

Thermal Decomposition of Potassium Trioxalato Chromate(III) Trihydrate: A Kinetic and Mechanistic Study

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Thermal decomposition of potassium trioxalato chromate(III) has been found to be involving dehydration, decomposition and oxidation, when heated in air with heating rate programmed at $1/6 \text{ K s}^{-1}$. The thermogravimetric data for the decomposition step has been analysed for kinetic parameters using Freeman-Carroll and Zsako methods. When α -T data of dehydration and decomposition steps were fed to computer for mechanistic analysis, both the steps were found to be following 1-1 random-nucleation mechanism.

INTRODUCTION

Oxalato complexes of transition metals have been widely studied, but their thermal studies have escaped proper attention. The object of the present investigation is to study the thermal decomposition of potassium trioxalato chromate(III) trihydrate in air, minimising the local factors and to study the kinetics and mechanism of dehydration of the compound.

EXPERIMENTAL

Sample of potassium trioxalato chromate(III) trihydrate was heated in air in Stanton Redcroft Thermobalance TG-750 with heating rate programmed at $1/6 \text{ K s}^{-1}$. Freshly prepared and dried complex was powdered and loosely poured over the crucible to minimise the local factors. For the purpose of synthesis, the standard method¹ of adding powdered potassium dichromate to the aqueous solution of potassium oxalate and oxalic acid was used. Small sample size of 7–8 mg was taken to minimise the influence of heat of decomposition over the sample. The thermogravimetric data obtained were used for mechanistic analysis of the dehydration and decomposition steps, and for kinetic analysis of the decomposition step, the Freeman-Carroll² and Zsako³ equations (Eq. 1–3) and the thermodynamic relation (Eq. 4) were used.

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

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

$$\log A = \bar{B} + \log Rq - \log E_a \quad (3)$$

$$\Delta S^\# = R \ln \frac{Ah}{KT_{1/2}} \quad (4)$$

where, $W_r = W_c - W$

W_c = Weight loss at completion of reaction.

W = total weight loss up to time 't'

q = heating rate.

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

α = degree of completion of reaction.

$p(x)$ = function of x (x depends upon T and E).

\bar{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 = Plank's constant

E = activation energy, A = frequency factor

$\Delta S^\#$ = activation entropy, b = order of reaction.

For mechanistic study, the $\alpha - T$ data were first recorded and then they were fed to computer for the search of suitable mechanistic model using the LOTUS-123 package developed by Rao⁴ *et al.* at Regional Research Lab. Bhubaneshwar. DTG curve was also obtained.

RESULTS AND DISCUSSION

The decomposition (Table-1) takes place in three distinct steps^{5,6} involving

TABLE-1
DIFFERENT STEPS OF THERMAL DECOMPOSITION OF THE COMPLEX

Complex	Steps	% Mass loss		Peak in DTG (K)
		obs	calcd.	
$K_3[Cr(C_2O_4)_3] \cdot 3H_2O$	1. $K_3[Cr(C_2O_4)_3] \cdot 3H_2O \xrightarrow{303-433 K} K_3[Cr(C_2O_4)_3]$	10.71	11.09	323
	2. $K_3[Cr(C_2O_4)_3] \xrightarrow{613-753 K} \frac{3}{2} K_2O \cdot \frac{1}{2} Cr_2(CO_3)_3$	42.47	41.96	713
	3. $\frac{3}{2} K_2O \cdot \frac{1}{2} Cr_2(CO_3)_3 \xrightarrow{853-983 K} \frac{3}{2} K_2O + \frac{1}{2} Cr_2O_3$	49.99	50.25	913

dehydration, decomposition of the oxalate and its final conversion to oxide. The $\alpha - T$ plot of the steps don't show presence of period of induction⁷. However the mechanistic analysis of the dehydration step suggest that the rate controlling process assumes random nucleation involving one nucleus and one particle during dehydration. The same mechanism is adopted by the first step of decomposition, which is the main decomposition step. The least R^2 values indicating the best fitted mechanistic data have been given in Table-2.

TABLE-2
BEST FITTED MECHANISTIC DATA (R^2 VALUES)

Complex	One Dim. Cyl. Sym.	Two Dim. Sphe. Sym.	Three Dim.	Three Dim. React. Extr.	Random Nucleation I, II, III	Phase Bou Cyl. Sym.	Phase Bou Sym.
$K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ (Step-I)					I 0.836062	0.706203	0.758892
					II 0.709258		
					III 0.439292		
					I 0.962478	0.933089	0.949798
$K_3[Cr(C_2O_4)_3]$ (Step-II)	0.892566	0.921385	0.933567	0.974259	II 0.962478		
					III 0.962478		

The order of reaction (b), activation energy (E_a), frequency factor (A), entropy activation (ΔS^\ddagger)-data as obtained by the Freeman-carroll and Zsako methods for decomposition (step II of Table-1) have been given in Table-3.

TABLE-3
COMPARATIVE KINETIC PARAMETER

Complex	Freeman-Carroll		Zsako			
	b	E_a (KJ (mole ⁻¹))	b	E_a (KJ (mole ⁻¹))	A (sec ⁻¹)	ΔS^\ddagger (KJ (mole ⁻¹))
$K_3[Cr(C_2O_4)_3] \cdot 3H_2O$	1.3	62.160846	2	54.758	1999695.6	-125.3134

The entropy values support the decomposition steps suggested above. They also indicate that there is appreciable rearrangement among various degrees of freedom, which is likely in such mechanism of decomposition.

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REFERENCES

1. John C. Bailar Jr. and Eldon M. Jones, *Inorganic Syntheses*, I (Ed. Harold Simmons Booth), McGraw Book Comapny (1939).
2. E.S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 294 (1958).
3. J. Zsako, *J. Phys. Chem.*, **72**, 2406 (1968).
4. K.K. Rao, Proc. VIII National Workshop on Thermal Analysis, p. 236.
5. Mukesh Kumar, Ph.D. Thesis, Magadh University, Bodh-Gaya (1991).
6. N.C. Bhattacharjee, Ph.D. Thesis, Magadh University, Bodh-Gaya (1993).
7. D.A. Young in *The Internationa Encyclopaedia of Physical Chemistry, Solid and Surface Kinetics*, Ed. Tompkins, Pergamon Press, 68 (1966).

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