Reactivity of acyl and aquo groups in metal–quinone aggregates of Photosystem-II

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Abstract

Because thermolytic products are analogous to photolytic products, non-isothermal TGA studies of metal–quinones involved in Photosystem-II have been undertaken. The compositions of the compounds C-1–C3 are $ML_2 \cdot x H_2O$. For C-1 and C-2, M = Co(II), $x = 2$, and L = Lw in the former and L = O-acylLwOx in the latter; for C-3, M = Ni(II), $x = 4$ and L = LwOx. The weight loss versus temperature data are treated using the Coats and Redfern relationship. In **C-1**, the water molecules are ligand participants in the coordination, while in **C-2** and **C-3** the water molecules are adsorbed. The kinetic data of the thermolysis throw light on the energetics of the $\overline{O \quad O}$ and $\overline{O \quad N \quad O}$ ligations in quinone chelates, together with their acyl and aquo functionalities.

The E_a values of Lw in **C-1** and of the acyl and LwOx functional moieties in **C-2**, are comparable: 55, 58 and 57 kJ mol^{-1} respectively. The aquation effect dominates in **C-1**, as the E_a of H_2O is ≈ 82 kJ mol^{-1}. The adsorbed water molecules in **C-3** have an $E_a \approx 7.5$ kJ mol^{-1}, while the outer-sphere water molecules participate in the hydrolysis of the O-acyl functional group during the pyrolytic reaction of **C-2**, which requires an energy ≈ 81.6 kJ mol^{-1}.

NOMENCLATURE

Lw   lawsone
LwOx   lawsonemonoxime
NQ   naphthoquinone
NSQ   naphthosemiquinone
WOC   water-oxidising complex
Q_A quinone acceptor

INTRODUCTION

It has been established that aggregates of acyl bridges, water molecules and quinone functions, together with metal centres, are integral parts of

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WOC biomodels [1–3]. But the roles of the different constituents in the electron-transfer mechanism in Photosystem-II (PS-II) are yet to be revealed. Recently we reported the thermolytic pathway of electron transfer in the chelates of hydroxyquinone oximes [4] which have considerable biological relevance [5]. In connection with that, we report here the mechanism of electron transport in O-acylLwOx (**I**) compared to that in its parent ligand lawsone (**II**). With the exception of a few reports [6–11], there is little of relevance in the literature.

EXPERIMENTAL

Materials

All the chemicals used in the preparation of the ligands and metal chelates were of AnalaR grade. Lawsone, 2-hydroxy-1,4-naphthoquinone, was obtained from Fluka. LwOx (**III**) and its O-acyl derivative (**I**) were synthesised using literature procedures [12,13]. The hydrated chelates of **I** and **II** with Co and of **III** with Ni were synthesised as reported earlier [4,12].

O-acyl LwOx (I)   Lw (II)   LwOx (III)
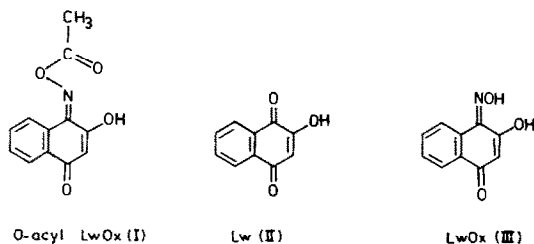
Thermal analysis

A laboratory built thermobalance, consisting of a chainomatic balance of 0.1 mg accuracy, a silica tube furnace, a pyrometer (Electroflow, England) of 10 °C accuracy to 1000 °C, a temperature controller (type 8D-1P, automatic, electric) and a chromel–alumel thermocouple placed in the vicinity of the sample, was employed in the work. A heating rate of between 2 and 4 °C min^{-1}, and 50–70 mg samples of 250–200 mesh particle size were used for the measurements. All measurements were carried out in static air atmosphere between room temperature and 700 °C in a quartz cup. The performance of the instrument was verified by the TG of $CaC_2O_4 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$. The temperatures were corrected for thermocouple non-linearity and are procedural temperatures.

IR studies

The IR spectra of the ligands and their metal chelates were recorded in nujol and fluorolube mulls (as necessary) on a Pye Unicam PU 9512 infrared spectrometer.

RESULTS AND DISCUSSION

The biological significance of the quinones Q_A in PS-II relates to their one (SQ), or two (CAT), electron-acceptor capabilities which, in turn, help in electron transport. Here we report the mechanistic electrodynamics during the pyrolysis of bis-(O-acylLwOx) Co(II) dihydrate compound.

Analytical data

The chemical compositions of **C-1**, **C-2** and **C-3** were established from their elemental analyses (Table 1).

IR studies

The significant IR data are given in Table 2, and are suggestive of $\overline{O\ \ O}$, $\overline{O\ \ \ N\ \ \ \ O}$ and $\overline{O\ \ \ N}$ chromophores in **C-1**, **C-2** and **C-3** compounds, where the coordination sites are the hydroxyl oxygen (i.e. 2-oxido), oximino nitrogen (C=N) and oximino acyl carbonyl groups. This is in accordance with previous reports [6,12,13]. However, the absence of the O-acyl frequency band at ≈ 1800 cm^{-1} on complexation implies an addi-

TABLE 1

Analytical data for chelates of cobalt and nickel

Compd.	Yield (%)	Decomp. temp. (°C)	Elemental analyses (%) [a]			
			C	H	Co/Ni	CoO/NiO
C-1	68	240	53.40	3.26	13.62	18.31
			(54.44)	(3.19)	(13.35)	(16.98)
C-2	63	80	47.95	3.79	10.55	14.00
			(51.90)	(3.63)	(10.61)	(13.49)
C-3	73	340	51.00	3.11	10.98	15.70
			(47.37)	(3.97)	(11.57)	(14.70)
C-3(a) [b]	70	320	51.19	2.91	13.61	18.78
			(55.22)	(2.78)	(13.43)	(17.20)

[a] Figures in parentheses are theoretically calculated percentage values. **C-1**, Co(Lw)$_2 \cdot$2H$_2$O; **C-2**, [Co(O-acylLwOx)$_2$]$\cdot$2H$_2$O; **C-3**, [Ni(LwOx)$_2$]$\cdot$4H$_2$O; **C-3(a)**, Ni(LwOx)$_2$.
[b] Compound prepared by heating **C-3** at ≈ 250°C for 1 h.

tional coordination through the oximino acyl carbonyl group in **C-2**, which gives a tridentate character to O-acylLwOx. The broad hydroxyl stretch absorptions are due to water molecules or oximinohydroxyl groups. The IR criteria as used in the literature [12] for NQ and NSQ coordinations suggest the probability of (NQ)(NQ) coordinations in **C-1**, and (NQ)(NSQ) coordinations in **C-2**.

Non-isothermal TG studies

The non-isothermal TG curves for the solid phase thermal decomposition of **C-1**, **C-2** and **C-3** are given in Fig. 1.

Pyrolysis in air resulted in two-step decompositions, with the final decomposition products being CoO.

TABLE 2

Significant absorptions in IR spectra of ligands **L-1–L-3** and chelates **C-1–C-3**

Compound	ν(OH)	ν(C=O)	ν(C=N)	ν(C=C aromatic)
L-1	3153 (sbr)	1678 (s)	–	1578 (m)
		1643 (s)		1563 (m)
L-2	3511 (sbr)	1801 (s) acyl	1561 (mbr)	1536 (m)
	3451 (w)	1631 (sbr) *p*-quinone	–	–
L-3	3494 (sbr)	1621 (sbr)	1581 (s)	1531 (sbr)
				1491 (s)
C-1	3300 (wbr)	1700 (wbr)	–	1580 (w)
		1650 (mbr)		
		1625 (mbr)		
C-2	3323 (mbr)	1623 (sh) acyl	1578 (s)	1578 (s)
		1603 (s) *p*-quinone		
C-3	3348 (wbr)	1618 (m)	1588 (m)	1548 (sh)
Compound	δ(OH phenolic)	ν(C–O)	ν(N–O)	Q absorption
L-1	1328 (s)	1233 (mbr)	–	1283 (m)
				1253 (m)
L-2	1361 (s)	1171 (s)	1021 (s)	1241 (s)
	1331 (m)		996 (s)	1231 (s)
L-3	1331 (s)	1176 (s)	1011 (s)	1261 (s)
				1256 (s)
C-1	–	1240 (mbr)	–	1270 (mbr)
C-2	–	1193 (sbr)	1063 (wbr)	1243 (mbr)
			1008 (wbr)	
C-3	–	1220 (sbr)	1028 (wbr)	1278 (mbr)

L-1, Lw; L-2, O-acylLwOx; L-3, LwOx; C-1, Co(Lw)$_2$·2H$_2$O; C-2, [Co(O-acylLwOx)$_2$]·2H$_2$O; C-3, [Ni(LwOx)$_2$]·4H$_2$O; Q, quinone.
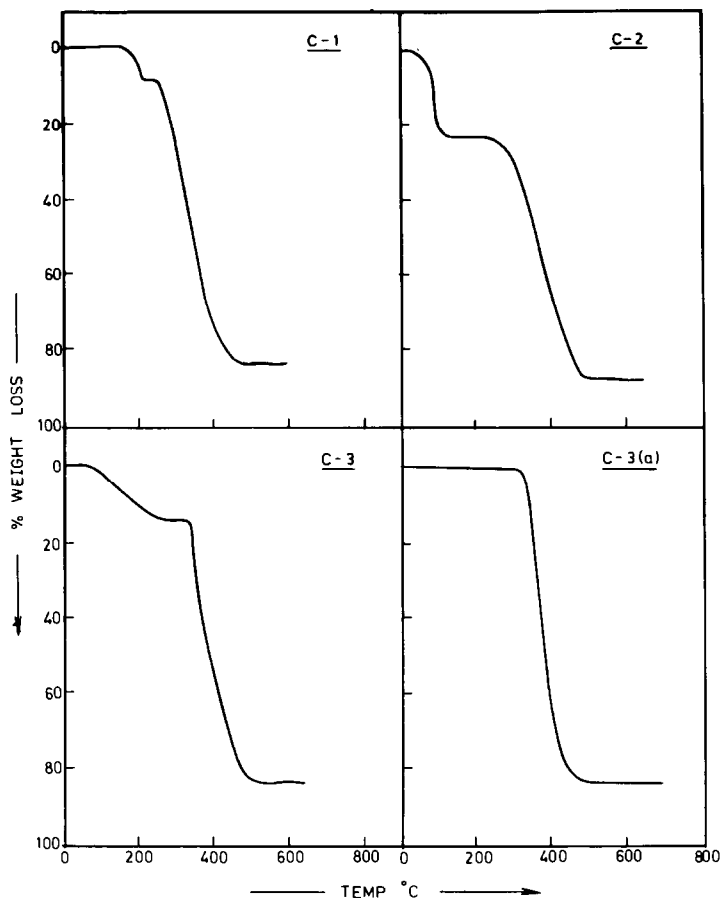s = strong, m = medium, w = weak, sh = shoulder, br = broad.

Fig. 1. Thermograms of **C-1–C-3a** compounds in air.

Decomposition temperature and thermal stability

The coordinations $\overbrace{O \quad O}$, $\overbrace{O \quad N}$ and $\overbrace{O \quad N \quad O}$ in **C-1**, **C-2** and **C-3**, when compared in the chelates, gave the thermal stability order **C-3 > C-1 > C-2** which is due to the bi- or tridenticity of the ligands forming five-membered rings in the respective chelates. The spins in **C-2** are distributed in two five-membered rings while such transfers occur in one five-membered ring in **C-1** and **C-3**. The strained ring formation in **C-2** is the reason for its low thermal stability.

Kinetic parameters from dynamic TGA

The dynamic TGA data with the % weight losses at different steps for **C-1**, **C-2** and **C-3** are given in Table 3. The kinetic parameters were calculated from the dynamic TG curves using the computer programs developed [14] using the rising temperature expression of Coats and

TABLE 3

Data from TGA in air for **C-1–C-3** chelates of cobalt and nickel

Compound	Step no.	Temp. range (°C)	% Wt. loss (calc)	Probable composition of group lost	Residue
C-1	I	170–200	8.30 (8.16)	$2H_2O$	$Co(Lw)_2$
	II	250–450	82.90 (83.01)	2Lw	CoO
C-2	I	80–160	22.50 (21.98)	$2H_2O + 2CH_3CO$	$Co(LwOx)_2$
	II	260–460	85.51 (85.74)	2LwOx	CoO
C-3	I	80–250	13.82 (14.20)	$4H_2O$	$Ni(LwOx)_2$
	II	350–510	18.25 (18.31)	2LwOx	NiO
C-3(a)	I	330–460	82.90 (82.80)	2LwOx	NiO

Redfern [15]. The kinetic plots are presented in Fig. 2. The different steps in the pyrolytic reactions, their order and energies of activation are summarised in Table 4.
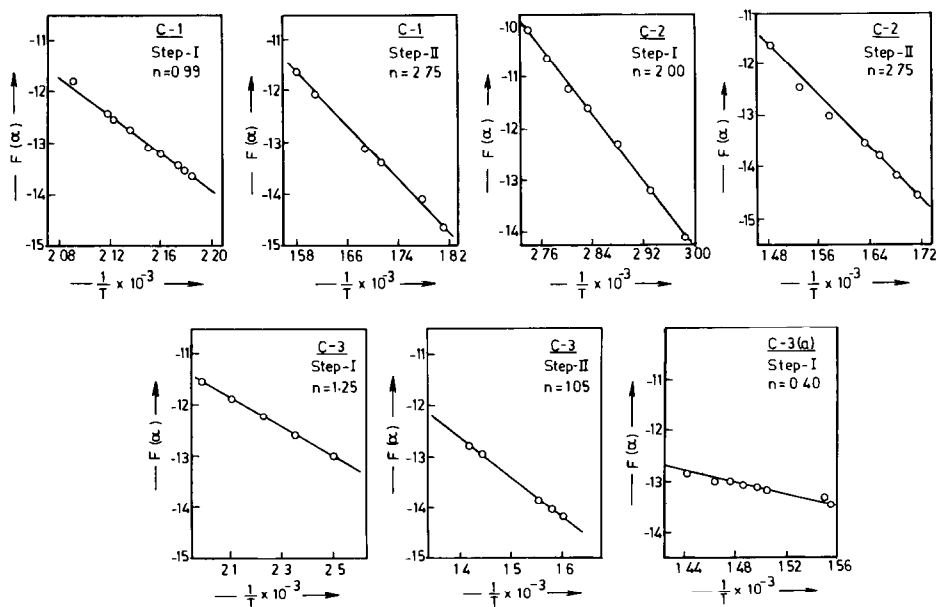

Fig. 2. Kinetic plots of **C-1–C-3a**.

TABLE 4

Data on activation energies from TGA in air

Comp. No.	Compound	Probable composition of group lost	Order n	E_a (kJ mol^{-1})
C-1	$Co(Lw)_2 \cdot 2H_2O$	$2H_2O$	0.99	164.50
		$2(Lw)$	2.75	111.20
C-2	$[Co(O\text{-}acylLwOx)_2] \cdot 2H_2O$	$2OH + 2CH_3CO$	2.00	131.70
		$2(LwOx)$	2.75	114.40
C-3	$[Ni(LwOx)_2] \cdot 4H_2O$	$4H_2O$	1.25	30.30
		$2(LwOx)$	1.05	63.67
C-3 [a]	$Ni(LwOx)_2$ [a]	$2(LwOx)$	0.40	41.35

[a] See footnote b of Table 1.

The role of the water molecules in quinone chelates

The dehydration step. In **C-1**, the water molecules participate in the complexation. The energy of activation needed for the water molecule in the coordination sphere in **C-1** is rather high, ≈ 82.5 kJ mol^{-1} compared with that for diaquobislawsone monoximatocobaltate(II) [4]. The effective spins in these chelates are determined by the water molecules in the inner or outer coordination spheres [16,17]. The role of the outer-sphere water molecules in the metal–quinone aggregates containing acyl functional groups as in WOC may be mimicked in this step of the **C-2** compound. However, its lawsone oxime derivative forms cobalt chelates with the water molecules in the inner coordination sphere, as reported earlier [4]. Here we compare **C-2** with the lawsone oximate of nickel, i.e. **C-3**, with adsorbed water molecules [18]. Because the latter nickel lawsone oximate has an E_a value that is the mean of the E_a of LwOx in its hydrated (**C-3**) and anhydrous (**C-3a**) compounds, ≈ 26.25 kJ mol^{-1}, it is comparable with its cobalt analogue (≈ 23 kJ mol^{-1}) [4]. The four water molecules are easily released at comparatively low temperatures (80 °C onwards) in **C-3** which requires an average energy of activation of ≈ 30.3 kJ mol^{-1}. Hence, the energy per adsorbed water molecule is ≈ 7.5 kJ mol^{-1}.

We can synthesise the anhydrous form of $Co(LwOx)_2 \cdot 2H_2O$ [4]. However, anhydrous **C-1** ($Co(Lw)_2$) cannot be synthesised, the result being a compound of molecular formula $[Co_2(Lw)_2(OH)_2] \cdot H_2O$. The TG residue, Co_2O_3, the chemical analysis and the IR spectrum (bridged hydroxyl stretch at ≈ 880 cm^{-1}) indicate its dimeric nature [19,20]. This again supports the characteristic behaviour of quinone chelates to form solvates [21].
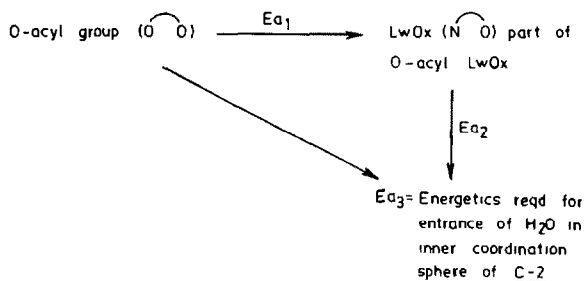
Correlation between the energetics for hydration in C-1 compared with C-2. **C-2** undergoes an acid hydrolysis reaction during thermolysis with the probable loss of two H_2O and two CH_3CO groups at temperatures from
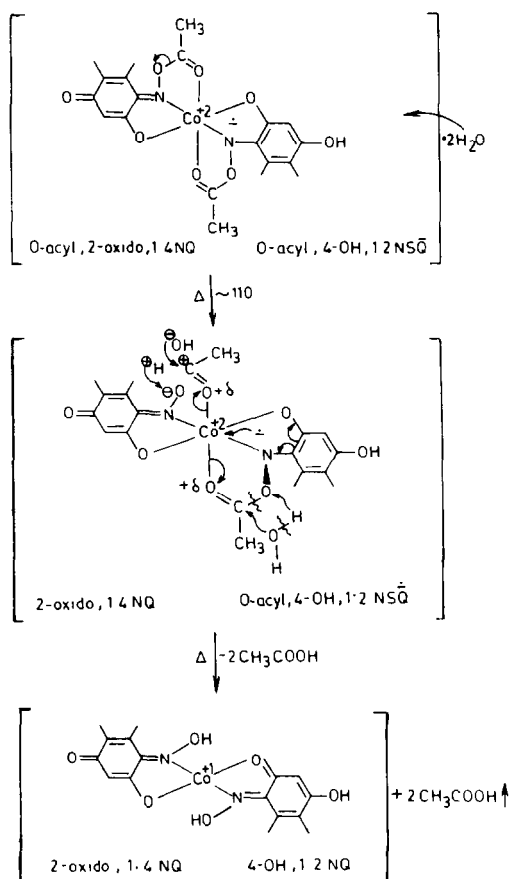
Scheme 1.

$110\,^{\circ}$C in the first step. The boiling point of CH_3COOH is in accordance with this temperature [22]. Hence the adsorbed water in C-2 enters the coordination sphere to react with the electrophile $CH_3\overset{\oplus}{C}O$ releasing CH_3COOH. Simultaneously, it protonates the oximino ligand (Scheme 1). Overall, there is loss of two OH and two CH_3CO groups with an energy of 131.7 kJ mol^{-1}. Using the additivity property of activation energy, the energy of activation for the CH_3CO group can be calculated as 58.27 kJ mol^{-1}. Here, the E_a required for the adsorbed water molecule is taken from the C-3 compound: E_a of CH_3CO per mole $= (131.7 - 7.575 \times 2)/2 = 58.275$ kJ mol^{-1}.

The first step of the thermolysis is due to the higher basic character of the ligand L-2. The second step in the thermogram indicates the decomposition of the oximino functional groups; the loss of 2LwOx requires an energy of activation of 57.2 kJ mol^{-1}. The E_a of the acyl functional group (58.27 kJ mol^{-1}) resulting from an acetate molecule is comparable with the

O-acyl group (O⌒O) $\xrightarrow{\quad Ea_1 \quad}$ LwOx (N⌒O) part of

O-acyl LwOx

$\downarrow Ea_2$

Ea_3= Energetics reqd for
entrance of H_2O in
inner coordination
sphere of C-2

Scheme 2.

E_a of Lw (55.6 kJ mol^{-1}) which has a (O⌒O) donor set. The log $^PK^H$ of both are similar (≈ 4) [23]. However, the E_a of the oximino part of C-2 (N⌒O), 57.2 kJ mol^{-1}, is also comparable with that of the above functional groups. This shows that the basicity of the oximino nitrogen in L-2 is reduced, due to substitution of the electron-withdrawing acyl group; hence, the Lewis base strength of the oximino ligand part in C-2 becomes equivalent to Lw. This accounts for the latter's hydrophilic character which results in the entrance of an H_2O molecule into the inner coordination sphere (see Scheme 1) [4].

Thus the energetics for the entrance of an H_2O molecule from the outer to the inner sphere during pyrolytic reactions in C-2, may be equated to the energy of water molecules in the coordination sphere of C-1 see Scheme 2.

The above reaction sequence shows good agreement with the Pythagorean type of relationship [24]

$$E_{a_3}(\text{calc}) = \left(E_{a_1}^2 + E_{a_2}^2\right)^{1/2}$$

$$= \left[(58.3)^2 + (57.2)^2\right]^{1/2}$$

$$= 81.67 \text{ kJ mol}^{-1}$$

$$= E_a \text{ of coordinated water in C-1 } (82.2 \text{ kJ mol}^{-1})$$

Finally, this suggests the roles of the different functional groups in water-oxidising complexes. The pH requirement of ≈ 4 for the medium may be fulfilled by the release of acetic acid during such biological processes. Hence, because the O⌒N⌒O function in C-2 incorporates all WOC essentialities with effective spin transfer due to the (NQ) (NSQ) coordination, it may be a good candidate for PS-II.

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