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Note

KINETICS OF THE NONISOTHERMAL DECOMPOSITION OF SOME METAL COMPLEXES OF ACETOPHENONE AND CHALCONE DERIVATIVES

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Singh and Rathi [1] have reported the synthesis and thermolysis of metal complexes of 2-hydroxy-5-bromo acetophenone (HBA) with Nd(III), Pr(III), La(III), Y(III), and of 2'-hydroxy-4'-methyl chalcone (HMC), 2'-hydroxy-4'-methyl-5'-chloro chalcone (HMCC), 2'-hydroxy-5'-chloro chalcone (HCC), and 2'-hydroxy-5'-bromo chalcone (HBC) with La(III). The literature reveals that the nonisothermal decomposition of these complexes has not been probed kinetically. The present communication concerns the evaluation of the kinetic parameters of the pyrolytic decomposition of these complexes using the procedures of Dave and Chopra [2].

EXPERIMENTAL

Acetophenone and chalcone derivatives were prepared using the methods of Noris and Sturgies [3] and Kerrer et al. [4], respectively. Metal complexes were synthesised according to the procedure adopted by Singh and Rathi [1]. Elemental analysis data collected with THERELEC agreed with the theoretical percentages.

Thermal investigations were carried out using a thermogravimetric balance with a Toshniwal furnace. Air dried samples were subjected to a continuous increase in temperature (5°C min^{-1}). The instrument was calibrated with calcium oxalate.

RESULTS AND DISCUSSION

Nonisothermal decomposition of the metal complexes of derivatives of acetophenone and chalcone resembles the type of reaction [5]

$$A_s \rightarrow B_s + C_g$$

The equations of Dave and Chopra [1,2] were employed for the kinetic studies of the pyrolytic decomposition of the complex.

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

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

The specific rate constant, k, at any time, t (or corresponding temperature T), was evaluated from eqn. (1) assuming $n = 1$. Values of log k were plotted vs. the reciprocal of the absolute temperature. The straight line so obtained in all cases confirms that the pyrolytic decompositon of all the complexes follows first order kinetics. The slope and intercept correspond to $-E/2.303\ R$ and log Z (Z = collision number), respectively.

On plotting

$$[\log(\mathrm{d}x/\mathrm{d}t)/\log(A-a)] \quad \text{vs.} \quad [T^{-1}/\log(A-a)]\ ,$$

fairly good straight-line plots are obtained in all cases, the slope and intercept being equal to $-E/2.303\ R$ and n, respectively.

A perusal of the data in Table 1 indicates that both procedures gave identical results. Looking to abnormally low values of log Z, it is concluded that the decomposition reactions of the metal complexes under study can be classed as slow reactions; no other probable reason can be given. Moreover, the values of n, E and Z are more dependable since this method, unlike other procedures for kinetic studies, does not involve measurement of the slopes of TG curves which is known to be sensitive. Secondly, the effect of small fluc-

TABLE 1

Values of E (energy of activation), n (order of reaction), and log Z (collision number) for the different reactions

Reaction	Method				
	Eqn. (1)			Eqn. (2)	
	n	E (kcal mole^{-1})	log Z	n	E (kcal mole^{-1})
$Y(HBA)_3 \rightarrow Y_2O_3 +$ dissociation products	1	7.32	0.55	0.93	9.15
$Pr(HBA)_3 \rightarrow Pr_2O_3 +$ dissociation products	1	6.95	0.50	0.92	7.64
$La(HBA)_3 \rightarrow La_2O_3 +$ dissociation products	1	6.77	0.60	0.84	7.32
$Nd(HBA)_3 \rightarrow Nd_2O_3 +$ dissociation products	1	6.77	0.40	0.88	9.15
$La(HMC)_3 \rightarrow La_2O_3 +$ dissociation products	1	9.15	1.20	1.10	9.15
$La(HMCC)_3 \rightarrow La_2O_3 +$ dissociation products	1	6.40	0.45	0.95	7.32
$La(HCC)_3 \rightarrow La_2O_3 +$ dissociation products	1	6.95	0.70	1.02	7.78
$La(HBC)_3 \rightarrow La_2O_3 +$ dissociation products	1	5.49	0.10	0.76	5.49

tuations due to heating rate and temperature variation in the TG curve is considerably minimised as the points in the DTG curve are joined by a smooth curve and the area enclosed is used in the calculations.

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