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Thermal studies of chromium, molybdenum and ruthenium complexes of chloranilic acid

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Abstract

Chromium, molybdenum and ruthenium complexes of chloranilic acid (H_2CA) were investigated by the thermogravimetric (TG) technique. The TG plot of $Cr(H_2CA)_3$ showed three decompositions in the temperature range 336–802°K. On the other hand, the TG plot of $MoO_3(HCA)$ complex displayed successive weight losses in four steps covering the temperature range 350–1278°K. The thermal decomposition of the cluster compound $Ru_3(CO)_{10}(\mu\text{-H})(HCA)$ occurred in three steps within the decomposition temperature range 302–764°K. Calculation of the reaction order of decompositions of the three complexes revealed that they follow first-order kinetics. The thermodynamic parameters for the different decomposition steps of the complexes were also determined from their DTG plots. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Direct reactions of quinones with metal carbonyls are commonly used for the preparation of binary quinone- and semiquinone complexes [1–9]. The importance of quinone complexes is related to the use of *o*-benzoquinones in oxidative-addition reactions to basic metals [3] and their relevance to metal catalyzed biological redox systems [10]. Reactions of the chromium and molybdenum hexacarbonyls with chrysenequinone and chrysenequinonemonoxime ligands gave several semiquinone derivatives. The spectroscopic and electrochemical investigation of these complexes illustrated interesting structural arrangements [5–7]. Also, reactions of chrysenequinone with the cluster compounds $M_3(CO)_{12}$, M=Ru and Os, yielded the quinone derivatives $M(CO)_3$ (chrysenequinone) [8]. On the other hand, $M_3(CO)_{12}$ reacted with 2,3-dihydroxyquinoxaline (DQ) in dimethylsulfoxide to give the complex $M(CO)_2(DQ)(DMSO)$. The IR and NMR spectroscopy showed that these complexes have trigonal bipyramidal structures with the two CO molecules differently bonded to the metal center; axially in the ruthenium complex and equatorially in the osmium complex [9].

In a preceding paper, we have described the reactions of $M(CO)_6$, M=Cr and Mo, as well as the reaction of the cluster compound $Ru_3(CO)_{12}$ with 2,5-dichloro-3,6-dihydroxy-*p*-quinone (chloranilic acid) [11]. The existence of these complexes in

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different structural arrangements, depending on the central metal atom, along with their higher thermal stability has prompted us to carry out a detailed thermal analysis to throw more light on their composition.

2. Experimental

Chromium and molybdenum hexacarbonyls as well as triruthenium dodecacarbonyl were supplied from Aldrich. 2,5-dichloro-3,6-dihydroxy-*p*-quinone, chloranilic acid (H_2CA), was purchased from Sigma. All the solvents used were of analytical reagent grade and purified by distillation according to the standard methods. $Cr(H_2CA)_3$, $MoO_3(HCA)$ and $Ru_3(CO)_{10}(\mu\text{-}H)(HCA)$ were prepared as described before [11].

Measurements of the thermogravimetric analysis (TG and DTG) were carried out under nitrogen atmosphere with a heating rate of 10°C/min using a Shimadzu DT-50 thermal. The mass spectra of the complexes were performed on Finnigan MAT SSQ 7000 spectrometer. Table 1 lists data for the most abundant peaks in the mass spectra in m/z units (m is the mass of the fragment ion and z is its charge).

2.1. Determination of reaction order of decomposition

The reaction order of decomposition of the chromium, molybdenum and ruthenium complexes were calculated from their DTG plots [12,13]. The weight fraction of the substance present at the DTG peak (C_s) can be determined from the following relation:

$$C_s = \frac{(W_s - W_f)}{(W_i - W_f)} \tag{1}$$

where W_s is the weight remaining at T_s (the temperature of DTG peak), and W_i and W_f are the initial and final weights of the substance. The order of the decomposition reaction (n) can then be calculated.

$$C_s = (n)^{1/1-n} \tag{2}$$

2.2. Calculation of kinetic and thermodynamic parameters

2.2.1. Integral method using the Coats–Redfern equation

For a first-order process, the activation energy E^* in J mol^{-1} can be calculated from the following equation [14]:

$$\log\left[\frac{\log(W_\infty/(W_\infty - W))}{T^2}\right] = \log\left[\frac{AR}{\phi E^*}\left(1 - \frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303RT} \tag{3}$$

where W_∞ is the mass loss at the completion of the decomposition reaction, W the mass loss up to temperature T, R the gas constant and ϕ the heating rate. Since $1-2RT/E^* \cong 1$, the plot of the left-hand side of Eq. (3) against $1/T$ would give a straight line. E^* was then calculated from the slope and the Arrhenius constant, A, was obtained from the intercept.

2.2.2. Approximation method using Horowitz–Metzger equation

For the first-order kinetic process, the Horowitz–Metzger equation [12,13] may be written in the form

$$\log\left[\log\frac{W_\infty}{W_r}\right] = \frac{\theta E^*}{2.303RT_s^2} - \log 2.303 \tag{4}$$

where T_s is the DTG peak temperature and $\theta = T - T_s$. A plot of log [log W_∞/W_r] versus θ will give a straight line and E^* can be calculated from the slope. The pre-exponential factor C was calculated from the

Table 1
Selected mass spectral data of the three complexes

Complex	m/z values[a]
$Cr(H_2CA)_3$	679.0, 605.15, 518.0, 459.9, 397.4, 378.15, 347.0, 309.4, 206.15, 159.95, 122.0, 45.95
MoO_3 (HCA)	670.4, 582.2, 474.2, 399.9, 385.9, 352.1, 336.0, 300.0, 242.0, 181.0, 144.0, 100.5, 58.0
$Ru_3(CO)_{10}(\mu\text{-}H)$ (HCA)	1045, 961.8, 929.4, 887.5, 854.5, 792.0, 769.4, 721.0, 598.2, 530.8, 492.0, 470.4, 354.8, 291.6, 370.0, 350.0, 314.1, 72.0, 56.0

[a] Most abundant peaks.

following equation [12,13]:

$$C = \left(\frac{\phi E^*}{RT_s^2}\right)\exp\left(\frac{E^*}{RT_s}\right) \tag{5}$$

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

$$S^* = 2.303\left(\log\frac{Ah}{kT}\right)R \tag{6}$$

$$H^* = E^* - RT \tag{7}$$

$$G^* = H^* - T_s S^* \tag{8}$$

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

3. Results and discussion

Reaction of chromium hexacarbonyl with chloranilic acid yielded the tris derivative $Cr(H_2CA)_3$. On the other hand, the corresponding reaction of $Mo(CO)_6$ with H_2CA in air gave the tri-oxo complex $MoO_3(HCA)$. The spectroscopic studies of the two complexes revealed that the chromium complex has an octahedral arrangement, with chloranilic acid bonded as a semiquinone, while the molybdenum one is trigonal bipyramid, with the ligand coordinated to two equatorial sites [11]. The proton of the coordinated hydroxyl group of the $MoO_3(HCA)$ was lost, probably via an oxidative addition which would result in the formation of a molybdenum (V) species. The cluster compound $Ru_3(CO)_{12}$ reacted with chloranilic acid in benzene to give the dark brown complex $[Ru_3(CO)_{10}(\mu\text{-}H)(HCA)]$. The appearance of the stretching frequency of the coordinated carbonyl of ligand at 1370 cm^{-1} suggested that it was bound to the metal as a catechol [11].

The thermal studies of the three complexes were carried out using the thermogravimetric (TG) and differential thermogravimetric (DTG) techniques. Typical TG and DTG plots for the three complexes are given in Fig. 1. The plots exhibited well-defined and non-overlapping decomposition steps. The temperature ranges of decompositions along with the corresponding mass loss of species are given in Table 1. Comparison between the mass spectral data of the complexes with the thermally decomposed species was performed to assist in proposing the thermal decomposition schemes.

The TG plot of $Cr(H_2CA)_3$ complex showed that it was decomposed in three steps. The first step, occurred in he temperature range 336–459°K, was consisted of two unresolved peaks with a net weight loss of 23.50% (Fig. 1). The percentage weight loss was consistent with the elimination of a water molecule and two chlorine molecules. On the other hand, the two decomposition peaks appeared in the temperature ranges 464–549 and 554–802°K were well separated with a net weight loss of 17.92 and 51.00%, respectively, and corresponded to material decomposition to give finally a metallic chromium (Table 2). The residual masses obtained from the three decomposition steps of the complex were found to be

Table 2
Thermal data for chromium, molybdenum and ruthenium complexes of chloranilic acid

Molecular formula	Molecular weight	DTG_{max} (°K)	Decomposition temperature (°K)	Weight loss (%)	Mass loss found (calculated)	Eliminated species	Solid decomposition product (%)
$[C_{18}H_6O_{12}C1_6Cr]$	678.95	386	336–459	23.50	160.00 (159.83)	$2C1_2$, H_2O	7.58
		498	464–549	17.92	122.00 (122.08)	$C_6H_2O_3$	(Cr)
		669	554–802	51.00	347.00 (345.05)	$C_6O_4C1_2$, $C_6H_2O_4$	
$[C_6HO_7Cl_2Mo]$	352.94	327,379	350–670	14.52	51.50 (51.45)	O, Cl	40.80
		812	712–860	16.38	58.00 (56.02)	2 CO	(MoO_3)
		1063	979–1278	28.30	100.50 (100.50)	C_4HOCl	
$[C_{16}H_2O_{14}Cl_2Ru_3]$	792.29	330	302–416	9.1	72.00 (72.02)	CO, CO_2	39.6
		526	440–583	44.2	350.00 (350.08)	$C_6HO_3Cl_2$ and $RuH(CO)_2$	$Ru_2C_4O_4$
		692	685–764	70	56 (56.02)	2CO	

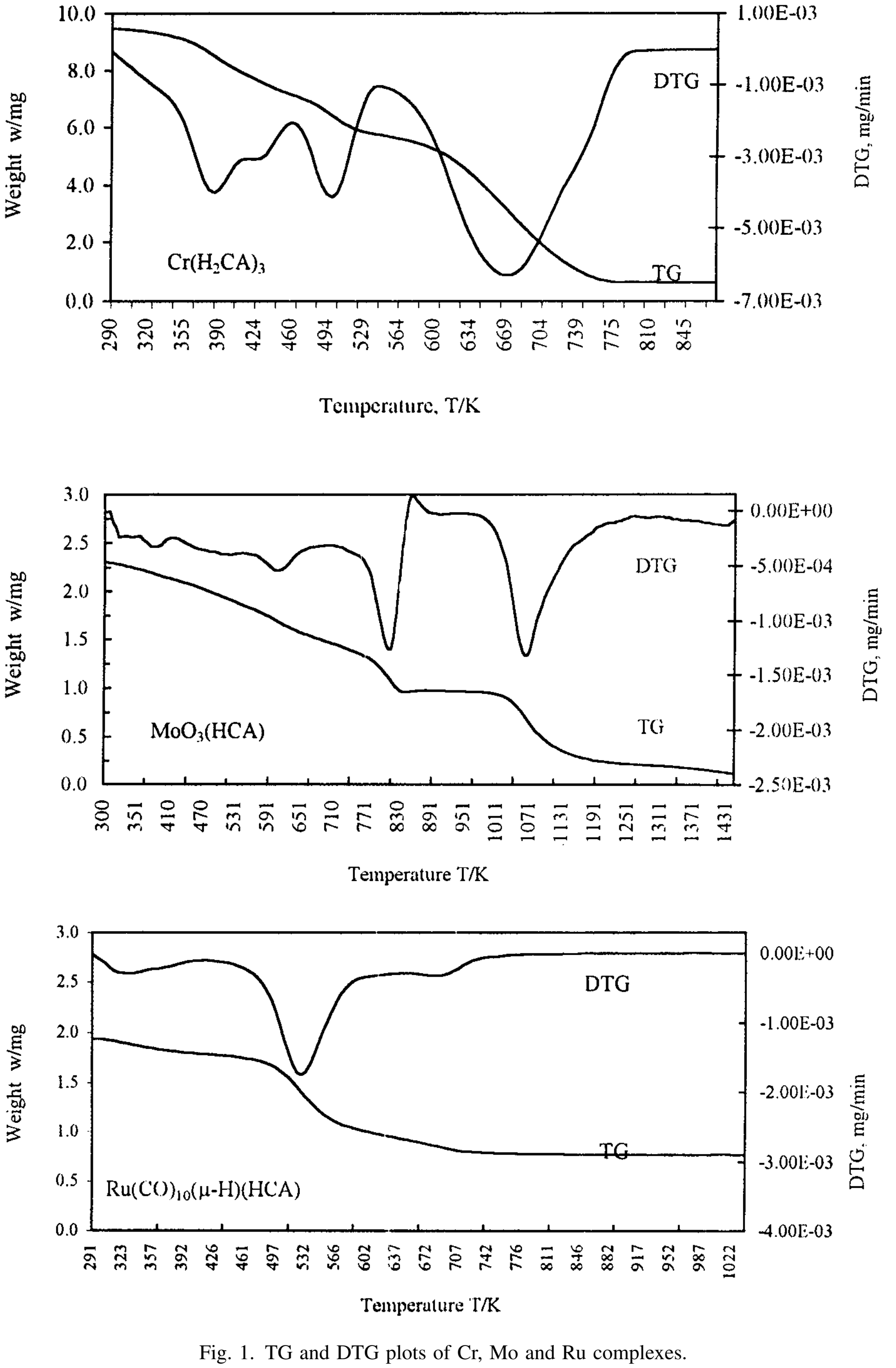
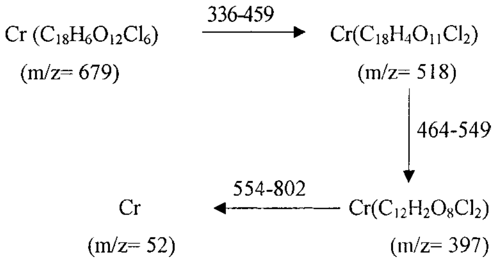


Fig. 1. TG and DTG plots of Cr, Mo and Ru complexes.



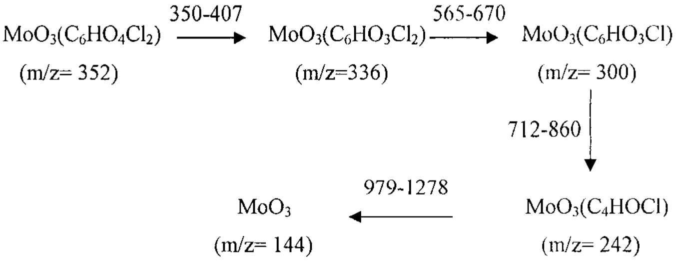
Scheme 1. The thermal decomposition steps of $Cr(H_2CA)_3$ complex.

consistent with the masses of the fragmentation patterns in its mass spectrum (Scheme 1).

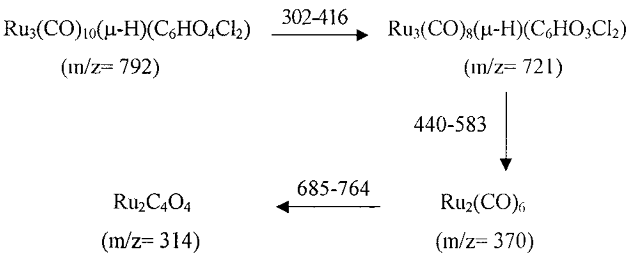
The thermogravimetric studies of the MoO_3(HCA) complex showed that it was decomposed in three steps (Fig. 1). The successive weight losses were observed in the temperature range 350–1278°K that ended with the formation of a stable metal oxide MoO_3 species (Table 2). The first decomposition peak occurred at 350–407°K was due to a loss of an oxygen; more conveniently from the ligand moiety. The following two decomposition peaks were due loss of a chlorine and two CO species. The expected decomposition species obtained from the three steps along with their matched masses obtained from the fragmentation patterns of the complex in its mass spectrum are illustrated in Scheme 2.

The TG plot of the cluster compound $Ru_3(CO)_{10}$-(μ-H)(HCA) showed that it decomposed in three steps within the temperature range 302–764°K The percentage weight loss in the first decomposition peak was attributed to the elimination of two CO and an oxygen atom. This is consistent with the mass spectrum of the complex. The second decomposition peak occurred at 440–583°K could be attributed to a material decomposition involving the loss of a volatile mononuclear ruthenium carbonyl species. Scheme 3 illustrates the expected decomposed species with their matched *m*/*z* values obtained from the fragmentation pattern of the complex in its mass spectrum.

If the maximum temperature of the first decomposition peak in the DTG plots of the investigated complexes (Table 2) is taken as a measure of their thermal stabilities, it can be concluded that: the chromium and molybdenum complexes have more higher thermal stability than the ruthenium one. This can be attributed to the higher affinity of both chromium and molybdenum to coordinate oxygen donor moieties. On the other hand, the carbonyl groups in the cluster



Scheme 2. The thermal decomposition steps of MoO_3(HCA) complex.



Scheme 3. The thermal decomposition steps of $Ru_3(CO)_{10}$(μ-H)(HCA) complex.

Table 3
The kinetic and thermodynamic data of the thermal decompositions of the three complexes

Complex	Decomposition temperature (°K)	E^* (kJ mol^{-1})		R^{2a}		A (s^{-1})		S^* (JK^{-1} mol^{-1})		H^* (kJ^{-1} mol^{-1})		G^* (kJ^{-1} mol^{-1})		C_s
		CR[b]	HM[c]	CR	HM	CR	HM	CR	HM	CR	HM	CR	HM	
Cr $(H_2CA)_3$	464–549	37.52	36.10	0.99	0.98	1157.25	1068.00	−190.56	−191.23	33.38	3195	124.82	127.18	0.33
	554–802	40.24	40.28	0.98	0.98	152.94	151.10	−209.84	−209.95	34.67	34.72	175.06	175.17	0.31
MoO_3(HCA)	712–860	123.59	123.72	0.95	0.97	2.1×10^7	2.1×10^7	−113.09	−113.27	116.83	116.97	208.66	208.94	0.34
	979–1278	64.38	64.91	0.99	0.96	63.41	106.90	−221.02	−216.67	55.54	56.07	290.48	286.40	0.29
$Ru_3(CO)_{10}$(μ-H) (HCA)	302–416	23.38	23.39	0.99	0.98	228.60	1282.90	−200.60	−186.29	20.63	20.61	86.84	82.08	0.31
	440–583	52.35	53.00	0.97	0.99	14416.9	41999.0	−170.00	−161.00	47.97	48.60	137.42	133.37	0.30
	685–764	42.08	43.09	0.96	0.99	194.29	193.81	−208.14	−208.15	36.32	37.34	180.35	181.39	0.29

[a] Correlation coefficient of the Arrhenius plots.

[b] Coats–Redfern method.

[c] Horowitz–Metzger method.

compound $Ru_3(CO)_{10}$(μ-H)(HCA) are more easily lost on heating. The mass spectrum of the complex showed a fragmentation pattern with a successive loss of CO groups [11].

The estimated values of C_s for the thermal decomposition of the three complexes were found in the range of 0.29–0.37 (Table 3). This range indicated that the decomposition reactions of the complexes followed first-order kinetics [12]. The values of activation energies, as well as the Arrhenius constants are given in Table 3. The values obtained from applying either Coats–Redfern or Horowitz–Metzger equations were comparable, Table 3. (The correlation coefficients of the Arrhenius plots of the thermal decomposition steps were found to be in the range 0.95–0.99 which indicated good fitness of the linear function). The low activation energy values (23.38–123.72 kJ mol^{-1}) could be retained to the organometallic nature of the complexes specially in the case of the $Ru_3(CO)_{10}$(μ-H) (HCA) complex [9] On the other hand, the negative values of S^* may indicate that the decomposition reactions were slower than the normal ones.

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