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Note

KINETIC STUDIES OF THE NON-THERMAL DECOMPOSITION OF CHELATES OF LAPACHOL WITH ALUMINIUM(III), CHROMIUM(III) AND IRON(III)

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Bhatia et al. [1,2] have studied the decomposition of complexes of lapachol with Be(II), ZrO(II), Pd(II), Ca(II), Ba(II) and Pb(II). The thermal decomposition of Al(III), Cr(III) and Fe(III) complexes with lapachol has not been probed kinetically using the equations of Horowitz and Metzger [3], Coats and Redfern [4] and Dave and Chopra [5]. In the present paper the results of such studies on $Al(C_{15}H_{13}O_3)_3 \cdot 1.25\ H_2O$, $Cr(C_{15}H_{13}O_3)_3 \cdot 0.75\ H_2O$, and $Fe(C_{15}H_{13}O_3)_3 \cdot 2\ H_2O$ are described.

EXPERIMENTAL

The ligand lapachol, 2-hydroxy-3-(3-methyl-2-butenyl-1-4 naphthoquinone) from Aldrich Chemical Inc. (U.S.A), was used without further purification. The metal lapacholates of Al(III), Cr(III) and Fe(III) were isolated by mixing, with constant stirring, a solution of lapachol in one equivalent of NaOH with metal ion solution taken in stoichiometric ratio. The coloured precipitate was digested on a steam bath for 0.5 h, filtered, washed finally with ice-cold water, and dried at 45°C. The metal content was estimated by complexometric titration with EDTA using suitable metal ion indicators. The carbon and hydrogen analysis was carried out on a Therelec electrofurnace. The IR spectra were recorded on a Perkin-Elmer 720 IR spectrophotometer using KBr disc/nujol mull technique. Thermograms of the chelates were recorded on a Cahn electrobalance with a heating rate of 8°C min^{-1} for the Al(III) and Cr(III) chelates, and 10°C min^{-1} for the Fe(III)–lapachol complex.

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METHOD EMPLOYED FOR THE CALCULATION OF ACTIVATION ENERGY (E)

The expression for the first order reaction

$$\log\log\left(\frac{W_0 - W_t}{W - W_t}\right) = \frac{E\theta}{RT_s{}^2} \tag{1}$$

due to Horowitz and Metzger was employed for the calculation of the energy of activation, where W is the mass remaining at a given temperature, W_0 and W_t are the initial and final masses, and T_s is the reference temperature, defined as a temperature at which

$$\frac{W - W_t}{W_0 - W} = \frac{1}{\mathrm{e}}$$

and

$$\theta = T - T_s$$

Kinetic data were also analyzed using the equation of Coats and Redfern.

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2}\right] = \log\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right] - \frac{E}{RT} \tag{2}$$

reduced to

$$\log\log\frac{1}{1-\alpha} - 2\log T = \log\frac{AR}{\beta E}\left[1 - 2\frac{RT}{E}\right] - \frac{E}{RT} \tag{3}$$

where α is the fraction of reaction completed, β is the reaction rate, T is the absolute temperature, A is the frequency factor, and R is the gas constant.

More reliable values of E and n for the pyrolysis of metal chelates of lapachol with Al(III), Cr(III), and Fe(III) could be obtained using the method of Dave and Chopra, which does not involve measurement of slopes of the thermogravimetric curves, known to be sensitive to several factors [3]. The Dave and Chopra procedure involves joining the points in the plot of $\mathrm{d}w/\mathrm{d}t$ vs. temperature by a smooth curve and the areas enclosed therein are used in the calculations, thereby minimizing the effect of fluctuations in the rate of heating and temperature variation in the TG curve.

The Dave and Chopra expression

$$k = \frac{(A/m^0)^{n-1}(-\mathrm{d}x/\mathrm{d}t)}{A-a} \tag{4}$$

and its reduced form for the first-order reaction

$$k = \frac{-\mathrm{d}x/\mathrm{d}t}{A-a} \tag{5}$$

have been used.

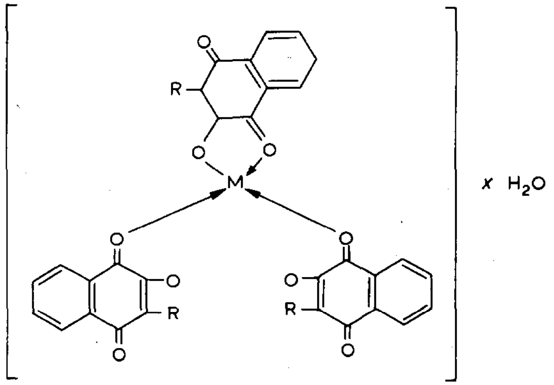
Another expression due to Dave and Chopra is

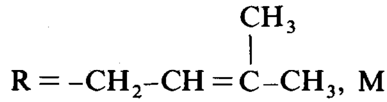
$$\frac{(-E/2.303)}{\log(A-a)}T^{-1} = -n + \frac{\log(\mathrm{d}x/\mathrm{d}t)}{\log(A-a)} \tag{6}$$

where A is the total peak area under the DTG curve, a is the area at time t, n is the order of reaction, and $\mathrm{d}x/\mathrm{d}t$ is the rate of weight loss.

IR SPECTRAL STUDIES

The free ligand shows bands at 1670 and 1650 cm^{-1} corresponding to the free and the hydrogen bonded $-\mathrm{C}=\mathrm{O}$, respectively. In the metal chelates of lapachol with Al(III), Cr(III) and Fe(III) this bond appeared at 1633, 1590 and 1595 cm^{-1}, respectively, indicating coordination of the carbonyl group with the metal ion. Broad absorption in the spectra of metal chelates in the 3400 cm^{-1} region showed the presence of H bonded O–H either of the lattice or of coordinated water. IR spectra revealed the involvement of both the hydroxyl and the carbonyl groups present in lapachol in chelation and that the complexes are bidentate. Thus the complexes are represented by the structure





where $\mathrm{R} = -\mathrm{CH_2}-\mathrm{CH}=\underset{}{\overset{\overset{\displaystyle \mathrm{CH_3}}{|}}{\mathrm{C}}}-\mathrm{CH_3}$, M = Al(III), Cr(III), Fe(III), and $x =$ 1.25, 0.75, 2.

RESULTS AND DISCUSSION

The thermal decomposition studies showed that the hydrated complexes are generally stable up to 60–80°C. The hydrated complexes began to lose water in the range 60–120°C, and the anhydrous complexes dissociated thereafter. Coupled with air oxidation they gave metal oxides as the final

TABLE 1

Analytical data

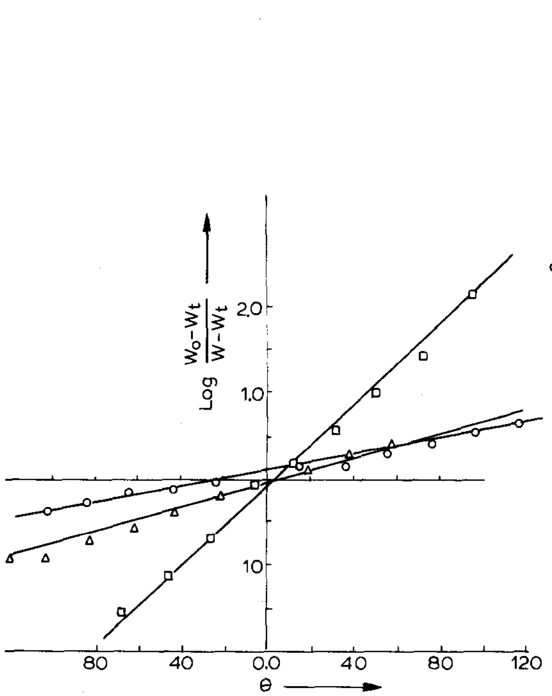
Chelates	C (%)		H (%)		Metal oxide (%)	
	Found	Calcd.	Found	Calcd.	Found	Calc.
$Al(C_{15}H_{13}O_3)_3 \cdot 1.25\ H_2O$	68.00	68.48	4.78	5.14	6.62	6.599
$Cr(C_{15}H_{13}O_3)_3 \cdot 0.75\ H_2O$	70.50	70.04	6.00	5.38	9.68	9.64
$Fe(C_{15}H_{13}O_3)_3 \cdot 2\ H_2O$	66.88	66.26	5.78	5.28	9.52	9.80

TABLE 2

Kinetic parameters for non-isothermal decomposition of metal lapacholate

Reaction	Temp. range (°C)	Method [a]								
		A		B		C			D	
		n	E	n	E	n	E	Z	n	E
$Al(C_{15}H_{13}O_3)_3 \rightarrow Al(C_{15}H_{13}O_3)0.31$ + dissocn. product.	200–880	1	5.16	1	2.97	1	5.90	0.35	0.78	4.11
$Cr(C_{15}H_{13}O_3)_3 \rightarrow Cr_2O_3$ + dissocn. product	160–660	1	4.12	1	7.62	1	5.55	0.75	0.84	4.90
$Fe(C_{15}H_{13}O_3)_3 \rightarrow Fe_2O_3$ + dissocn. product	140 560	1	8.72	1	7.49	1	8.66	6.31	1.23	9.15

[a] Methods of A, Horowitz and Metzger [eqn. (1)]; B, Coats and Redfern [eqn. (3)]; C, Dave and Chopra (DTG) expression for first order [eqn. (5)]; D, Dave and Chopra's second expression [eqn. (6)].



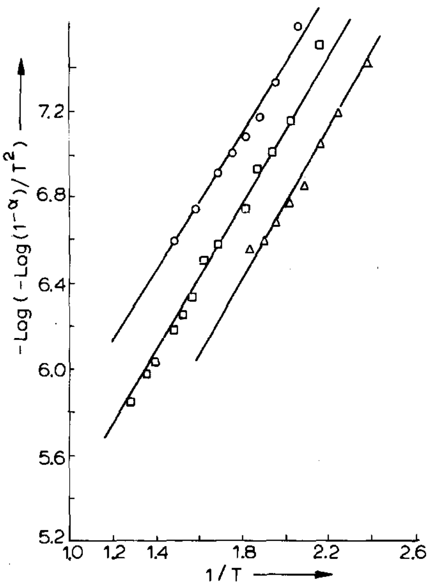


Fig. 1. Linear plot for the determination of activation energy ($n = 1$) using the Horowitz and Metzger equation, eqn (1). ○, Al(III) lapacholate; △, Cr(III) lapacholate; □, Fe(III) lapacholate.

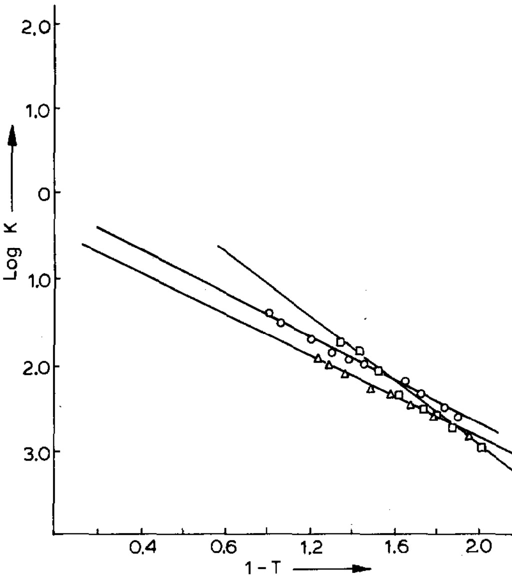
Fig. 2. Linear plot for the determination of activation energy ($n = 1$) using the the Coats and Redfern equation, eqn. (3). ○, Al(III) lapacholate; △, Cr(III) lapacholate; □, Fe(III) lapacholate.

residue. Table 1 gives the percentage of carbon, hydrogen and metal oxide. Non-isothermal decomposition of the metal complexes under study resembles the type of reaction $A_s \rightarrow B_s + C_g$ [6] which can be probed kinetically for evaluation of kinetic parameters with the aid of the methods of Horowitz and Metzger [3], Coats and Redfern [4] and Dave and Chopra [5].

A Horowitz and Metzger plot of log log $(W_0 - W_t)/(W - W_t)$ (reciprocal of fraction pyrolized) against θ (Fig. 1), and a Coats and Redfern plot of $\log[-\log(1 - \alpha/T^2]$ against the reciprocal of temperature (Fig. 2) yielded straight lines with slopes E/RT_s^2 and $E/2.303R$, respectively.

Values of log k calculated using eqn. (4) were plotted against the reciprocal of temperature $1/T$. A straight line with slope $E/2.303R$ and an intercept equal to log Z were obtained in each reaction (Fig. 3), thus supporting the idea that non-isothermal decomposition of metal complexes of lapachol with Al(III), Cr(III) and Fe(III) follows first-order kinetics. Equation (6), similar to that of Freeman and Caroll [6], was employed for kinetic parameters for the different reactions. A plot of $\log(\mathrm{d}x/\mathrm{d}t)/\log(A - a)$ vs. $T^{-1}/\log(A - a)$ gave a straight line of slope $E/2.303R$ and intercept equal to order of reaction (n) (Fig. 4).

Quite comparable values of activation energy (E) and order of reaction



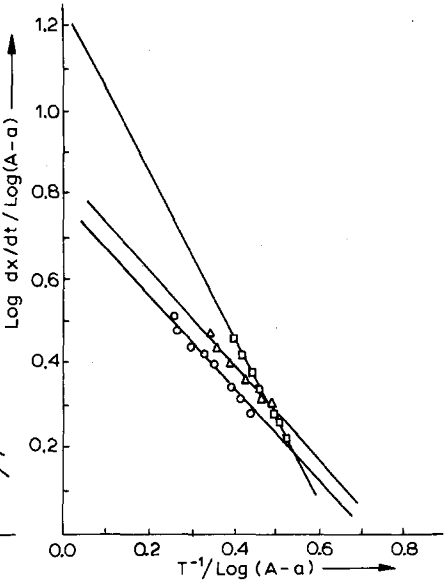


Fig. 3. Linear plot for the determination of activation energy ($n = 1$) using the Dave and Chopra (DTG) expression, eqn. (5). ○, Al(III) lapacholate; △, Cr(III) lapacholate; □, Fe(III) lapacholate.

Fig. 4. Linear plot for the determination of activation energy using the Dave and Chopra equation, eqn. (6). ○, Al(III) lapacholate; △, Cr(III) lapacholate; □, Fe(III) lapacholate.

have been obtained by the different methods (Table 2). Further, the small value of $\log Z$ indicates that the pyrolytic decomposition of metal complexes could be regarded as a slow reaction.

REFERENCES

1 B.M.L. Bhatia and S.S. Sawhney, Thermochim. Acta, 47 (1981) 363.
2 B.M.L. Bhatia and N. Vohra, Thermochim. Acta, 53 (1982) 361.
3 H.H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
4 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
5 N.G. Dave and S.K. Chopra, Z. Phys. Chem. N.F., 48 (1966) 257.
6 E.S. Freeman and B. Caroll, J. Phys. Chem., 62 (1958) 394.