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Note

THERMAL ANALYSIS AND DETERMINATION OF THE KINETIC PARAMETERS OF THE NON-ISOTHERMAL DECOMPOSITION OF LAWSONE AND SOME OF ITS METAL COMPLEXES USING THERMOGRAVIMETRIC DATA

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Sawhney et al. [1–3] proved kinetically the non-isothermal decomposition of some metal derivatives of hydroxy-1,4-naphthoquinone. The literature further reveals that physico-chemical studies have been made on some metal–lawsone derivatives [4,5], including the 1:2 oxovanadium–lawsone complex [6]. The present note explains the pyrolysis curves of lawsone and its gallium, oxovanadium and chromium complexes and the determination of the kinetic parameters from a mathematical simplification due to Coats and Redfern (linearization of initial differential equation) [7]

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

where α = fraction of substance at time t, A = frequency factor, a = a linear heating rate, and E = activation energy of the reaction.

EXPERIMENTAL

All the chemicals used were of analar grade. The metal derivatives of lawsone (Fluka, Switzerland) were obtained by adding slowly with constant stirring, sodium lawsonate to the metal solution. The coloured precipitate immediately appeared and was filtered, washed with distilled water and dried at 30–35°C. Elemental analysis displayed a tally between theoretical and experimental data (VOL_2, GaL_2, $CrL_3 \cdot 3.5\ H_2O$, L = anion of lawsone).

Du Pont instruments were used for thermal analysis. The parameters applied are:

TG
Range = 2 mV cm^{-1}
Time constant = 5 s

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Weight = 1.88, 3.11 and 3.6 g for lawsone, GaL_2, VOL_2 and $CrL_3 \cdot 3.5\ H_2O$
Atm = N_2
Flow rate = 50 ml min^{-1}
Time axis: progress rate = 10°C min^{-1}; range = 25°C cm^{-1}.
DTA
Range = 100 mV cm^{-1}
Reference = alumina
Atm = ambient
Time axis: progress rate = 10°C min^{-1}; range = 0.2 mV cm^{-1}; heat = 650°C; ISO = 75°C

RESULTS AND DISCUSSION

The lawsone TG curve showed no loss up to 125°C. From 125 to 200°C, 68.8% loss was observed; slow decomposition regions, losses being 3.2% (200–300°C) and 8% (300–450°C), were also detected. From 450 to 550°C no loss occurred. A DTA endotherm at 200°C and two exotherms at 400 and 550°C were observed.

Analysis of the TG curve for GaL_2 revealed no loss from 20 to 100°C; loss between 100 and 200°C amounted to 52%. Further, a plateau (loss being nil from 200 to 237°C) corresponding to $GaL_{0.75}$ was observed; after 237°C the decomposition slowed down and 24% loss from 237 to 650°C was observed. The DTA trace pointed to an endotherm at 193°C and an exotherm at 475°C, with the peak height at 521°C.

The VOL_2 pyrolysis curve displayed stability up to 50°C after which it decomposed till 162°C, with 34% loss. From 162 to 237°C the complex decomposed very slowly, with only 2% loss, probably indicating the existence of an intermediate compound with probable stoichiometry $VOL_{1.25}$. An exotherm as seen in the DTA trace began at 300°C, with peak height at 360°C; another exotherm with peak height at 415°C was observed.

Loss of 3.5 water molecules from $CrL_3 \cdot 3.5\ H_2O$ occurred as manifested by its pyrolysis curve in the temperature range 40–100°C. No loss between 100 and 125°C, indicating a plateau corresponding to CrL_3, was observed; between 125 and 225°C, CrL_3 broke up very slowly (only 2% loss), after which the rapid decomposition, loss being 56% from 225 to 650°C, was noticed. An endotherm, supporting lattice water in the complex, was observed at 100°C in the DTA curve. The exotherm beginning at 340°C with peak height at 409°C was in agreement with the decomposition of CrL_3 as indicated in the TG trace.

To ensure accurate temperature measurements and linear heating rate, small samples [7] were used. The thermal decomposition of the compounds under study resembles the reaction

$$A(s) \rightarrow B(s) + C(g)$$

TABLE 1

Kinetic parameters for the non-isothermal decomposition of lawsone and its metal complexes

Reaction	Temp. range (°C)	n	E (kcal mole^{-1})
Lawsone → Carbon + gaseous decompn. products	125–200	1	2.85
$VOL_2 \rightarrow VOL_{1.25} + 0.75$ L	50–162	1	6.10
$VOL_{1.25} \rightarrow V_2O_5$ + gaseous decompn. products	237–650	1	2.97
$GaL_2 \rightarrow GaL_{0.75} + 1.25$ L	100–200	1	19.22
$GaL_{0.75} \rightarrow GaO$ + gaseous decompn. products	237–650	1	5.49
$CrL_3 \cdot 3.5\ H_2O \rightarrow CrL_3 + 3.5\ H_2O$	40–100	1	3.43
$CrL_3 \rightarrow Cr_2O_3$ + gaseous decompn. products	125–650	1	6.29

L = Anion of lawsone (2 hydroxy-1,4-naphthoquinone).

which could be kinetically proved by a mathematical simplification due to Coats and Redfern with the use of Du Pont instruments. All the conditions required for the application of Coats and Redfern's expression for the determination of kinetic parameters from TG data were ensured during the present study. In previous communications, Sawhney et al. [1–3], assuming $n = 1$ for the non-isothermal decomposition of some metal complexes of some hydroxy-1,4-naphthoquinones, calculated the values of other kinetic parameters using the method of Dave and Chopra. Against this background, assuming the pyrolytic decomposition of lawsone and its metal complexes follows first order kinetics ($n = 1$), the value of E was determined following Coats and Redfern's eqn. (1) where the expression

$\log(AR/aE)(1 - 2RT/E)$ is sensibly constant. A plot of

$-\log[-\log(1-\alpha)/T^2]$ vs. $1/T$ gave a straight line (all reactions) of slope $E/2.\ 3R$. The kinetic data are given in Table 1.

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REFERENCES

1 S.S. Sawhney and B.M.L. Bhatia, Thermochim. Acta, 43 (1981) 243.
2 B.M.L. Bhatia and S.S. Sawhney, Thermochim. Acta, 47 (1981) 363.
3 S.S. Sawhney, R.M. Sati and Surya K. Chandel, Thermochim. Acta, 55 (1982) 363.
4 S.S. Sawhney, Thesis, Meerut University, India, 1972.
5 N.C. Trehan, Thesis, Garhwal University, India, 1978.
6 N. Vohra, Thesis, Garhwal University, India, 1979.
7 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68