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# KINETICS OF DEHYDRATION IN CHELATES OF QUINONES INVOLVED IN PHOTOSYSTEM-II

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The solid-state deaquation of the *trans*- and *cis*-oximates of lawsone (I) and phthiocol (II) with cobalt(II) was investigated by means of non-isothermal thermogravimetry. The modes of deaquation during the thermolyses of hydrated oximates of (I) and (II) with compositions $CoL_2 \cdot 2H_2O$ were compared. The weight loss *vs.* temperature data were treated by using the Coats and Redfern relations. The kinetic data support a rearrangement-type mechanism for the deaquation of the oximate of phthiocol. The $E_a$ values for both the ligands and water molecules were found to be ~23 kJ/mol.

Notations

LwOx = lawsonemonoxime
PhthOx = phthiocolmonoxime
NSQ = naphthosemiquinone oxime radical
$E_a$ = energy of activation
L = ligand
PS-II = photosystem-II

Quinone complexes generally show a marked tendency to form solvates, which may be non-stoichiometric after a few hours at room temperature [1, 2]. Such complexes of quinones are known to be involved in the reactions of photosystem-II [3]. Therefore, it is of interest to examine the role of water in quinone chelates. To reveal the mechanisms, the reaction products in photolysis may be compared with their thermolysis products [4]. Except for a few reports [5–7], the kinetics and mechanism of metal-quinone chelates have not been thoroughly investigated. In the present paper, we try to interpret the reaction mechanism involved in the

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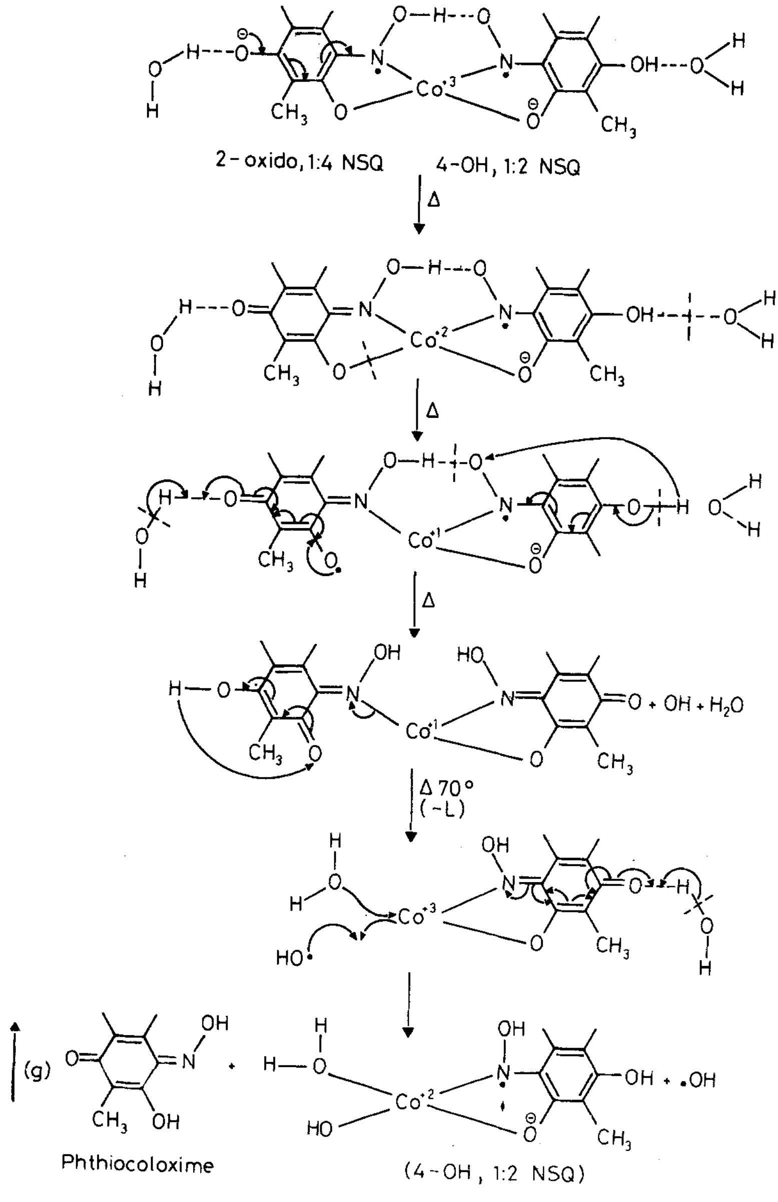
thermolysis of some hydrated and anhydrous compounds containing quinone oxime ligands (I, II) which may lead to another route to explain the photolytic reactions in PS-II.

**Scheme 1**



## Experimental

### *Instrumentation*

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

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

Elemental analyses of ligands and their metal chelates were performed in the microanalytical laboratory of the University of Poona. Metal estimation was carried out according to the procedure given by Vogel [8].

## Syntheses

All the chemicals used in the preparation of the ligands and metal chelates were A.R. grade. Lawsone (2-hydroxy-1,4-naphthoquinone) was obtained from Fluka company. Phthiocol (3-methyl-2-hydroxy-1,4-naphthoquinone) was prepared according to Fieser's procedure [9]. 1-Monoximes of lawsone and phthiocol were synthesized as per the procedures given in the literature [10].

The hydrated chelates of cobalt(II) with LwOx and PhthOx *C–2* and *C–4* were synthesized by employing procedures similar to those for the copper complexes reported earlier [10].

The procedure used to synthesize the anhydrous oximates of (I) and (II) by using triethyl orthoformate was similar to that for rare earth chelates [11].

## Results and discussion

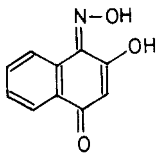
The anhydrous (*C–1* and *C–3*) and hydrated (*C–2* and *C–4*), reddish-brown cobalt(II) complexes of (I) and (II) have the compositions $CoL_2$ and $CoL_2 \cdot 2H_2O$, respectively (Table 1).

**Table 1** Analytical data on anhydrous and hydrated chelates of cobalt

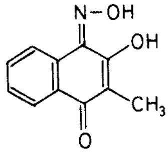
| No. | Compound | Yield, % | Decomp. temp., °C | Elemental analyses (calc.) | | | |
|---|---|---|---|---|---|---|---|
| | | | | C, % | H, % | N, % | Metal, % |
| *C–1* | $Co(LwOx)_2$ | 70 | 270 | 54.9 | 3.1 | 6.3 | 13.3 |
| | | | | (55.1) | (2.8) | (6.4) | (13.5) |
| *C–2* | $Co(LwOx)_2 \cdot 2H_2O$ | 65 | 290 | 49.9 | 3.5 | 6.0 | 12.4 |
| | | | | (50.1) | (3.4) | (5.9) | (12.5) |
| *C–3* | $Co(PhthOx)_2$ | 65 | 240 | 56.8 | 3.8 | 5.9 | 12.6 |
| | | | | (57.0) | (3.5) | (6.0) | (12.7) |
| *C–4* | $Co(PhthOx)_2 \cdot 2H_2O$ | 75 | 240–250 | 52.6 | 4.1 | 5.7 | 11.6 |
| | | | | (52.8) | (4.0) | (5.6) | (11.8) |

*IR studies*

Trans isomer(III) is detected in *C–1* from OH stretch absorption observed at 3400 and 3200 $cm^{-1}$, while the *cis* (IV) configuration in *C–3* is confirmed by the total absence of OH absorption [12], which is due to strong intra- and intermolecular H-bonding.

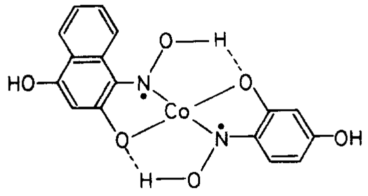


(I)



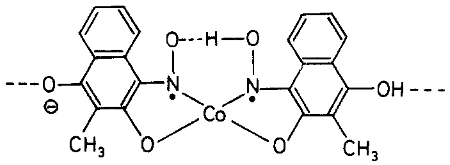
(II)

*trans (III)*



(III)

*cis (IV)*



(IV)

The NSQ coordination of both ligands in all compounds is assigned from $\nu_{C-O}$ and $\nu_{C-N}$ at ~1600 and 1575–1585 $cm^{-1}$, respectively [10]. In compounds *C–1* and *C–2*, $\nu_{C-N}$ is raised on coordination as compared with the ligand [13], but in compounds *C–3* and *C–4* the lowering of the imine absorptions governs the probability of the "back-coordination effect" [14–19], which may result in the oxidation of Co(II) to Co(III) (Scheme 1).

## *TG studies*

The TG curves for compounds *C–1* to *C–4* are presented in Fig. 1. The stoichiometries of the pyrolytic reactions of these compounds at different stages were ascertained. The weight loss curves for the anhydrous compounds *C–1* and *C–3* show one-step decomposition (~85%), while those for *C–2* and *C–4* display

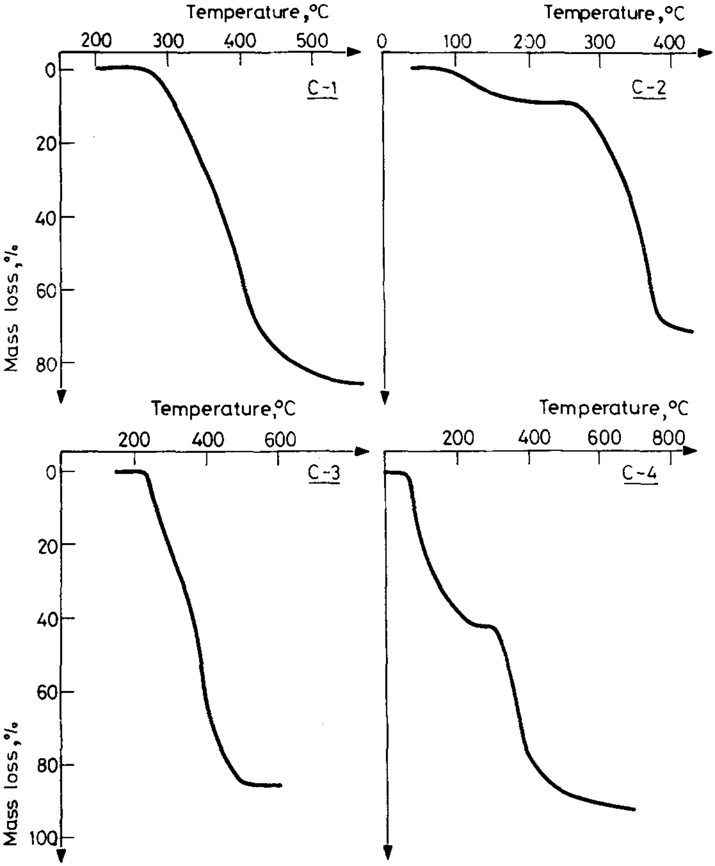


Fig. 1 TG curves of *C–1* to *C–4* compounds in air atmosphere

two steps. Since the pyrolysis is carried out in air atmosphere, the final decomposition product is CoO. The thermal stability sequence for these four chelates can be given as *C–4* < *C–3* < *C–1* < *C–2*. Comparison of the thermal stabilities shows that the compounds of LwOx (*C–1* and *C–2*) are thermally more stable than those of PhthOx (*C–3* and *C–4*). However, the sequence of their thermodynamic stability constants in solution is found to be the reverse [20]. This supports the pronounced "chelation" effect in PhthOx compounds as compared with LwOx compounds, which can be attributed to the methyl substituent at position 3 in (II).

The kinetic parameters were determined from the rising temperature expressions of Coats and Redfern [21]. The data on the steps of the thermal decomposition reactions, their order and the energy of activation are shown for all compounds in Table 2. The kinetic plots based on a nucleation growth mechanism as decomposition model are shown in Fig. 2.

**Table 2** Data on activation energies from dynamic TG in air

| No. | Compound | Step | Probable groups lost | Order, *n* | $E_a$, kJ/mol |
|---|---|---|---|---|---|
| *C–1* | $Co(LwOx)_2$ | I | 2 L | 0.33 | 45.42 |
| *C–2* | $Co(LwOx)_2 \cdot 2H_2O$ | I | $2\,H_2O$ | 2.00 | 46.41 |
| | | II | 2 L | 0.33 | 46.42 |
| *C–3* | $Co(PhthOx)_2$ | I | 2 L | 0.95 | 47.86 |
| *C–4* | $Co(PhthOx)_2 \cdot 2H_2O$ | I | L | 2.00 | 25.52 |
| | | II | $L+2\,H_2O$ | 0.66 | 71.80 |

The following inferences are made from the kinetic studies:

The anhydrous compounds *C–1* and *C–3* lose two ligands, starting at ~280°, which requires an average energy of activation of ~47 kJ/mol. Therefore, the mean activation energy to break the M–L bond for each ligand is ~23.5 kJ/mol. The hydrated compounds *C–2* and *C–4* undergo two-step decompositions, but these compounds follow different routes. Compound *C–2* loses two water molecules at lower temperature, requiring an energy of ~46.4 kJ/mol. This is comparable with the behaviour of the complex $Ni(Py)_4(SCN)_2$ [22]. Therefore, the mean activation energy for metal-hydrate bond rupture is ~23 kJ/mol, which is in the range of aquation energies reported by Wendlandt for cobalt complexes [23]. Since this energy is comparable with the activation energy of the ligand, PhthOx, there is a competition between their coordinations, which makes compound *C–4* thermally unstable. Hence, it shows the lowest decomposition temperature in this series. In the first step, compound *C–4* loses one ligand molecule, and in the second step two

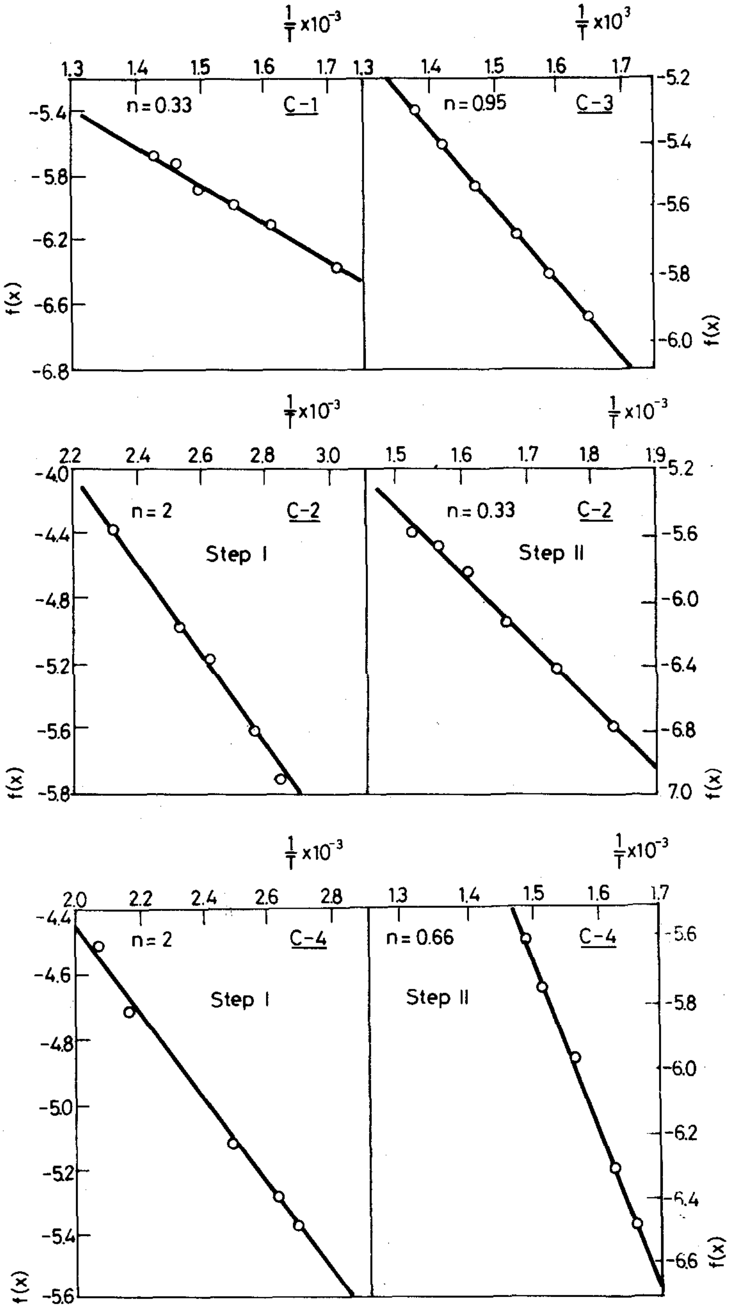


**Fig. 2** Kinetic plots of *C-1* to *C-4* compounds

water molecules are lost, together with the remaining ligand. $E_a$ for the first step, ~25 kJ/mol, corresponds to the loss of one ligand, but in the second step the overall activation energy is ~72 kJ/mol. This could be expressed as the sum of two intermediate processes, the losses of L and $2H_2O$ ($23.9+46.0 = 69.9$ kJ/mol). The additivity of the activation energy values could be validated in this series of compounds owing to the equivalence of the molecular compositions of the LwOx and PhthOx complexes.

Such different mode of reactions for compounds *C–2* and *C–4* may be due to the *trans* (III) and *cis* (IV) structures of these chelates, respective.y In compound *C–4*, the water molecule may be able to slip into the interstitial position causing little lattice distortion [24]. The water molecules in *C–4* are categorized as lattice-trapped water according to Berg's [25] third class. In compound *C–2*, the water molecules take part in coordination, which corresponds to the constitutional category. A slightly higher energy is required to lose the water molecules in compound *C–4* than in compound *C–2*, which is a measure of the high strength of the hydrogen-bonding in compound *C–4*. The reaction mechanism for the substitution of the water molecule/$OH^-$ in the coordination sphere after loss of the ligand, PhthOx, in *C–4* is similar to that of the deaquation process for the chromium complex [26]. The deaquation step in *C–4* could be illustrated as follows:

$$[\mathrm{Co}^{+3}(\text{2-oxido-1,4-NSQ}^{-2})(\text{4-OH-1,2-NSQ}^{-1})]\cdot 2\mathrm{H_2O(s)} \xrightarrow{70^\circ}$$

$$[\mathrm{Co}^{+2}(\text{4-OH-1,2-NSQ})(\mathrm{H_2O})(\mathrm{OH})](\mathrm{s}) + (\text{2-OH-1,4-NQ})(\mathrm{g})\uparrow$$

The detailed mechanism shown in Scheme 1 can be interpreted as involving ligand rearrangement reactions. In this compound *C–4*, the cobalt may be present in the +3 oxidation state, according to the electroneutrality principle and due to a back-bonding effect, but at elevated temperature it may transform into the +2 state [27, 28] and it becomes kinetically labile for ligand substitution, as it possesses less CFSE than the $Co^{3+}$ state.

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**Zusammenfassung** — Mittels nichtisothermer Thermogravimetrie wurde die Dehydratation der trans- und cis-Kobalt(II)-oximate von Lawson (I) und Phthiokol (II) untersucht. Die Arten der Dehydratation während der Thermolyse der hydratierten Oximate von (I) und (II) mit der Zusammensetzung $CoL_2 \cdot 2H_2O$ wurden verglichen. Bei der Auswertung der Massenverlust-Temperatur-Daten wurden Coats–Redfern Beziehungen angewendet. Die kinetischen Daten bekräftigen einen Umlagerungsmechanismus für die Dehydratation des Oximates von Phthiokol. Die $E_a$ Werte betragen sowohl für die Liganden als auch für Wasser etwa 23 kJ/mol.

**Резюме** — Методом неизотермической термогравиметрии изучено твердотельное обезвоживание транс- и цис-оксимов лавсона (I) и фтиокола (II) с двухвалентным кобальтом. Сопоставлен характер дегидратации хелатных соединений I и II состава $CoL_2 \cdot 2H_2O$ во время их термолиза. Температурные зависимости потери веса обрабатывались с помощью уравнений Коутса–Радферна. Кинетические данные дегидратации оксима фтиокола указывают на механизм реакции типа перегруппировки. $E_a$ значения как дла молекул лигандов, так и воды были равны приблизительно 23 кдж · моль$^{-1}$