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Note

THERMOGRAVIMETRIC ANALYSIS AND KINETICS OF THE NON-ISOTHERMAL DECOMPOSITION OF MOLECULAR COMPLEXES OF 8-HYDROXYQUINOLINE (OXINE) WITH POTASSIUM DICHROMATE, POTASSIUM CHROMATE AND POTASSIUM PERMANGANATE

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Attempts have been made in the past to determine the kinetics of solid state reaction, based upon different mathematical expressions due to Kofstad [1], Freeman and Caroll [2], Doyle [3], and Coats and Redfern [4]. In 1966 Dave and Chopra [5] listed some mathematical expressions [eqns. (1)–(3)], which have been applied together with DTG curves, accounting for their preference for other procedures for the determination of kinetic parameters of the pyrolytic decomposition of metal complexes of derivatives of naphthaquinone, acetophenone, and amino acid by Sawhney et al. [6–8].

$$k = \frac{(A/m_0)^{n-1}(-\mathrm{d}x/\mathrm{d}t)}{(A-a)^n} \tag{1}$$

or

$$k = \frac{-\mathrm{d}x/\mathrm{d}t}{A-a} \tag{2}$$

for $n = 1$

$$\frac{-E/2.303R(T^{-1})}{\log(A-a)} = -n + \frac{\log(\mathrm{d}x/\mathrm{d}t)}{\log(A-a)} \tag{3}$$

where k = specific rate constant, m_0 = initial mole fraction of the reaction, A = total area under the curve for complete reaction, a = area under the curve at time t, $\mathrm{d}x/\mathrm{d}t$ = height at different points, n = order of reaction, and E = activation energy of the reaction.

The literature reveals that no attempt appears to have been made to synthesize and characterize the molecular complexes of oxine with $KMnO_4$, $K_2Cr_2O_7$ and K_2CrO_4. The present communication deals with TG analysis, followed by the determination of the kinetic parameters of the pyrolytic decomposition of the aforesaid oxine molecular complexes using the expressions of Dave and Chopra.

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EXPERIMENTAL

All the chemicals used were of BDH quality. For the synthesis of the molecular complexes of oxine with $KMnO_4$, $K_2Cr_2O_7$ and K_2CrO_4, 1 g of the salt in 10 ml of water was mixed slowly with constant stirring with X g of oxine in 10 ml of glacial acetic acid (where $X = 1.85$, 1.85 and 1.52 for $KMnO_4$–, K_2CrO_4–, and $K_2Cr_2O_7$–oxine complexes). The precipitate immediately appeared, and was refluxed over a water bath for 1/2 h, cooled to room temperature, filtered, washed successively with water and 10% glacial acetic acid, and dried at 60–70°C. Elemental analysis showed agreement between theoretical and experimental data for $KMnO_4 \cdot 4.5$ OX, $K_2CrO_4 \cdot 2$ OX and $K_2Cr_2O_7 \cdot 6.5$ OX. Thermogravimetric evaluation of air-dried oxine molecular complexes was carried out in air with a modern thermogravimetric balance with a Toshniwal furnace. Samples were subjected to conditions of continuous increases in temperature (10°C min^{-1}). The instrument was standardized with calcium oxalate.

RESULTS AND DISCUSSION

Thermogravimetric pyrolysis of molecular complexes of oxine with $KMnO_4$, $K_2Cr_2O_7$ and K_2CrO_4 indicated initially the loss of 0.75, 1.25 and 1.0 oxine molecules, respectively, as gaseous decomposition products in the ranges 60–120°C, 70–280°C and 120–540°C, respectively. Plateaus corresponding to 120–280°C, 280–370°C and 540–580°C pointed to $KMnO_4 \cdot 3.75$ OX, $K_2Cr_2O_7 \cdot 5.25$ OX and $K_2CrO_4 \cdot$ OX, respectively, which further dissociated between 280 and 560°C, 370 and 520°C, and 580 and 760°C, respectively. The residues were $KMnO_4$, $K_2Cr_2O_7$, and K_2CrO_4, respectively.

If the minimum decomposition temperature is taken as a rough criterion of the thermal stability, the order for oxine molecular complexes would be $K_2CrO_4 > K_2Cr_2O_7 > KMnO_4$ ($120 > 70 > 60$°C).

The solid state reactions under investigation resemble

$$A_s \rightarrow B_s + C_g$$

which could be kinetically probed using the expressions of Dave and Chopra. The separate sigmoidal traces were analyzed individually for the investigation of the kinetics of the non-isothermal decomposition of the oxine molecular complexes of $KMnO_4$, $K_2Cr_2O_7$ and K_2CrO_4.

For the calculation of the energy of activation, order of reaction and frequency factor, values of A and a and dx/dt from DTG curves were calculated using a planimeter. Values of $\log k$, calculated from the equation for a first order reaction (2) were plotted against the reciprocal of absolute temperature. A straight line was obtained in each case, showing that various

TABLE 1

Kinetic parameters for the non-isothermal decomposition of oxine molecular complexes for $KMnO_4$, $K_2Cr_2O_7$ and K_2CrO_4

Reaction	Temp. range (°C)	% Loss		Eqn. (1)			Eqn. (2)	
		Found	Calcd.	*n*	*E* (kcal/ mole^{-1})	*Z*	*n*	*E* (kcal/ mole^{-1})
$KMnO_4 \cdot 4.5\ OX \rightarrow KMnO_4 \cdot 3.75\ OX + 0.75\ OX$	60–120	12.83	13.42	1	16.02	1.79		
$KMnO_4 \cdot 3.75\ OX \rightarrow KMnO_4 + 3.75\ OX$	280–560	80.82	80.51	1	17.16	0.19	0.60	22.88
$K_2Cr_2O_7 \cdot 6.5\ OX \rightarrow K_2Cr_2O_7 \cdot 5.25\ OX + 1.25\ OX$	70–280	13.66	14.65	1	9.15	0.30	0.72	13.73
$K_2Cr_2O_7 \cdot 5.25\ OX \rightarrow K_2Cr_2O_7 + 5.25\ OX$	370–520	77.05	76.22	1	18.08	2.09	0.69	41.18
$K_2CrO_4 \cdot 2\ OX \rightarrow K_2CrO_4 \cdot OX + OX$	120–540	34.40	30.00	1	5.15	0.21	0.58	5.34
$K_2CrO_4 \cdot OX \rightarrow K_2CrO_4 + OX$	580–760	61.50	60.00	1	22.88	0.16	0.63	22.88

OX = Oxine.

rate controlling steps follow first order kinetics. Slope ($-E/2.303\ R$) and intercept ($\log Z$) of the straight line yielded values of activation energy of the reaction and collision number (Z).

A plot of $\log(dx/dt)/\log(A-a)$ vs. $T^{-1}/\log(A-a)$ also gave a straight line of $E/2.303\ R$ slope and the n (order of reaction) intercept [eqn. (3)]. The kinetic data in Table 1 indicate that both eqns. (2) and (3) gave identical results. From the abnormally low values of Z it is concluded that the loss of oxine molecules from the molecular complexes under study may be classed as slow reactions.

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