

# THERMAL STUDY OF CHROMIUM AND MOLYBDENUM COMPLEXES WITH SOME NITROGEN AND NITROGEN–OXYGEN DONORS LIGANDS

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The complexes of chromium and molybdenum with salicylidene-2-aminophenol (shaH<sub>2</sub>), salicylidene-2-aminoanisole (salanH<sub>2</sub>), salicylidene-2-aminoaniline (salphenH<sub>2</sub>) and biquinoline (biq) were studied using the thermogravimetric techniques. The thermal decomposition of all complexes was found to be first order reaction and the thermodynamic parameters corresponding to the different decomposition steps were reported. Molybdenum complexes were found to be more thermally stable and the order of stability was [Mo(CO)<sub>4</sub>(biq)] > [MoO(salphen)] > [MoO<sub>2</sub>(salphenH<sub>2</sub>)] > [MoO<sub>4</sub>(salan)] > [MoO(sha)]. Similar trend was found for chromium complexes where [Cr(CO)<sub>4</sub>(biq)] > [Cr(CO)<sub>2</sub>(salphen)] > [CrO<sub>2</sub>(CO)<sub>2</sub>(shaH<sub>2</sub>)] > [CrO<sub>2</sub>(CO)<sub>2</sub>(salan)].

**Keywords:** chromium, kinetics of thermal decomposition, molybdenum, Schiff bases, thermogravimetric studies

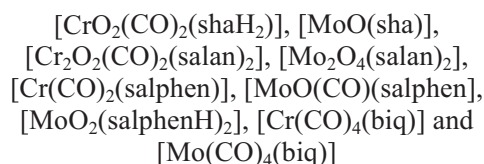
## Introduction

In the use of transition metal carbonyls as reactive species in homogeneous catalytic reactions such as hydrogenation, hydroformylation and carbonylation, carbon monoxide served simply as a ligand providing the complex with the necessary reactivity and/or stability to allow reaction to ensue [1]. On the other hand, the presence of ligands having donor atom sets like N<sub>2</sub>O<sub>2</sub> and N<sub>4</sub> have been found to be useful catalysts especially for epoxidation reactions [2]. In the same aspect a large number of Schiff bases and their complexes have been studied for their interesting and important properties, e.g. their ability to reversibly bind oxygen [3], catalytic activity in the hydrogenation of olefins [4], transfer of an amino group [5], photochromic properties [6], complexing ability towards some toxic metals [7]. In previous work the preparation and the structures of chromium and molybdenum with salicylidene-2-aminophenol (shaH<sub>2</sub>), salicylidene-2-aminoanisole (salanH<sub>2</sub>), salicylidene-2-aminoaniline (salphenH<sub>2</sub>) and biquinoline (biq) were reported [8–11]. In this article we throw more light on the thermal stability of these complexes and report the thermodynamic parameters of the different decomposition steps of the complexes.

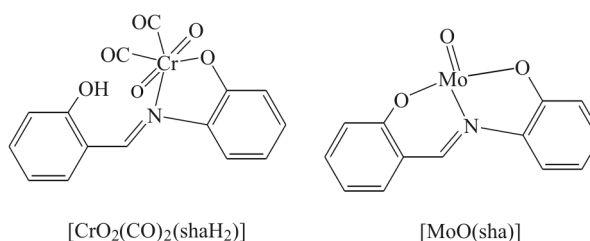
## Experimental

Chromium and molybdenum complexes with N-salicylidene-2-hydroxyaniline (shaH<sub>2</sub>), N-salicyli-

dene-2-aminoanisole (salanH<sub>2</sub>), N-salicylidene-2-aminoaniline (salphenH<sub>2</sub>) and biquinoline (biq) were prepared and their structures were reported [8–11]. The molecular formulae were proved as Schemes 1–4.



Measurements of the thermogravimetric analysis (TG and DTG) were carried out under nitrogen atmosphere with a heating rate of 10 K min<sup>-1</sup> using a Shimadzu DT-50 thermal analyzer.



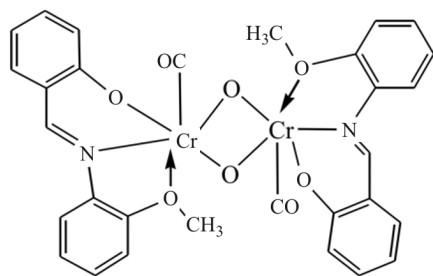
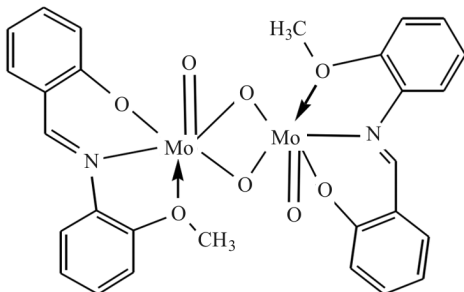
Scheme 1

### Kinetics of the decomposition of the complexes

#### Determination of reaction order of decomposition

The Horowitz and Metzger [12] equation  $C_s = n^{1/n}$ , where  $n$  is the order of the reaction and  $C_s$  is the mass

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[Cr<sub>2</sub>O<sub>2</sub>(CO)<sub>2</sub>(salan)<sub>2</sub>][Mo<sub>2</sub>O<sub>4</sub>(salan)<sub>2</sub>]

Scheme 2

fraction of the substance present at the DTG peak temperature;  $T_s$ , is given by:

$$C_s = (W_s - W_f) / (W_0 - W_f) \quad (1)$$

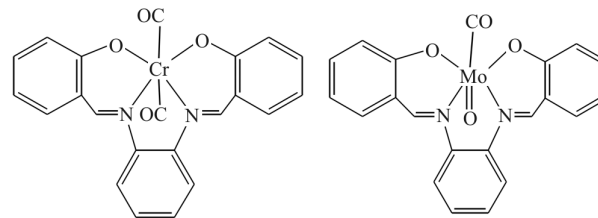
and was used for the determination of the values of the reaction order. Here  $W_s$  stands for the mass remaining at a given temperature  $T_s$ , i.e. the DTG peak temperature,  $W_0$  and  $W_f$  are the initial and final masses of the substance, respectively.

Integral method using the Coats–Redfern equation

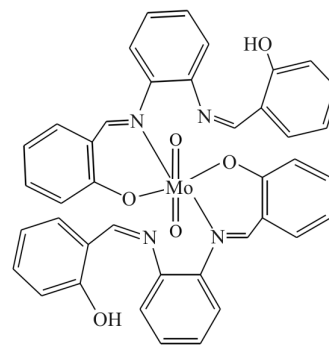
For a first order process the Coats–Redfern equation [13] may be written in the form:

$$\begin{aligned} \log \left[ \frac{\log(W_f / W_r)}{T^2} \right] &= \\ &= \log \left[ \frac{AR}{\theta E^*} \left( 1 - \frac{2RT}{E^*} \right) \right] - \frac{E^*}{2303RT} \end{aligned} \quad (2)$$

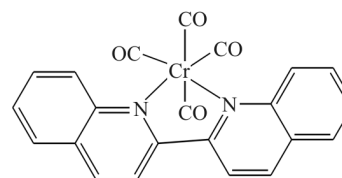
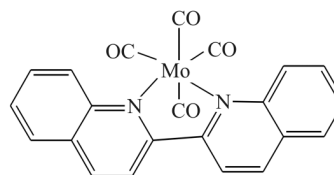
where  $W_f$  is the mass loss at the completion of the reaction,  $W$  is the mass loss up to temperature  $T$ ; ( $W_r = W_f - W$ ),  $R$  is the gas constant,  $E^*$  is the activation energy in J mol<sup>-1</sup>,  $\theta$  is the heating rate. Since  $1 - 2RT/E^* \cong 1$ , a plot of the left hand side of Eq. (2) vs.  $1/T$  was drawn which gave straight lines where  $E^*$  and  $A$  (Arrhenius constant) were calculated from the slope and the intercept, respectively.

[Cr(CO)<sub>2</sub>(salphen)]

[MoO(CO)(salphen)]

[MoO<sub>2</sub>(salphen)<sub>2</sub>]

Scheme 3

[Cr(CO)<sub>4</sub>(biq)][Mo(CO)<sub>4</sub>(biq)]

Scheme 4

Approximation method using Horowitz–Metzger equation

For the first order kinetic process, the Horowitz–Metzger equation [12, 14] may be written in the form:

$$\log \left( \frac{W_\infty}{W_r} \right) = \frac{\theta E^*}{2303RT_s^2} - \log 2.303 \quad (3)$$

where  $T_s$  = DTG peak temperature and  $\theta = T - T_s$ . A plot of  $\log[\log W_\infty/W_r]$  vs.  $\theta$  will give a straight line and  $E^*$  can be calculated from the slope. The pre-exponential factor  $C$  was calculated from the following equation [12, 13]:

$$C = (\theta E^* / RT_s^2) \exp(E^* / RT_s) \quad (4)$$

The activation entropy  $\Delta S^*$ , the activation enthalpy  $\Delta H^*$  and the free energy of activation  $\Delta G^*$  were calculated using the following equations:

$$\Delta S^* = 2.303 \left( \log \frac{Ah}{kT} \right) R \quad (5)$$

$$\Delta H^* = E^* - RT \quad (6)$$

$$\Delta G^* = \Delta H^* - T_s \Delta S^* \quad (7)$$

where  $k$  and  $h$  are the Boltzman and Planck constants, respectively.

## Results and discussion

The thermal studies of the chromium and molybdenum complexes were carried out using the thermogravimetric (TG) and differential thermogravimetric (DTG) techniques. Typical TG and DTG plots for some complexes were represented in Fig. 1. The temperature ranges of decompositions along with the corresponding mass loss of species are given in Tables 1–4.

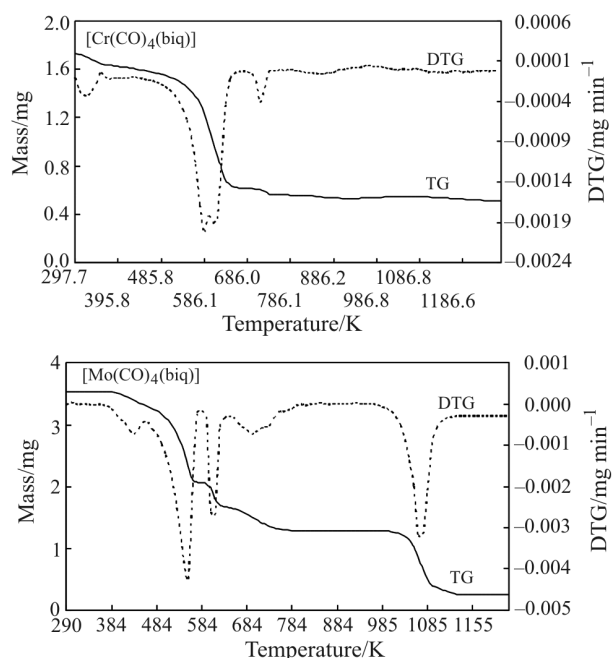


Fig. 1 TG and DTG plots of biquinoline complexes

### $[\text{Cr}(\text{O})_2(\text{CO})_2(\text{shaH}_2)]$ complex

The TG plot of  $[\text{Cr}(\text{O})_2(\text{CO})_2(\text{shaH}_2)]$  displayed four successive decomposition steps which could be treated as two decomposition steps for simplicity. The first two steps were broad and existed over a wide temperature range; 330–460 K, with a net mass loss of 15.90% which may be due to partial decomposition

of the complex through successive elimination of two CO groups. The other decomposition steps occurred in the temperature ranges 544–806 K with a net mass loss of 60.34% may be assigned to the elimination of the Schiff base moiety leaving  $\text{CrO}_2$  as metallic residue;  $\text{CrO}_2$  (23.74%).

### $[\text{MoO}(\text{sha})]$ complex

$[\text{MoO}(\text{sha})]$  complex displayed also two decomposition steps in the temperature range 490–820 K. The first decomposition step occurred in the temperature range 490–700 K with a net mass loss of 28.50% corresponding to the partial decomposition of the Schiff base molecule through the elimination of a  $\text{C}_6\text{H}_4\text{O}$  moiety. The second decomposition step occurred in the temperature range 720–820 K with a mass loss of 31.91% and corresponded to the removal of the rest of the Schiff base molecule as  $\text{C}_7\text{H}_5\text{N}$  to give finally the residue  $\text{MoO}_2$  (39.62%).

### $[\text{Cr}_2\text{O}_2(\text{CO})_2(\text{salan})_2]$ complex

The decomposition of  $[\text{Cr}_2\text{O}_2(\text{CO})_2(\text{salan})_2]$  complexes has been taken place in two steps. The first decomposition step occurred in the temperature range 392–502 K with a net mass loss of 13.39% was assigned to the elimination of two carbonyls (2CO) and the two methyl groups as ethane moiety ( $\text{C}_2\text{H}_6$ ). The second decomposition step is a composite one of three successive and unresolved peaks and was found in the temperature range 602–723 K. The mass loss associated with this decomposition step was 63.0% corresponding to the elimination of the rest of the Schiff base molecule with the formation of  $\text{Cr}_2\text{O}_3$  as metallic residue (23.30%).

### $[\text{Mo}_2\text{O}_4(\text{salan})_2]$ complex

$[\text{Mo}_2\text{O}_4(\text{salan})_2]$  decomposed in two separate steps with two resolved and non overlapping DTG peaks. The first decomposition peak was found to take place in the temperature range 670–740 K with a net mass loss of 30.0% which may be assigned for the partial decomposition of the two bulk Schiff base molecules via the equal elimination of two  $\text{C}_6\text{H}_4\text{OCH}_3$  species. The second decomposition step found in the temperature range 1050–1240 K with a net mass loss of 70.0% may be assigned for the volatilization of the rest of the complex including the metallic nuclei.

### $[\text{Cr}(\text{CO})_2(\text{salphen})]$ complex

Chromium complex with salphen;  $[\text{Cr}(\text{CO})_2(\text{salphen})]$  decomposed in four successive steps in a wide range of temperature; 340–1273 K. The first two steps with very

**Table 1** Thermal analysis data for salicylidene-2-aminophenol (shaH<sub>2</sub>) complexes

Complex	Molecular mass	DTG <sub>max</sub> /K	Decomposition step/K	Mass loss/%	Molecular mass found (calculated)	Eliminated species	Solid residue/%
[CrO <sub>2</sub> (CO) <sub>2</sub> (shaH <sub>2</sub> ) <sub>2</sub> ]	353.25	391	330–410	7.95	28.01 (28.00)	CO	CrO <sub>2</sub> (23.74)
		440	420–460	7.95	28.01 (28.00)	CO	
		589	544–702	30.33	107.13 (107.00)	C <sub>7</sub> H <sub>7</sub> O	
		769	705–806	30.04	106.11 (106.00)	C <sub>6</sub> H <sub>4</sub> NO	
[MoO(sha)]	323.08	410	490–700	28.50	92.10 (92.00)	C <sub>6</sub> H <sub>4</sub> O	MoO <sub>2</sub> (39.59)
		633	720–820	31.91	103.12 (103.00)	C <sub>7</sub> H <sub>5</sub> N	

**Table 2** Thermal analytical data of salicylidene-2-aminoanisole (salanH<sub>2</sub>) complexes

Molecular formula	Molecular mass	DTG <sub>max</sub> /K	Decomposition step/K	Mass loss/%	Molecular mass found (calculated)	Eliminated species	Solid residue/%
Cr <sub>2</sub> O <sub>2</sub> (CO) <sub>2</sub> (salan) <sub>2</sub>	644.53	442	392–502	13.39	86.30 (86.00)	2CO, C <sub>2</sub> H <sub>6</sub>	Cr <sub>2</sub> O <sub>3</sub> (23.61)
		642	602–723	63.00	406.05 (406.00)	C <sub>13</sub> H <sub>9</sub> NO <sub>2</sub> , C <sub>13</sub> H <sub>9</sub> NO	
Mo <sub>2</sub> O <sub>4</sub> (salan) <sub>2</sub>	708.48	717	670–740	30.00	212.54 (214.00)	2C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	–
		1090	1050–1240	70.00	495.50 (494.48)	Me <sub>2</sub> O <sub>4</sub> (salan-C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> ) <sub>2</sub>	

**Table 3** Thermal analytical data for salicylidene-2-aminoaniline (salphenH<sub>2</sub>) complexes

Molecular formula	Molecular mass	DTG <sub>max</sub> /K	Decomposition step/K	Mass loss/%	Molecular mass found	Eliminated species	Solid residue/%
[CrO <sub>2</sub> (CO) <sub>2</sub> (salphen)]	422.37	420	340–483	6.63	28.01	CO	CrO <sub>2</sub> (18.74)
		615	490–733	19.41	82.00	CO+C <sub>2</sub> H <sub>2</sub> N <sub>2</sub>	
		840	740–933	9.96	42.08	C <sub>3</sub> H <sub>6</sub>	
		1086	940–1273	44.10	186.21	C <sub>15</sub> H <sub>6</sub>	
[MoO(CO)(salphen)]	454.27	420	353–488	6.16	28.01	CO	Mo (21.13)
		650	490–733	16.75	76.10	C <sub>6</sub> H <sub>4</sub>	
		857	773–1083	34.15	155.18	C <sub>11</sub> H <sub>7</sub> O	
		1171	1090–1273	21.80	99.06	C <sub>3</sub> H <sub>3</sub> +N <sub>2</sub> +O <sub>2</sub>	
[MoO <sub>2</sub> (salphen) <sub>2</sub> ]	758.71	402	350–453	4.22	32.00	O <sub>2</sub>	Mo (13.10)
		506	460–653	17.06	129.45	C <sub>5</sub> H <sub>10</sub> +N <sub>2</sub> +O <sub>2</sub>	
		892	660–1083	49.34	374.37	2(C <sub>12</sub> H <sub>13</sub> )+N <sub>2</sub> +O <sub>2</sub>	
		1170	1093–1268	16.28	123.50	C <sub>11</sub> H <sub>4</sub>	

broad DTG peaks was found in the temperature range 340–733 K with a total mass loss of 26.04% (mass=109.98) which may be related to the partial decomposition of the complex through the removal of two carbonyl groups and part of the ligand as  $C_2H_2N_2$ . The last decomposition steps found in the temperature range 740–1273 K with a mass loss of 54.06% (mass=228.29) may be assigned for the removal of the rest of the ligand molecule leaving  $CrO_2$  as the metallic residue.

#### [MoO(CO)(salphen)] complex

[MoO(CO)(salphen)] complex decomposed in four thermal decomposition steps within the whole temperature range 353–1273 K. The first two merged decomposition step with a relatively sharp DTG peak was found in the temperature range 353–733 K. The mass loss corresponded to this step was 22.91% (mass=104.11) which may be due to the removal of CO and  $C_6H_4$  moieties. The third decomposition step was broadened over the temperature range 733–1083 K with a net mass loss of 34.15% (mass=155.18). This mass loss may be assigned for the decomposition of major parts of the ligands in the form of  $C_6H_4O$  and  $C_5H_3$ . The rest of the ligand ( $C_3H_3+O_2+N_2$ ) was removed in the final step in the temperature range 1090–1273°C leaving Mo as the metallic residue.

#### [MoO<sub>2</sub>(salphen)<sub>2</sub>] complex

[MoO<sub>2</sub>(salphen)<sub>2</sub>] decomposed thermally in four steps within the temperature range 350–1268 K. The first two decomposition steps, found in the temperature range 350–653 K, with a mass loss of 21.28 ( $M=161.45$ ) was assigned for partial decomposition of the ligand with the removal of two  $O_2$  molecules in addition to one molecule  $N_2$  and  $C_5H_{10}$  moiety. The third step found in the temperature range 660–1083 K with a mass loss of 49.34% (mass=374.37) may be assigned for further decomposition of the ligand moiety with the removal of two  $C_{12}H_{13}$  and  $N_2+O_2$  molecules (net mass of 374.40). The rest of the ligand moiety was removed in the last decomposition step in the temperature range 1093–1268 K with a mass loss of 16.28% (mass=123.50). The metallic residue remained at the end of decomposition was assigned as metallic Mo (13.10).

#### [Cr(CO)<sub>4</sub>(biq)] complex

The complex decomposed in three steps, the first one occurred in the temperature range 295–367 K, with a mass loss of 6.65% (mass=22.95) which is consistent with the elimination of CO group. The second and third decomposition steps (498–752 K) with net mass

loss of 66.61% which corresponded to the elimination of the biquinoline moiety. The metallic residue (19.98%) remained after the decomposition was attributed to  $CrO_2$  species.

#### [Mo(CO)<sub>4</sub>(biq)] complex

The thermal decomposition of [Mo(CO)<sub>4</sub>(biq)] was reported [11]. The complex was further heated up to 1145 K. A new decomposition step appeared in the temperature range 982–1145 K. The mass losses for the five decomposition steps with the corresponding mass losses and the suggested species eliminated are tabulated in Table 4.

#### Kinetics of thermal decomposition

The calculated values of  $\Delta E^*$ ,  $A$ ,  $\Delta S^*$ ,  $\Delta H^*$  and  $\Delta G^*$  for the decomposition steps are given in Tables 5–8.

[CrO<sub>2</sub>(CO)<sub>2</sub>(shaH<sub>2</sub>)] complex showed considerable thermal stability which is reflected from the moderately high values of the activation energy averaged to 60.71 kJ mol<sup>-1</sup>. On the other hand, [MoO(sha)] was found to be comparatively more stable which is reflected from the relatively higher activation energy ranging from 92.94–149.60 kJ mol<sup>-1</sup> (average values) which may be explained on the basis that molybdenum complex is less sterically hindered with no carbonyl moiety which often decomposed at lower temperatures compared with the organic moiety coordinated to the metal [15].

[CrO<sub>2</sub>(CO)<sub>2</sub>(salan)<sub>2</sub>] showed a weak thermal stability which is reflected from the very low activation energy of the sum of the decomposition steps ranging from 37.10–40.73 kJ mol<sup>-1</sup> with a sum of 38.92 kJ mol<sup>-1</sup>. On contrary, [Mo<sub>2</sub>O<sub>4</sub>(salan)<sub>2</sub>], showed high thermal stability which is reflected from the relatively very high energy of activation ranging from 257.80–381.99 kJ mol<sup>-1</sup> with a sum of 639.79 kJ mol<sup>-1</sup>.

The complexes of salphen with chromium and molybdenum showed high thermal stability which is reflected from their energies of activation ranging from 16.97–79.73, 21.22–255.12, 21.93–210.76 kJ mol<sup>-1</sup>, with sums of 96.70, 324.12, 309.44 kJ mol<sup>-1</sup> for [Cr(CO)<sub>2</sub>(salphen)], [MoO(salphen)] and [MoO<sub>2</sub>(salphenH)<sub>2</sub>], respectively.

[Cr(CO)<sub>4</sub>(biq)] complex showed moderate thermal stability as reflected from the activation energy of the different decomposition steps ranging from 33.53 to 263.55 kJ mol<sup>-1</sup>. [Mo(CO)<sub>4</sub>(biq)] complex showed a wide variation of activation energies of the decomposition steps ranging from 36.59 to 606.09 kJ mol<sup>-1</sup>.

In general and based on the sum of the energies of activation, the molybdenum complexes were found to be more stable than chromium complexes. The order of

**Table 4** Thermal analytical data for biquimoline (biq) complexes

Molecular formula	Molecular mass	DTG <sub>max</sub> /K	Decomposition temperature/K	Mass loss/%	Molecular mass found	Eliminated species	Solid residue/%
[Cr(CO) <sub>4</sub> (biq)]	420.35	323	295–367	6.65	27.95	CO	CrO <sub>2</sub> (19.98)
		589	498–659	66.61	280.0	C <sub>20</sub> H <sub>12</sub> N <sub>2</sub>	
		714	661–752	6.10	28.0	CO	
[Mo(CO) <sub>4</sub> (biq)]	464.29	429	400–476	33.61	128.19+28.01	C <sub>9</sub> H <sub>6</sub> N+CO	–
		538	475–572	12.70	56.03	2CO	
		679	599–652	20.57	95.67	Mo	
		1069	663–783	27.62	128.24	C <sub>9</sub> H <sub>6</sub> N	

**Table 5** The kinetic and thermodynamic data of the thermal decompositions of (shaH<sub>2</sub>) complexes

Complex	Decomposition temperature/K	$\Delta E^*/\text{kJ mol}^{-1}$		$R^2$		$A/\text{s}^{-1}$		$\Delta S^*/\text{J K}^{-1} \text{mol}^{-1}$		$\Delta H^*/\text{kJ mol}^{-1}$		$\Delta G^*/\text{kJ mol}^{-1}$		$C_s$
		CR	HM	CR	HM	CR	HM	CR	HM	CR	HM	CR	HM	
[CrO <sub>2</sub> (CO) <sub>2</sub> (shaH <sub>2</sub> )]	391–841	53.42	68.00	0.99	0.99	$3.63 \cdot 10^2$	$1.38 \cdot 10^4$	-203.27	-173.01	47.44	62.02	193.59	186.42	0.30
[MoO(sha)]	490–700	81.60	104.28	0.90	0.85	$1.78 \cdot 10^9$	$1.44 \cdot 10^{13}$	-70.49	4.36	78.19	100.88	107.09	99.09	0.29
	720–820	137.63	161.57	0.98	0.98	$7.94 \cdot 10^{10}$	$1.05 \cdot 10^{13}$	-42.51	-1.94	132.37	157.31	159.28	157.54	0.31

**Table 6** The kinetic and thermodynamic data of the thermal decompositions of (salanH<sub>2</sub>) complexes

Complex	Decomposition temperature/K	$\Delta E^*/\text{kJ mol}^{-1}$		$R^2$		$A/\text{s}^{-1}$		$\Delta S^*/\text{J K}^{-1} \text{mol}^{-1}$		$\Delta H^*/\text{kJ mol}^{-1}$		$\Delta G^*/\text{kJ mol}^{-1}$		$C_s$
		CR	HM	CR	HM	CR	HM	CR	HM	CR	HM	CR	HM	
[CrO <sub>2</sub> (CO) <sub>2</sub> (salan) <sub>2</sub> ]	392–520	32.67	35.44	0.99	0.98	$5.77 \cdot 10^2$	$7.38 \cdot 10^3$	-194.82	-173.63	29.22	32.00	109.88	103.88	0.23
	602–723	4.43	5.29	0.98	0.98	$2.13 \cdot 10^4$	$2.41 \cdot 10^5$	-168.17	-143.36	1.01	5.90	212.82	100.90	0.26
[Mo <sub>2</sub> O <sub>4</sub> (salan) <sub>2</sub> ]	660–744	246.10	269.50	0.98	0.99	$4.85 \cdot 10^{17}$	$4.60 \cdot 10^{19}$	86.48	124.37	240.20	263.60	178.89	175.42	0.25
	1050–1240	372.99	390.56	0.97	0.98	$6.77 \cdot 10^{16}$	$2.15 \cdot 10^{18}$	66.55	95.28	363.94	381.51	291.61	277.75	0.29

**Table 7** The kinetic and thermodynamic data of the thermal decompositions of (salphenH<sub>2</sub>) complexes

Complex	Decomposition temperature/K	$\Delta E^*/\text{kJ mol}^{-1}$		$R^2$		$A/\text{s}^{-1}$		$\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$		$\Delta H^\ddagger/\text{kJ mol}^{-1}$		$\Delta G^\ddagger/\text{kJ mol}^{-1}$		$C_s$
		CR	HM	CR	HM	CR	HM	CR	HM	CR	HM	CR	HM	
[Cr(CO) <sub>2</sub> (salphenH <sub>2</sub> )]	340–733	11.81	22.13	0.99	0.99	0.12	5.34	-268	-237	6.70	17.02	172.01	162.80	0.29
	740–1273	70.51	88.95	0.99	0.99	54.41	1722	-222	-193	61.47	79.92	303.07	290.32	0.28
[MoO(salphenH <sub>2</sub> )]	353–733	16.15	26.28	0.99	0.99	1.70	112.70	-244	-209	12.22	22.34	127.81	121.44	0.29
	773–1083	39.80	55.76	0.96	0.96	5.20	228	-240	-208	32.34	48.63	238.37	227.37	0.33
	1090–1273	245.8	264.44	0.99	0.99	4.9·10 <sup>9</sup>	1.45·10 <sup>11</sup>	-70	-42	236.1	254.71	318.88	304.61	0.32
[MoO <sub>4</sub> (salphenH <sub>2</sub> )]	350–653	17.33	26.53	0.99	0.98	1.39	68	-246	-214	13.12	22.32	137.89	130.72	0.30
	660–1083	70.13	83.37	0.99	0.98	3.5·10 <sup>2</sup>	9.3·10 <sup>4</sup>	-205	-178	62.69	76.00	246.27	235.14	0.27
	1093–1268	261.4	160.12	0.97	0.96	2.61·10 <sup>10</sup>	5.46·10 <sup>8</sup>	-57	-87	251.7	152.68	318.28	230.27	0.31

**Table 8** The kinetic and thermodynamic data of the thermal decompositions of (biq) complexes

Complex	Decomposition temperature/K	$\Delta E^*/\text{kJ mol}^{-1}$		$R^2$		$A/\text{s}^{-1}$		$\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$		$\Delta H^\ddagger/\text{kJ mol}^{-1}$		$\Delta G^\ddagger/\text{kJ mol}^{-1}$		$C_s$
		CR	HM	CR	HM	CR	HM	CR	HM	CR	HM	CR	HM	
[Cr(CO) <sub>4</sub> (biq)]	295–367	33.53	37.15	0.91	0.91	8.22·10 <sup>2</sup>	4.30·10 <sup>5</sup>	-190	-138	30.84	34.45	92.15	78.92	0.31
	498–659	131.12	162.34	0.95	0.94	1.34·10 <sup>14</sup>	1.41·10 <sup>14</sup>	-38	20	126.22	157.45	148.36	145.50	0.29
	661–752	253.12	263.55	0.92	0.91	1.89·10 <sup>16</sup>	1.18·10 <sup>19</sup>	59	113	247.18	257.61	204.72	176.92	0.31
[Mo(CO) <sub>4</sub> (biq)]	400–476	36.59	38.76	0.97	0.97	0.96·10 <sup>2</sup>	1.33·10 <sup>4</sup>	-211	-169	33.03	35.20	123.20	107.71	0.28
	475–572	88.32	100.31	0.99	0.98	1.77·10 <sup>7</sup>	2.29·10 <sup>9</sup>	-111	-70	83.84	95.83	143.59	133.85	0.32
	599–652	174.17	177.19	0.88	0.89	1.45·10 <sup>13</sup>	8.54·10 <sup>14</sup>	1.09	35	169.10	172.12	168.44	150.78	0.30
	663–783	51.54	58.11	0.95	0.96	5.15·10 <sup>3</sup>	3.15·10 <sup>3</sup>	-219	-185	45.73	52.30	199.00	181.66	0.29
	982–1145	538.42	606.09	0.99	0.99	9.31·10 <sup>25</sup>	2.64·10 <sup>29</sup>	241	308	529.53	597.21	271.20	268.21	0.30

CR – Coats–Redfern method; HM – Horowitz–Metzger method;  $R^2$  – correlation coefficient of the Arrhenius plots

thermal stability according to the coordinated ligands was found to be  $\text{biq} > \text{salphenH}_2 > \text{salanH}_2 > \text{shaH}_2$ . This can be explained on the basis that  $\text{biq}$  (NN donor) is less sterically hindered than the other complexes. On the other hand  $\text{salphenH}_2$  is strong NNOO tetradentate ligand compared with the NOO tridentate  $\text{salanH}_2$  and  $\text{shaH}_2$ . This trend is found to be  $\text{biq} > \text{salphenH}_2 > \text{shaH}_2 > \text{salanH}_2$  for chromium complexes.

The entropy change,  $\Delta S^*$ , for the formation of the most of the activated complexes from the starting reactants, is in most cases of negative values. The negative sign of the  $\Delta S^*$  suggests that the degree of structural 'complexity' (arrangement, 'organization') of the activated complexes was lower than that of the starting reactants and the decomposition reactions are slow reactions [16].

The values of  $C_s$  for the thermal decomposition of the complexes are in the range 0.23–0.33 which indicates that the decomposition follows first order kinetics [12, 14].

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