Thermochimica Acta, 71 (1983) 381–386
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

THERMAL AND pH-METRIC STUDIES ON COMPLEXES OF Hg(II) AND Er(III) WITH 2-HYDROXY-3-(3-METHYL-2-BUTENYL)-1,4-NAPHTHOQUINONE (LAPACHOL)

S.S. SAWHNEY and S.S. BAINS

Department of Chemistry, D.A.V. (P.G.) College, Dehra Dun 248001 (India)

(Received 11 July 1983)

Sawhney et al. [1–4] reported investigations on metal–lapachol complexes; slope-dependent and slope-independent methods [5,6] have also been used for the kinetics of the non-isothermal decomposition of metal–lapachol complexes. In this note, the solution and solid-state studies on Hg(II)–lapachol and Er(III)–lapachol complexes are detailed.

EXPERIMENTAL

B.D.H. or Aldrich chemicals were used. Lapachol/metal chloride solutions were prepared in ethanol/distilled water. The metal content was estimated by standard methods. For solution studies, solutions having identical concentrations of the common ingredient in different sets were prepared as recommended by Bjerrum and Calvin. The pH was corrected for non-aqueous media (50% v/v, ethanol–water) according to Van Uitert and Haas [7] and was measured on a Metrhom Harisau E-520 pH-meter calibrated with suitable buffers. The ionic strength was maintained at 0.1 M KCl.

The complexes of Hg(II) and Er(III) with lapachol were extracted by adding sodium lapacholate solution to the metal ion solution. The precipitate, which was formed immediately, was filtered, washed with ice-cooled water and dried at 35–40°C.

The metal complexes were pyrolysed in air on a modern thermogravimetric balance equipped with a Toshniwal furnace, which was standardised with calcium oxalate and maintained at 10°C min^{-1} for all runs. Chemical analyses were obtained using THERELEK and a Perkin–Elmer Infra Cord spectrophotometer was used for IR studies.

RESULTS AND DISCUSSION

Values of $\bar{n}_H$, $\bar{n}$ and pL were calculated using Irving–Rossotti expressions [8]. Proton–ligand stability constants ($^PK^H$) were determined from linear

0040-6031/83/$03.00

TABLE 1

Stability constants and thermodynamic data of Hg(II)–lapachol and Er(III)–lapachol systems

Temp. (°C)	Method [a]	$\log_{10}k_1$	$\log_{10}k_2$	$\log_{10}k_3$	$\log_{10}\beta_2/\beta_3$	ΔG^0	ΔH^0	ΔS^0
Hg(II)–lapachol system								
20	A	4.05	3.91					
	B	4.13	3.33					
	C	4.00	3.93					
		4.09 [b]	3.58 [b]		7.67/–	−14.75		
40	A	3.83	3.57					
	B	3.98	4.03					
	C	3.65	3.61					
		3.82 [b]	3.79 [b]		7.61/–	−15.63	−1.26	+30.80
Er(III)–lapachol system								
20	A	4.34	3.50	3.11				
	B	4.66	3.58	2.95				
	C	4.46	3.49	3.15				
		4.49 [b]	3.52 [b]	3.07 [b]	–/11.08	−14.86		
40	A	3.98	3.70	3.57				
	B	4.14	3.27	3.66				
	C	3.79	3.65	3.37				
		3.97 [b]	3.54 [b]	3.87 [b]	–/11.38	−16.30	+6.29	+72.18

[a] A, Graphical method; B, pointwise calculation method; C, from eqn. (1).

[b] Mean.

TABLE 2

Thermogravimetric results

Stable phase	Temp. range (°C)	Wt. loss due to	Wt. loss		Metal oxide	
			Found (%)	Calcd. (%)	Found (%)	Calcd. (%)
$Hg(C_{15}H_{13}O_3)_2 \cdot 0.25\ H_2O$	$\leqslant 60$					
	60–140	$0.25\ H_2O$	0.70	0.66		
$Hg(C_{15}H_{13}O_3)_2$	140–220					
HgO	220–540	organic matter	69.01	70.62		
	540–700				30.78	31.51
$Er(C_{15}H_{13}O_3)_3 \cdot 6\ H_2O$	$\leqslant 40$					
	40–200	$6\ H_2O$	10.86	10.82		
$Er(C_{15}H_{13}O_3)_3$	200–240					
	240–660	organic matter	78.17	81.21		
Er_2O_3	$\geqslant 660$				19.46	19.16

plots of $\log(1-\bar{n}_H)/\bar{n}_H$ vs. pH or $\bar{n}_H$ vs. pH. $\mathrm{Log}_{10}{}^{\mathrm{P}}K^{\mathrm{H}}$ was found to be 6.38 at 20°C and 6.12 at 40°C.

Hg(II)–Lapachol and Er(III)–lapachol systems could not meet the conditions of the Bjerrum half-integral method ($\log_{10}k_1/k_2 \geqslant 2.5$) and hence this method could not be applied. Formation curves neither corresponded to $0<\bar{n}<2$ nor $2<\bar{n}<3$ ($N=3$ and $k_1 \simeq k_2 \gg k_3$). Absence of the condition, $k_1 \gg k_2 \simeq k_3$ was observed in the formation curves. Further, the formation curves lost their wave-like character, thus concluding the similarity in the stability of successive complexes, a condition which has been observed from the values of successive stability constants (Table 1). A set of trial constants obtained through

$$\log_{10}k_n = \mathrm{pL}_{n-0.5}$$

were refined by successive approximations using eqn. (1).

$$\log_{10}k_{\bar{n}} = \mathrm{pL}_{\bar{n}} + \log_{10}\left\{ {}^{t=n-1}_{t=0}\Sigma(\bar{n}-t)\beta_t[\mathrm{L}]^t \Big/ {}^{t=N}_{t=n}\Sigma\frac{(t-\bar{n})\beta_t[\mathrm{L}]^{t-1}}{k_n} \right\} \tag{1}$$

Pointwise calculations and graphical methods were employed for stepwise formation constants. Table 1 gives the stability constants and thermodynamic data of the systems under study. It shows the metal–lapachol reaction to be a spontaneous process as ΔG^0 becomes more negative as the temperature increases. The negative enthalpy (ΔH^0) for the Hg(II)–lapachol system favours complexation while the positive value of ΔH^0 for the Er(III)–lapachol system points to the endothermic nature of the reaction. The positive entropy (ΔS^0) for both reactions also favours complex formation.

A gradual increase in the $\bar{n}$ values as the pH increases indicates the participation of the anionic form of lapachol; this fact found support in the titration of metal–lapachol mixtures with compositions of 0 : 1, 1 : 1, 1 : 2, 1 : 3 and 1 : 4, which revealed the liberation of protons on the reaction of the metal with lapachol, the limiting conditions being reached with 1 : 2 for the Hg(II)–lapachol system and 1 : 3 for the Er(III)–lapachol system. Afterwards, overlapping occurs indicating the liberation of two and three protons, respectively.

Thermal studies

$$\frac{-E/2.303R\Delta T^{-1}}{\Delta\log_{10}W_r} = -n + \frac{\Delta\log_{10}\mathrm{d}w/\mathrm{d}t}{\Delta\log_{10}W_r} \tag{2}$$

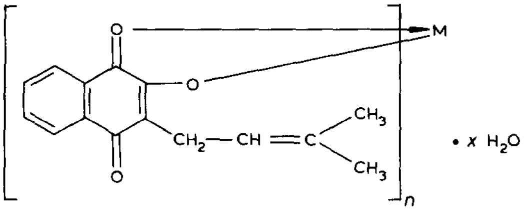
$$k = \frac{(A/m_0)^{n-1}(\mathrm{d}x/\mathrm{d}t)}{(A-a)^n} \tag{3}$$

$$\frac{-E/2.303RT^{-1}}{\log_{10}(A-a)} = -n + \frac{\log_{10}\mathrm{d}x/\mathrm{d}t}{\log_{10}(A-a)} \tag{4}$$

The pyrolysis curve of $Hg(C_{15}H_{13}O_3)_2 \cdot 0.25\ H_2O$ showed the stability of the complex up to 60°C, after which desolvation of the solvated complex started and continued up to 140°C with a levelling off up to 220°C; this plateau indicated the appearance of a new compound, $Hg(C_{15}H_{13}O_3)$, which lost organic matter from 220 to 540°C. The plateau from 540°C and onwards corresponded to HgO.

The Er(III)–lapachol complex $[Er(C_{15}H_{13}O_3)_3 \cdot 6\ H_2O]$ was stable up to 40°C and lost six molecules of water in the range 40–200°C in a one-step process: further decomposition took place above 240°C and was completed at 660°C. The constant weight recorded at $\geqslant$ 660°C was due to Er_2O_3 (see Table 2).

Analytical data including IR studies which indicated the shifting of frequency from 1650 to 1630 and 1588 cm^{-1} for Hg(II)–lapachol and Er(III)–lapachol complexes, respectively, showed the structure to be



Where M = Er, $n = 3$, $x = 6$ or
M = Hg, $n = 2$, $x = 0.25$.

Kinetic studies

A, *a* and $\mathrm{d}x/\mathrm{d}t$ were calculated from the derivative thermogravimetric curves, derived manually from the TG curves by the differential method.

TABLE 3

Kinetic data

Reaction [a]	Eqn. (2)		Eqn. (3)		Eqn. (4)	
	n	*E* (kcal $mole^{-1}$)	*n*	*E* (kcal $mole^{-1}$)	*n*	*E* (kcal $mole^{-1}$)
$HgL_2 \cdot 0.25\ H_2O \rightarrow$ $HgL_2 + 0.25\ H_2O$	0.12	12.81	1	11.90		
$HgL_2 \rightarrow HgO + $ d.p.	0.02	0.91	1	5.03	0.60	4.93
$ErL_3 \cdot 6\ H_2O \rightarrow$ $ErL_3 + 6\ H_2O$	0.75	9.61	1	9.15	0.51	12.71
$ErL_3 \rightarrow Er_2O_3 + $ d.p.	0.46	6.59	1	7.32	0.49	5.34

[a] d.p. = dissociation products, $L = C_{15}H_{13}O_3$.

$\mathrm{Log}_{10}k$ [eqn. (3)] was then calculated and plotted vs. $1/T$; the resulting linear plots indicate that the pyrolytic decomposition of the complexes follows first-order kinetics. E and Z were obtained from the slope $(-E/2.303R)$ and intercept $(\log_{10}Z)$. Using the kinetic data obtained from eqn. (4), a straight-line relationship was obtained on plotting $T^{-1}/\log_{10}(A-a)$ vs. $\log_{10}(\mathrm{d}x/\mathrm{d}t)/\log_{10}(A-a)$. The values of n and E nearly tallied with the data obtained from eqn. (3) and eqn. (2) due to Freeman and Carroll. Further, the low value of Z showed the reactions to be slow processes.

Table 3 gives the kinetic data.

REFERENCES

1 S.S. Sawhney and B.M.L. Bhatia, Thermochim. Acta, 43 (1981) 243.
2 S.S. Sawhney, R.M. Sati, N. Chandra and N. Vohra, Thermochim. Acta, 54 (1982) 373.
3 S.S. Sawhney, N. Vohra and S.K. Chandel, Thermochim. Acta, 52 (1982) 349.
4 S.S. Sawhney and S.D. Matta, J. Indian Chem. Soc., 57 (1980) 497.
5 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
6 N.G. Dave and S.K. Chopra, Z. Phys. Chem. N.F., 48 (1966) 257.
7 L.G. Van Uitert and C.G. Haas, J. Am. Chem. Soc., 75 (1953) 451.
8 H. Irving and H. Rossotti, J. Chem. Soc., (1953) 3397.