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Note

KINETICS OF THE NON-ISOTHERMAL DECOMPOSITION OF DIODOQUIN COMPLEXES OF BARIUM(II), MAGNESIUM(II) AND CADMIUM(II) FROM DIFFERENTIAL THERMOGRAVIMETRIC CURVES

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Some metal complexes of diodoquin (5,7-diiodo-8-hydroxyquinoline) have been thermally studied by Thomas [1], Dupuis [2], Borrel and Paris [3], Berg [4] and Majumdar [5]. Attempts, assuming the region of slow pyrolytic decomposition as a plateau, have been made by Mittal et al. [6] for the kinetics of the non-isothermal decomposition of diodoquin complexes of Ba(II), Mg(II) and Cd(II), employing the methods of Freeman and Carroll [7], Coats and Redfern [8] and Horowitz and Metzger [9]. The present communication concerns a review of the situation by overruling the said assumption, and the probing of the kinetics of the pyrolytic decomposition of these diodoquin complexes using Dave—Chopra [10] equations (1, 2) and DTG curves.

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

$$\frac{-E/2.303(T^{-1})}{\log(A-a)} = -n + \frac{\log(\mathrm{d}x/\mathrm{d}t)}{\log(A-a)} \tag{2}$$

where A is the total area under the differential thermogravimetric curve for any reaction, a is the area for the reaction up to time t, $\mathrm{d}x/\mathrm{d}t$ is the height of the curve at time t, m_0 is the initial mole fraction of the reactant, and n is the order of the reaction with respect to reactant.

EXPERIMENTAL

The thermograms used in the present study are those recorded by Mittal et al. [6] who used a Stanton self-recording thermobalance of 1 mg sensitivity, 100 mg of sample in a platinum crucible, and a heating rate of 6°C min^{-1}.

RESULTS AND DISCUSSION

The non-isothermal decomposition of the diodoquin complexes of Ba(II),

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Mg(II) and Cd(II) under study resembles the reaction of type [7]

$A_s \rightarrow B_s + C_g$

the kinetics of which can be studied thermally. In each diodoquin complex pyrolysis, the TG curve follows a relatively simple sigmoidal path, a fact which has been overlooked by Mittal et al. [6] while studying the kinetics of diodoquin complexes by different methods, which fundamentally involve initial weight of the substance. It is strange that the whole process of decomposition in the case of each complex has been regarded by Mittal et al. to be taking place in two steps, such deviation does not correspond to the actual situation in the pyrolysis curve, which involves only a sigmoid. The values of the kinetic parameters as estimated by Mittal et al. are therefore not dependable.

To obtain better, more reliable results, the Dave—Chopra method, which could be employed in a situation where slight errors in the measurements of the variables such as temperature, heating rate and the reproduction of the geometry of the crucible which are known to influence the TG tracing and therefore the kinetic parameters derived from Freeman—Carroll, Coats—Redfern and Horowitz—Metzger methods, are not serious as the measurements of areas under the differential thermogravimetric curves can be made accurately and any isolated reading is not of too much significance. Assuming *n* (order of reaction) to be equal to 1, log *k* values were calculated using eqn. (1) and

TABLE 1

Kinetic parameters for non-isothermal decomposition of diodoquin complexes

Method *	*n*	*E* (kcal mole^{-1})	*Z*
Reaction: $Ba(DIHQ)_2 \rightarrow BaCO_3$ + dissociation products [1]			
A	1	5.72	2.16
B	0.64	5.49	
C	0.0	27.45	
D	1	28.76	2.6×10^5
E	1	29.16	2.28×10^5
Reaction: $Mg(DIHQ)_2 \rightarrow MgO$ + dissociation products			
A	1	5.75	2.75
B	0.61	3.20	
C	0.0	18.06	
D	1	17.56	1.7×10^2
E	1	17.60	1.58×10^2
Reaction: $Cd(DIHQ)_2 \rightarrow CdO$ + dissociation products			
A	1	5.72	3.31
B	0.67	3.20	
C	0.0	29.16	
D	1	18.53	2.11×10^2
E	1	18.45	2.0×10^2

* A = Dave—Chopra method [eqn. (1)]; B = Dave—Chopra method [eqn. (2)]; C = Freeman—Carroll method; D = Coats—Redfern method; E = Horowitz—Metzger method.

the DTG curves corresponding to different temperatures. Since the Arrhenius plot (log k vs. $1/T$) gave a straight line for each reaction, it follows that non-isothermal decomposition follows first order kinetics which has found support in the use of another Dave—Chopra equation (2).

Table 1 incorporates the values of E, Z and n, calculated using eqns. (1) and (2), and other methods employed by Mittal et al. It shows that the abnormally low values of Z (collision numbers) support the view that the pyrolytic decomposition of the diodoquin complexes is a slow process.

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