

SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF ADDUCTS

8-quinolinol with the photoproduct of octacyanomolybdate(IV) and -tungstate (IV) with ethylenediamine and triethylenetetramine

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Abstract

The photoproduct of octacyanomolybdate(IV) and -tungstate(IV) with ethylenediamine and triethylenetetramine give complexes of the type $K_3[Mo(O_2)(O)(OH)(C_9H_7ON)] \cdot 3C_9H_7ON$ I, $K_2[W(O_2)(O)(C_9H_7ON)_3]$ II and $K_3[Mo(CN)_3(OH)_4(C_9H_7ON)] \cdot 2C_9H_7ON \cdot 3H_2O$ III with 8-quinolinol (oxine). The IR spectra of the complex III shows the presence of $\nu(CN)$ peaks in the range 2047–2108 cm^{-1} and oxine group $\nu(C-O)$ in the complex I, II and III in the range of 1100–1150 cm^{-1} . The lower region of IR spectra shows the $M=O$ stretching while the higher the $\nu(N-H)$ and $\nu(OH)$. Thermal studies show the removal of uncoordinated water at 131°C from complex III. The decomposition of complexes I and II start from 150 and 212°C respectively. Oxine and cyano molecules were removed in stages at higher temperatures. The final product of the thermal decomposition was oxide which was of polymeric nature. The kinetic parameters viz. order of reaction 'n' and activation energy 'E' were determined by different methods.

Keywords: adducts, complexes

Introduction

The adducts and complexes of 8-quinolinol with metals in different oxidation states have been the subject of investigation in recent years. Certain inner transition metals form oxinate of the type $[M(Ox)_nOxH]$ [1] (M =uranium(IV) and (VI) and plutonium (VI) and Ox =oxine) and transition elements, $[MCl_n(Ox)]$ [2–5] (M =Sn, Ti). Many workers [6–11] have studied the thermal dissociation, heat stabilities and crystallographic structure of 8-quinolinol and its complexes with metals. The bonding of extra oxine molecule in thorium pentaaxinate

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[Th(Ox)₄OxH] and uranium trioxinate [UO₂(Ox)₂OxH] have been discussed [12–13]. The adducts of octacyanomolybdate(IV) and (V) and octacyanotungstate(IV) and (V) with 8-quinolinol have been synthesised and characterised [14–15]. On ultra violet irradiation octacyanomolybdate (IV) and tungstate(IV) give substitution reaction of CN⁻ by H₂O molecule giving intermediate species [M(CN)₇H₂O]³⁻, and the final photoproduct, [M(CN)₄O(OH)]³⁻ (M=Mo, W) depending upon the time of irradiation [16]. Recently, on exposure to ultra violet light in the ligand field band ≈365 nm of octacyanomolybdate(IV) and tungstate(IV) complexes with 8-quinolinol of the type K₃[Mo(CN)₇(C₉H₇ON)₇·5H₂O, K₂WO₂(CN)₂(C₉H₇ON)₄·0.5H₂O, MoO₂(C₉H₇ON)₂ and WO₂(C₉H₇ON)₂ have been synthesised and characterised [17].

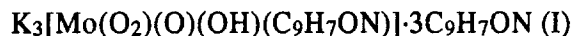
In this paper we report the synthesis, characterisation and thermal dissociation studies of the adduct and complexes of oxine with the photoproducts of potassium octacyanomolybdate(IV) and -tungstate(IV) with ethylenediamine and triethylenetetramine.

Experimental

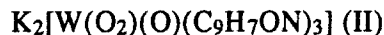
Materials and methods

Potassium octacyanomolybdate(IV) dihydrate, K₄[Mo(CN)₈]·2H₂O and potassium octacyanotungstate(IV) dihydrate K₄[W(CN)₈]·2H₂O were prepared by the method of Leipoldt *et al.* [18]. For the preparation of 8-quinolinol solution 2 g of AR oxine was dissolved in 100 cm³ of 2 M acetic acid and then ammonia was added dropwise until turbidity began to appear. The solution was made clear by the addition of a little acetic acid [19]. Determination of carbon, nitrogen and hydrogen were carried out by micro analysis method.

Synthesis of complexes



0.1M aqueous solution of ethylenediamine (en) was added into 0.1 M of K₄[Mo(CN)₈] aqueous solution and irradiated under ultra violet light, ≈365 nm. The colour of the solution changed from light yellow to red within 15 min. The oxine solution was added dropwise into the red solution, when a black precipitate of the complex was formed. The precipitate was filtered, washed with ethanol-water mixture and dried over fused CaCl₂. The chemical analysis gave for K₃[Mo(O₂)(O)(OH)(C₉H₇ON)]·3C₉H₇ON (%) C=50.1, H=3.3, N=7.1 against required (%) C=50.3, H=3.0, N=6.5.



0.1M solution of ethylenediamine was added into 0.1M aqueous solution of K₄[W(CN)₈] and irradiated with ultra violet light ≈365 nm. The colour of the

solution changed from dark yellow to red within 15 min. The oxine solution was added dropwise into the red solution, when an almond colour precipitate of the complex was formed. The chemical analysis gave for $K_2[W(O_2)(O)(C_9H_7ON)_3]$ (%) C=43.3, H=2.7, N=5.8 against required (%) C=43.4, H=2.8, N=5.6.

$K_3[Mo(CN)_3(OH)_4(C_9H_7ON)] \cdot 2C_9H_7ON \cdot 3H_2O$ (III)

0.1M solution of triethylenetetramine (trien) was added into 0.1M aqueous solution of $K_4[Mo(CN)_8]$ and irradiated with ultra violet light ≈ 365 nm. The colour of the solution changed from light yellow to red within 15 min. The oxine solution was added dropwise into the red solution, when a reddish brown precipitate of the complex was formed. The chemical analysis gave for $K_3[Mo(CN)_3(OH)_4(C_9H_7ON)] \cdot 2C_9H_7ON \cdot 3H_2O$ (%) C=42.9, H=3.7, N=9.3 against required (%) C=42.4, H=3.6, N=9.9.

Physical measurements

IR spectra were recorded in the range of 400–4000 cm^{-1} in KBr matrix with Perkin-Elmer-782 infra red spectrophotometer. Thermal studies of the complexes were carried out on thermal analyser, STA-780 series, Stanton Redcroft, U.K. at the heating rate of 15°C min^{-1} . Due to the insolubility of the complex compounds in most of the organic solvents conductance measurements could not be performed.

Results and discussion

Potassium octacyanomolybdate(IV) and tungstate(IV) when irradiated in the ligand field band with ethylenediamine or triethylenetetramine gave photoproducts $[M(CN)_6(en)]^{2-}$ and $[M(CN)_4(trien)]$ respectively [20, 21]. These photoproducts when made to react with 8-quinolinol gave adducts and complexes of various compositions. The elemental analysis of the complexes show that they are of the type $K_3[Mo(O_2)(O)(OH)(C_9H_7ON)] \cdot 3C_9H_7ON$ (I), $K_2[W(O_2)(O)(C_9H_7ON)_3]$ (II) and $K_3[Mo(CN)_3(OH)_4(C_9H_7ON)] \cdot 2C_9H_7ON \cdot 3H_2O$ (III).

In I and II, all the cyano group and ethylenediamine have been substituted, whereas in III, trien molecule and one cyano group have been substituted. The infra red spectra in the frequency region where cyanide stretching, metal-oxygen stretching, M–OH deformation modes and $\nu(C-O)$ band usually occur are summarized for each complex in (Table 1).

IR spectrum of III shows the presence of strong band at 2100 cm^{-1} (vs) in the range 2020–2140 cm^{-1} (Fig. 1), which implies the presence of cyano group with the mode M–CN [22]. The $\nu(CN)$ in the complex III is shifted to higher

Table 1 Important IR frequencies of the complexes $K_3[Mo(O_2)(O)(OH)(C_9H_7ON)] \cdot 3C_9H_7ON$ (I), $K_2[W(O_2)(O)(C_9H_7ON)_3]$ (II) and $K_3[Mo(CN)_3(OH)_4(C_9H_7ON)] \cdot 3H_2O$ (III) and their assignment

Complex I		Complex II		Complex III	
Frequency/ cm ⁻¹	Assignment	Frequency/ cm ⁻¹	Assignment	Frequency/ cm ⁻¹	Assignment
500(s)	metal-ligand	410(s)		400(s)	
520(m)	$\delta_{sym}(C-C-O)$	440(w)	M-N	500(m)	metal-ligand
540(vs)	$\delta_{sym}(C-C-O)$	470(w)	$\delta_{sym}(O-C-O)$	520(m)	
620(s)	$\nu(C-O-Mo-O)$		M-N	540(m)	$\delta_{asym}(O-C-O)$
640(vs)		505(s)	metal-ligand	570(m)	$\nu(M-O)$
740(vs)	C-H band	545(vs)	$\delta_{sym}(C-C-O)$	590(m)	ring vibration
790(vs)	$\delta_{asym}(O-C-O)$	570(s)	$\nu(M-O)$	620(s)	$\nu(C-O-Mo-O)$
810(vs)	$\nu(Mo=O)$	580(m)	ring vibration	640(s)	
				750(vs)	C-H band
830(vs)	$\nu(Mo-O)$ stretching	635(sh)	$\nu(C-O-W-O)$	785(s)	
		650(s)		810(s)	$\nu(Mo=O)$
921(vs)	$\nu(Mo=O)$	750(vs)	$\nu(Mo=O)$	825(s)	
1057(m)	$\nu(M-O-H)$	770(s)	$\delta_{asym}(O-C-O)$	918(s)	$\nu(M=O)$
1100(vs)	$\nu(C-O)$ of oxine	795(s)	$\delta_{asym}(O-C-O)$	935(s)	
		810(s)		1035(m)	$\nu(N-O)$
1170(s)	asym ring vibration	835(vs)	W-O stretching	1057(m)	$\nu(M-O-H)$
				1110(vs)	$\nu(C-O)$ of oxine
		900(vs)		1140(m)	
				1170(m)	asym ring vibration
1240(vs)	$\nu(-N=O)$	920(s)			
1260(vs)		1035(s)		1240(s)	$\nu(-N=O)$
1320(vs)	$\nu_{sym}(C-O)$	1060(s)	$\nu(N-O)$	1265(vs)	
				1325(vs)	$\nu_{sym}(C-O)$
1380(s)		1100(vs)	$\nu(C-O)$ of oxine	1380(s)	
				1425(m)	
1420(s)		1140(s)		1470(vs)	$\nu_{sym}(C=O)$
1470(vs)	$\nu_{sym}(C=O)$	1170(vs)	asym ring vibration	1500(vs)	-N=O or ring vibration

w (weak), m (medium), br (broad), s (strong), sh (shoulder)

Table 1 Continued

Complex I		Complex II		Complex III	
Frequency/ cm ⁻¹	Assignment	Frequency/ cm ⁻¹	Assignment	Frequency/ cm ⁻¹	Assignment
1500(vs)	-N=O or ring vibration	1235(s)	v(-N=O)	1570(vs)	v(C=N)
		1320(vs)	v _{asym} (C-O)	1605(m)	v(=N-H)
		1380(vs)	v(-N=N-)	2100(vs)	v(CN)
1580(vs)	N=H bonding	1400(s)	v(-N=N-)	3060(br)	
1605(m)	v(=N-N)	1430(s)		3400(br)	v(OH)
3060(s)		1470(vs)	v _{sym} (C=O)		
3440(br)	v(OH)	1500(vs)	-N=O or ring vibration		
		1585(vs)	v(OH), v(N=H)		
		1600(w)	v _{asym} (=N-H)		
		3060(s)			
		3460(br)	v(OH)		

w (weak), m (medium), br (broad), s (strong), sh (shoulder)

frequency from 2078 cm⁻¹(vs) in [Mo(CN)₈]⁴⁻ to 2100 cm⁻¹(vs) in K₃[Mo(CN)₃(OH)₄(C₉H₇ON)]·2C₉H₇ON·3H₂O.

The CN acts as a σ -donor by donating electrons to metal and as a π -acceptor by accepting electrons from the metal. σ -donation tends to raise the ν (CN) since electron is removed from the 5 σ orbital, which is weakly antibonding (16). In the adduct of potassium octacyanomolybdate (IV) and octacyanotungstate(IV) with 8-quinolinol [14], frequency band at 1569 cm⁻¹(s) and 1554 cm⁻¹(vs) respectively is assigned to the ν (C=N) stretching. In the present work for complex III, ν (C=N) is observed at 1570 cm⁻¹(vs). The ν (OH) in III is in the region 3100–3300 cm⁻¹; it is a broad band and attributed to the water molecule in uncoordinated form. A strong band at 1600 cm⁻¹(s) in various photohydrolysed molybdenum complexes with nitrogen containing ligands indicate the N–H stretching vibration [23]. The frequencies in the doublet form in the range of 1580–1605 cm⁻¹ for I and in the range of 1585–1600 cm⁻¹ for II are due to the N–H stretching vibrations, but N–H stretching frequency in III is shifted to higher frequency by 5 cm⁻¹ from 1600(s) to 1605 cm⁻¹(m).

The presence of oxine in I, II and III is indicated by the band in the region 1100–1140 cm⁻¹ (Fig. 1). For several metal complexes with oxine, the ν (C–O) band is observed at 1120 cm⁻¹ [24]. The position of this band undergoes a shift depending upon the electronegativity and oxidation state of the metal. In the present investigation, these bands are observed at 1100 cm⁻¹ for I & II and at 1110 cm⁻¹(vs) for III. The shift to lower frequency is 20 cm⁻¹ for I & II and

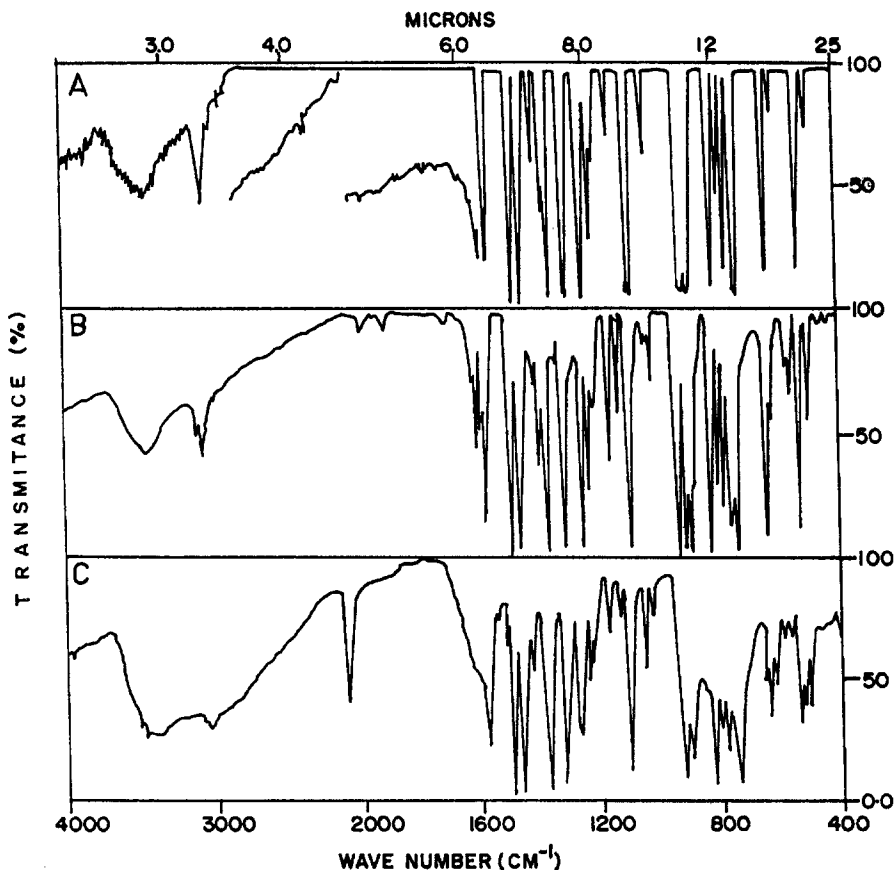


Fig. 1 IR spectra of (A) for $K_3[Mo(O)_2(O)(OH)(C_9H_7ON)] \cdot 3C_9H_7ON$ (B) $K_2[W(O_2)(O)(C_9H_7ON)_3]$ (C) $K_3[Mo(CN)_3(OH)_4(C_9H_7ON)] \cdot 2C_9H_7ON \cdot 3H_2O$

10 cm^{-1} for III. The free oxine ligand exhibits $\nu(\text{NO})$ at 1050 cm^{-1} while this $\nu(\text{NO})$ peak is found at 1240 cm^{-1} (vs) in complex I and III and at 1235 cm^{-1} (s) in II. This shift is due to the fact that increase in electron density at Mo atom leads to an increase in the repulsive forces with non bonding electrons.

The M-OH band at 1072 (s) and 1057 cm^{-1} (m) have been assigned [25] to the photohydrolysis products of $[W(\text{CN})_8]^{4-}$ and $[Mo(\text{CN})_8]^{4-}$ respectively. In the present work M-OH deformation modes occur at 1057 cm^{-1} (m) for I and III and no peak in this region has been observed for II. The lower frequency region of the complexes show the mode of bonding between Mo/W and ligands. The presence of bands at 500 cm^{-1} in I, III and at 440 and 470 cm^{-1} for II is due to M-N. Three bands for Mo=O stretching frequencies in the region $700-1000 \text{ cm}^{-1}$ are observed in $MoO(\text{OH})_3$. A value of 967 cm^{-1} has been assigned for the Mo=O stretching frequency in K_2MoOCl_5 and strong band in

this region is expected for all the compounds containing an $M=O$ band [26]. Lippard [25] has assigned $\nu(M=O)$ bands to the photohydrolysis products of potassium octacyanomolybdate (IV) and tungstate(IV) in this region. The peaks at $921\text{ cm}^{-1}(s)$ and $810\text{ cm}^{-1}(s)$ for I and $918\text{ cm}^{-1}(s)$ and $810\text{ cm}^{-1}(m)$ for III are assigned to $\nu(Mo=O)$ stretching and at $900\text{ cm}^{-1}(s)$ and $750\text{ cm}^{-1}(s)$ in II are assigned to $\nu(W=O)$ stretching.

Thermal studies

The TG of complex I shows that the decomposition occurs in two steps (Fig. 2). One molecule of oxine, (C_9H_7ON) and KOH each are removed in a single step in the temperature range 100 to 450°C . The observed weight loss is 23.5% as against the calculated weight loss 24.0% . The rate of the decomposition in this step is very slow. The remaining compound $K_2[Mo(O_2)(O)](O)$

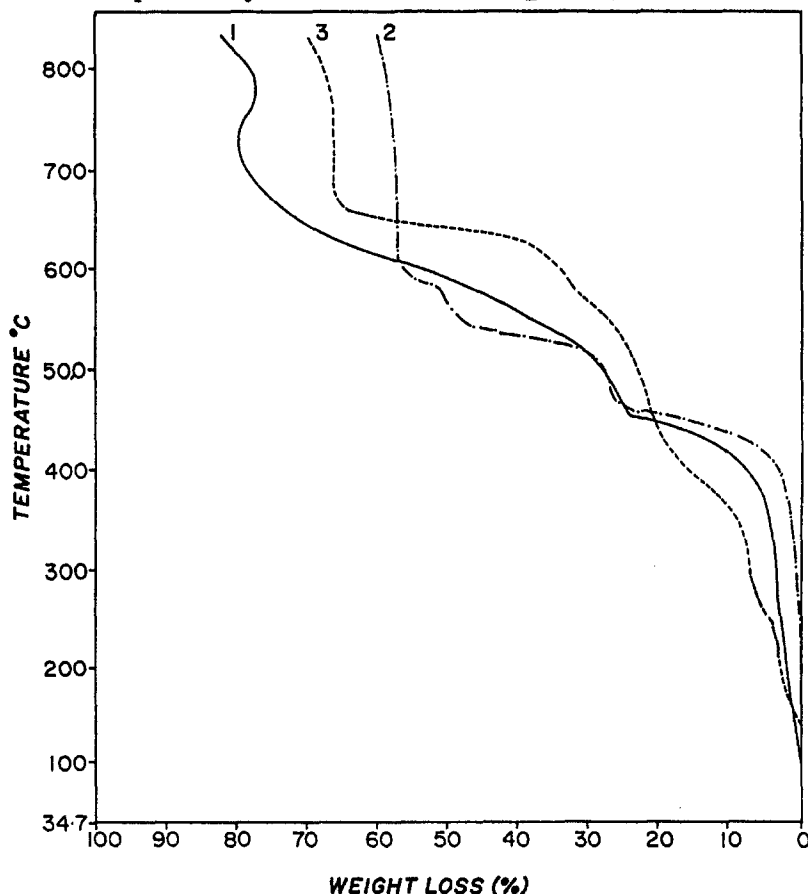
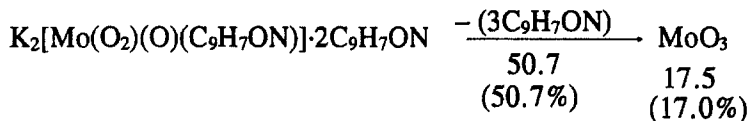
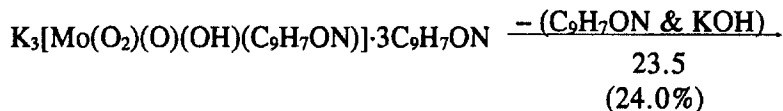


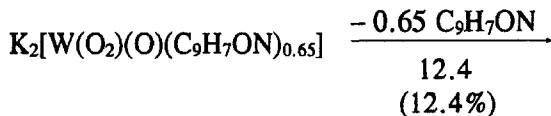
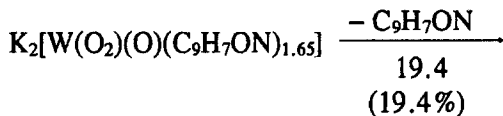
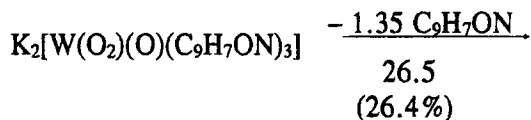
Fig. 2 TG curves (1) for $K_3[Mo(O)_2(O)(OH)(C_9H_7ON)] \cdot 3C_9H_7ON$
 (2) $K_2[W(O_2)(O)(C_9H_7ON)_3]$ (3) $K_3[Mo(CN)_3(OH)_4(C_9H_7ON)] \cdot 2C_9H_7ON \cdot 3H_2O$



Scheme I

(C₉H₇ON)]·2C₉H₇ON lost its three molecules of oxine in a single step in the temperature range 450–690°C. The observed weight loss is 50.7% as against the calculated weight loss 50.7%. The rate of decomposition in this step is faster. The end product is MoO₃ (17.5% as against the calculated value, 17.0%). The thermal dissociation is represented in Scheme I.

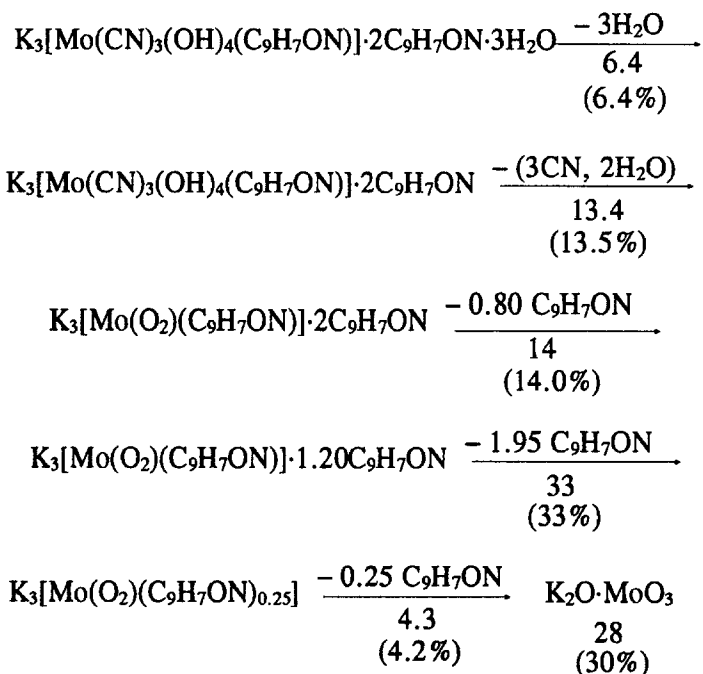
The TG of complex II shows that the decomposition occurs in three steps (Fig. 2). The complex is stable upto 212°C. Three oxine molecules are then lost in the range 212–620°C in three steps. In the first step 1.35 molecules of oxine are removed in the range 212–470°C. The observed weight loss is 26.5% as against the calculated weight loss 26.4%. The rate of decomposition in this step is slow. In the second step one molecule of oxine is removed in the range 470–535°C. The observed weight loss is 19.4% as against the calculated weight loss 19.5%. The rate of the decomposition in this step is higher. In the third step, 0.65 molecule of oxine is removed in the temperature range 535–620°C. The observed weight loss is 12.4% as against the calculated 12.4%. There is no appreciable change after 620°C and possibly the polymeric oxide K₂O·WO₃ is



Scheme II

formed. The residual weight is 40.0% against the calculated value 43.7%, Scheme II.

The TG of complex III shows that the decomposition occurs in five steps (Fig. 2). Three water molecules are removed upto 272°C. The observed weight loss is 6.3% as against the calculated weight loss 6.4%. The anhydrous complex loses 3CN⁻ and 4OH⁻ from the inner sphere in the range 272–430°C. The observed weight loss is 13.4% as against the calculated value of 13.5%. The loss of three oxine molecules occurs in the range 430–700°C in three steps. In the first step, the complex loses 0.8 molecule of oxine between 430–580°C. The observed weight loss is 14.0% as against the calculated value 14% and in the second step 1.95 molecules of oxine are removed in the range 580–675°C. The observed weight loss is 33% as against the calculated value 33%. The remaining 0.25 molecule of oxine is removed in the range 675–700°C. The observed weight loss is 4.1% as against the calculated value 4.2%. The end product may be the polymeric oxide K₂O·MoO₃ (28.0% as against the calculated value of 30%). The thermal dissociation is represented in Scheme III. It is observed from the TG curves that at the end of thermal dissociation of the complexes, there is increase in weight which implies that the lower oxides formed are converted into higher oxides. This effect is more pronounced in I and III.



Scheme III

Kinetic parameters

The thermal decomposition takes place in two steps for complex I, three steps for II and four steps for III. The order of reaction ' n ' and activation energy ' E ' was calculated using the Coats-Redfern equations [27], for $n=1$

$$\log_{10} \left[-\log_{10} \frac{(1-\alpha)}{T^2} \right] = \log_{10} \frac{AR}{HE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT}$$

and for $n \neq 1$

$$\log_{10} \left[\frac{1 - (1-\alpha)^{1-n}}{T^2(1-n)} \right] = \log_{10} \frac{AR}{HE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT}$$

where α is the fraction decomposed, ' A ' is the probability factor (solid state reaction), ' E ' is the activation energy and ' H ' is heating rate. The linear plot of

$$\log_{10}[-\log_{10}(1-\alpha)/T^2] \text{ vs. } 1/T \text{ for } n=1$$

and

$$\log_{10}[1-(1-\alpha)^{1-n}/T^2(1-n)] \text{ vs. } 1/T \text{ for } n \neq 1$$

were drawn for different values of ' n ' in the range of 0 to 3 and the order parameter was fixed from the two values of ' n ' which gave the best fit line for a

Table 2 Kinetic parameters for the thermal decomposition of complexes $K_3[Mo(O_2)(O)(OH)(C_9H_7ON)] \cdot 3C_9H_7ON$ (I), $K_2[W(O_2)(O)(C_9H_7ON)_3]$ (II) and $K_3[Mo(CN)_3(OH)_4(C_9H_7ON)] \cdot 3H_2O$ (III)

Complex	Stage	Sample mass/mg	$T_i/$ °C	$T_f/$ °C	$T_r/$ °C	$E/\text{kcal mol}^{-1}$		
						Coats&Redfern	Doyle	Dharwadkar
I	one	3.49	321	436	451	19.7	19.3	21.1
	two		451	609	728	10.1	10.1	13.8
II	one	5.20	212	443	462	31.6	30.5	32.8
	two		462	528	538	27.6	25.7	24.4
	three		538	589	590	6.1	3.8	5.1
III	one	3.30	135	240	273	4.3	6.1	5.8
	two		273	391	433	6.5	6.7	7.9
	three		433	554	583	5.7	6.3	8.2
	four		583	641	670	24.8	18.1	21.7

particular stage. The order parameters for all the three complexes were found to be one. The activation energy was found to be 19.7 kcal mol⁻¹ and 10.0 kcal mol⁻¹ for stage one and two respectively in complex I. 'E' was found to be 31.7, 27.6 and 6.1 kcal mol⁻¹ for stage one, two and three respectively in the case of complex II. The activation energy was found to be 4.3, 6.5, 5.7 and 24.8 kcal mol⁻¹ for stages 1, 2, 3 and 4 respectively in the thermal decomposition of complex III (Table 2).

The activation energy was also calculated using the Horowitz-Metzger [28] equation as modified by Dharwadkar and Karkhanawala [29] which is given below:

$$\log[\log(1-\alpha)^{-1}] = 100 E \theta / 2.303 RT_i^2 (T_f - T_i) - \log 2.303$$

where α is the fraction decomposed, T_f is the temperature of completion of the reaction, T_i is the initial temperature of reaction, θ is the difference between the inflection temperature and temperature under consideration and R is the gas constant. Activation energy 'E' was calculated from the slope of the plot of $\log(\log(1-\alpha)^{-1})$ vs. θ , which gave a linear curve. E was found to be 21.1 and 13.9 kcal mol⁻¹ for stage one and two respectively in I and 32.8, 24.4 and 5.1 kcal mol⁻¹ for stage one, two and three respectively in II. For complex III it was found to be 5.8, 7.9, 8.2 and 21.7 kcal mol⁻¹ for stages one, two, three and four respectively. Doyle equation also [30, 31] gave activation energies close to the values obtained by the above methods.

The low values of activation energies may be due to the broad TG changes observed at some stages of the complexes in their thermal dissociation which may not be temperature controlled under dynamic temperature conditions.

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