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Note

KINETICS OF THE PYROLYTIC DECOMPOSITION OF MOLECULAR COMPLEXES OF 8-HYDROXYQUINOLINE (OXINE) WITH POTASSIUM DICHROMATE, POTASSIUM CHROMATE AND POTASSIUM PERMANAGANATE

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Sawhney et al. [1] probed kinetically each sigmoid of the TG curves of the molecular complexes under study, pyrolysed on a manually operated thermogravimetric balance with a Toshniwal furnace (10°C min^{-1}), using the method of Dave and Chopra [2]. This method, unlike slope-dependent procedures [3–6], provides dependable kinetic data even if the samples are pyrolysed without maintaining procedural parameters such as heating rate, particle size, temperature variation, etc., constant throughout the investigation. The present note concerns the estimation of kinetic data for the non-isothermal decomposition of molecular complexes of oxine with potassium dichromate, potassium chromate and potassium permanganate, using the expression of Coats and Redfern [6]

$$\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - E/2.3RT$$

which, when $n = 1$, reduces to

$$\log_{10}\left[-\log_{10}\frac{(1-\alpha)}{T^2}\right] = \log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - E/2.3RT \qquad (1)$$

where α = fraction decomposed at time t, A = frequency factor, a = a linear heating rate, and T = absolute temperature. The use of this equation depends on the accurate measurement of temperature and no departure from a linear heating rate due to endo- or exothermic reactions.

EXPERIMENTAL

Syntheses of the molecular complexes, $KMnO_4 \cdot 4.5$ OX, $K_2Cr_2O_7 \cdot 6.5$ OX and $K_2CrO_4 \cdot 2$ OX, have been reported previously, and their course of decomposition explained [1]. To meet the conditions of the Coats and Redfern procedure, a Stantov thermobalance Model TR-1 was employed in the present study, using the parameters: heating rate, 4°C min^{-1}; chart speed, 6 in. h^{-1}; maximum temperature, 1000°C; balance accuracy, 1 mg g^{-1}.

RESULTS AND DISCUSSION

α was determined using the relationship

$$\alpha = \frac{W_0 - W}{W_0 - W_f}$$

where W_0 = initial weight, W = weight at time, t, and W_f = final weight.

Each sigmoidal trace was kinetically probed, Non-isothermal decomposition of the molecular complexes with reference to each sigmoid follows first order reaction ($n = 1$), following the use of Dave and Chopra expressions, according to Sawhney et al. [1]. For the loss of 8-hydroxyquinoline as the temperature increases, E was determined by plotting $\log_{10}[-\log(1-\alpha)/T^2]$ vs. $1/T$; the ensuing straight line of slope $-E/2.3R$ yielded the value of E.

The term $\log_{10}(AR/aE)[1-(2RT/E)]$ in the Coats and Redfern expression is sensibly constant.

Table 1 contains the kinetic data together with the data due to Dave and Chopra expressions.

TABLE 1

Kinetic data for the non-isothermal decomposition of molecular complexes of oxine with $KMnO_4$, $K_2Cr_2O_7$ and $K_2Cr_2O_4$

Reaction [a]	Range of a studied (°C min^{-1})	E(kcal mole^{-1}) [b]			n [b]		
		A	B	C	A	B	C
$KMnO_4 \cdot 4.5$ OX → $KMnO_4 \cdot 3.75$ OX + 0.75 OX	0.05–0.81	25.42	16.02		1	1	
$KMnO_4 \cdot 3.74$ → $KMnO_4$ + 3.75 OX	0.06–0.34	14.30	17.16	22.88	1	1	0.60
$K_2Cr_2O_7 \cdot 6.5$ OX → $K_2Cr_2O_7 \cdot 5.25$ OX + 1.25 OX	0.04–0.79	8.80	9.15	13.73	1	1	0.72
$K_2Cr_2O_7 \cdot 5.25$ OX → $K_2Cr_2O_7$ + 5.25 OX	0.27–0.89	25.42	18.08	41.18	1	1	0.69
$K_2CrO_4 \cdot 2$ OX → K_2CrO_4 OX + OX	0.12–0.82	7.38	5.15	5.34	1	1	0.58
$K_2CrO_4 \cdot$OX → K_2CrO_4 + OX	0.18–0.88	38.13	22.88	22.88	1	1	0.63

[a] OX = oxine.

[b] A = Coats and Redfern's method.
B = Dave and Chopra's expression $k = (-dx/dt)/(A-a)$ for $n = 1$.
C = Dave and Chopra's expression $[-E/2.303R(T^{-1})]/\log(A-a) = -n + [\log(dx/dt)/\log(A-a)]$.

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