¹	ΔS* JK ⁻¹ mol ⁻¹
Th(MNP) ₂ (NO ₃) ₄	1st stage	FC	16.56	-	-
		CR	11.62	2.66 × 10 ⁴	-157.8
		HM	18.40	3.65 × 10 ⁴	-155.2
	2nd stage	FC	16.56	-	-
		CR	18.82	2.34 × 10 ⁴	-162.2
		HM	17.25	3.77 × 10 ⁴	-158.25
	3rd stage	FC	35.37	-	-
		CR	32.53	5.13 × 10 ⁴	-160.5
		HM	34.73	1.09 × 10 ⁴	-173.4
UO ₂ (MNP) ₂ (NO ₃) ₂	1st stage	FC	22.56	-	-
		CR	20.94	1.01 × 10 ⁵	-147.1
		HM	24.22	1.18 × 10 ⁵	-140.7
	2nd stage	FC	17.53	-	-
		CR	14.07	6.22 × 10 ⁴	-157.4
		HM	19.59	8.45 × 10 ⁴	-154.8
	3rd stage	FC	26.53	-	-
		CR	24.63	7.21 × 10 ⁴	-158.3
		HM	29.55	3.45 × 10 ⁴	-164.4

$$\text{and } \log \left\{ \frac{-\log(1-\alpha)}{T^2} \right\} = \log \left\{ \frac{AR}{aE^*} \frac{(1-2RT)}{E} - \frac{E^*}{2.3RT} \right\} \text{ for } n=1 \quad (5)$$

where α = fraction of compound at time 't' = $\frac{W_0 - W}{W_0 - W_y}$ and W_0 , W and W_y are initial weight, weight at time 't' and final weight respectively of the sample under investigation and a = rate of heating.

All other symbols have usual meanings. We have applied these equations for our present data and observed that plots of

$$\log \left\{ \frac{-\log(1-\alpha)}{T^2} \right\} \text{ vs } 1/T \quad (6)$$

are straight lines in decomposition reactions of these two complexes. This justifies that the reactions may have order unity ($n=1$) as it is observed on the basis of Freeman-Carroll method. E^* values for these reactions are obtained from the slopes of the plots (as $-E^*/2.3R$) and A from intercept.

ΔS^* values for each of the reactions is obtained from the following equation.

$$\Delta S^* = R \ln \{ Ah/kT_s \} \quad (7)$$

Results obtained on applying this method are given in Table 2.

Horowitz-Metzger Method¹³: Horowitz-Metzger method is illustrative of the approximation methods

These authors derive the relation for a first order reaction which may be written as

$$\log \left\{ \log \frac{W_{\alpha}}{W_r} \right\} = \frac{E^* \theta}{2.3 RT_s^2} - \log 2.3 \quad (8)$$

where $\theta = T - T_s$ and T_s = peak temperature where dW/dt is maximum.

We have tried to apply this approximation method to our present data and observed that plots of $\{\log W_{\alpha}/W_r\}$ vs θ are straight lines. E^* for these reactions is calculated from the slope of the lines and A is calculated using the following equation:

$$\frac{E^*}{RT_s^2} = \frac{A}{a \cdot \exp \{-E^*/RT_s\}} \quad (9)$$

ΔS^* values are calculated according to equation (7). The results of this method are given in Table 2.

The kinetic parameters obtained by employing Coats-Redfern, Horowitz-Metzger and Freeman-Carroll equations are summarized in Table-2. The values of E^* , A and ΔS^* are appreciable and E values are sufficiently high while ΔS^* have negative values; these are comparable with other observations⁵⁻⁷. These complexes show similar type of thermal behaviour as is shown by the E^* and A values for each reaction.

Horowitz-Metzger method gives reasonably good results but it is less accurate mathematically than integral methods. Coats-Redfern method seems to be more accurate but it is a considerable time-consuming method.

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