Thermal and spectral properties of alkali metal complexes of vitamin K3 analogue phthiocol

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Abstract Hydroxynaphthoguinones, alkali, and alkali metal salts were used to synthesize several biologically important molecules. As hydroxynaphthoquinones act also as potential ligands, it is possible that alkali metal complexes may be formed as intermediates in such reactions. To ensure this, the reactions of 2-hydroxy-3-methyl-1,4naphthoquinone (phthiocol, a vitamin K3 analogue) with sodium metal, alkali such as NaOH and KOH, and alkali metal salts such as CH₃COONa, Na₂CO₃ and K₂CO₃ were studied in the present investigation. The products were characterized by various analytical techniques, namely elemental analysis, FT-IR, ¹H NMR, UV-Vis, thermogravimetric (TG) analysis, GC-MS, and DSC studies. 100 % reduction of the ligand was observed in Phth-1 with sodium metal as reducing agent. The solution of CH₃ COONa, NaOH, KOH, and K₂CO₃ in methanol facilitates the reduction of phthiocol ligand. The reduction of the ligands may be probably due to disproportionate reaction of the 'catechol' form and the fully oxidized naphthoquinone form of the ligand. The radical signatures of the ligands in complexes were detected by EPR studies and also by carbonyl frequencies in FT-IR spectra. Non-isothermal TG studies confirm the presence of adsorbed and coordinated water molecules. Residue formed after complete decomposition was observed to be 1/2 Na₂O in Phth-1 to Phth-3, K₂O in Phth-4, and 1/2 K₂O in Phth-5. Based on GC-MS

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and TG studies, three decomposition mechanisms are being proposed for all complexes.

Keywords Vitamin K3 · Phthiocol · Hydrogen bonding · TG studies · Vapochromic behavior · Hydroxy naphthoquinone · Naphthosemiquinone

Introduction

2-methyl-1,4-naphthoquinone is used as a vitamin K3 in mammals. Vitamin K3 in combination with vitamin C was studied for the potential treatment for prostate cancer [1-5]. Vitamin K prevents bleeding by increasing hepatic biosynthesis of prothrombin and other coagulation factors. It is also needed for healthy bones. Vitamin K3 is used as a source of vitamin K in the treatment of hypoprothrombinemia against vitamin K deficiency. Menadione is a vitamin precursor of vitamin K2, which can be converted in the liver to active menaquinones by chemical alkylation in vivo [6, 7]. Phytonadione (vitamin K1) and menaquinone (vitamin K2) occur in plants and are consumed in the diet.

Vitamin K is an essential nutrient often associated with the clotting cascade and has been the focus of considerable research in recent years, demonstrating an anticancer potential [6, 7]. Vitamin K is usually identified as a critical factor in blood coagulation; recent research has found that vitamin K is also a cofactor in bone metabolism [6]. Naphthoquinones and their substituents have been widely studied for their application in biological functions. Therefore, when the naphthoquinone ring is substituted by an appropriate alkyl chain, these compounds tend to exhibit anticancer and antitumor activity [7]. They also do present an antihemorrhagic activity, depending on the molecular

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structure. There are many synthetic forms of vitamin K, such as vitamin K3, vitamin K4, and vitamin K5, which are used in several areas including the pet food industry (vitamin K3) and to inhibit fungal growth (vitamin K5). Menadione (vitamin K3) is a synthetic derivative of the naturally occurring vitamins K1 and K2.

Thermal and spectral properties of naphthoquinone and their metal complexes were studied by several workers [8-10]. The decomposition of naphthoquinone ligands with loss of water molecules over the temperature range and solid phase transformation, melting, etc., can be detected by thermal studies. The activation energy of naphthoquinone ligands varies in metal complexes, as these ligands coordinate to metal ions in various oxidation states [11, 12]. Hydroxynaphthoquinones are redox active ligands. Scheme 1 shows the three different oxidation states of phthiocol.

KOH, NaOH, and alkali metal salts such as Na₂CO₃, K_2CO_3 and CH₃COONa are used to synthesize hydroxynaphthoquinone derivatives. Intrinsic radicals are observed in polycrystalline powder form of these derivatives. To find the origin of EPR signals in the hydroxy naphthoquinones, the reaction of 2-hydroxy-3-methyl-1,4-naphthoquinone (phthiocol; phth) was studied with 'Na' metal, alkali NaOH and KOH, and alkali metal salts CH₃COONa and K_2CO_3 in the present investigation. The abbreviations of the complexes are as follows: the synthesis with sodium metal (Phth-1), CH₃COONa (Phth-2), NaOH (Phth-3), KOH (Phth-4), and K_2CO_3 (Phth-5). Thermal and spectral properties of all the compounds have been studied, and decomposition mechanisms were proposed based on GC–MS and thermogravimetric studies.

Experimental

All the chemicals used in synthesis were of analytical grade. Menadione (2-methyl-1,4-naphthoquinone) was recrystallized from methanol prior to synthesis. Sodium metal was obtained from SD Fine chemicals. Milli-Q water was used for the experimental work of flame photometry. Anhydrous methanol was purified using the procedure reported in the literature [13].

Physical measurements

Elemental analysis was performed on Thermo Finnigan EA 1112 Flash series elemental analyzer. FT-IR spectra of phthiocol ligand and complexes Phth-1 to Phth-5 were recorded between 4000 and 400 cm⁻¹ as KBr pellets on SHIMADZU FT 8400 spectrometer. The concentration of Na⁺ and K⁺ ions in Phth-1 to Phth-5 were determined on SYSTRONICS flame photometer 128. AR-grade NaCl and KCl were used as standards for flame photometry analysis. UV-Vis spectra of all compounds were recorded on SHI-MADZU UV 1650 in methanol between 200 and 800 nm. The X-band EPR spectrum of all complexes was recorded at room temperature (298 K) and liquid nitrogen temperature(133 K) with VARIAN, E112 EPR SPECTRO-METER with microwave frequency 9.5 GHz with sensitivity of 5 \times 10¹⁰ spins and modulation of frequencies from 100 to 15 Hz at SAIF-IIT Powai, Mumbai, India.

DSC curves were recorded on TA waters model Q2000 instrument. Tzero aluminum pan was used as sample holder in DSC studies. Gas chromatograph-mass spectrums (GC-MS) were recorded on Shimadzu, GC-MS-QP5050. Liquid chromatograph-mass spectrums (LC-MS) were recorded on Shimadzu, LCMS-2010EV, with ESI source for ionization.

TG analyses have been performed on laboratory-constructed instrument. The details of each component are given below.

Balance

An electrical single-pan analytical balance, K-14 Super (K. Roy and Co., India), of 100 g capacity with an accuracy of \pm 0.1 mg is used and was mounted on a vibration-free, horizontal platform.

Furnace

Nichrome wire resistance furnace using a quartz tube with 32 mm (internal diameter) \times 250 mm (length) was constructed with good thermal insulation of approximately 3 cm above the windings. This assembly was then set into a

Scheme 1 Various redox forms of 2-oxido-3-methyl-1,4naphthoquinone. *I* oxidized naphthoquinone form (NQ⁻); *II* naphthosemiquinone form (NSQ⁻⁻), and *III* catechol form (CAT)



cement pipe of approximately 250 mm (height) and 70 mm (internal diameter). The inner space between the furnace and this cement pipe was filled up using slurry of plaster of paris, silica, and asbestos wool.

Thermocouple

The tip of the chromel-alumel thermocouple (24 gauze wires) was kept in the vicinity of the sample, and terminals were connected to a direct temperature measuring pyrometer with range 0–1200 °C (\pm 5 °C).

Temperature regulator

The terminals of the furnace were connected to a temperature regulator (Argo Transformers Co. Ltd., India, 15 Amp capacities).

Standardizations of thermobalance

The instrument was standardized by carrying out dynamic TG of standard sample such as $CaC_2O_4.H_2O$ and $CuSO_4.5H_2O$. The dynamic and non-isothermal TG experiments in air were perforated on this thermobalance.

Sample size	50-70 mg
Particle Size	200–250 mesh (55–70 µ)
Rate of heating	3–5 °C/min
Temperature range of study	30–900 °C
Thermocouple	Chromel-alumel
Sample container	Cylindrical quartz glass cup 6 mm (diameter), 20 mm (height)
Atmosphere	Static air

Synthesis

Synthesis of 2-hydroxy-3-methyl-1,4-naphthoquinone (*phthiocol*)

The preparation followed a minor modification of the published procedure [14]. Menadione (1.0 g; 5.8 mmol) was dissolved in 10 mL methanol and chilled in an ice bath. A solution of 0.2 g of anhydrous Na₂CO₃ and 1 mL of 30 % H₂O₂ in 5 mL of water was then added, and the reaction mixture was maintained at 0 °C. Addition of 100 mL of chilled water led to the precipitation of 2-methyl-1,4-naphthoquinoneoxide as colorless crystals, which were collected by filtration and dried in air. The solid obtained was treated with 5 mL concentrated H₂SO₄ and allowed to stand for 10 min. The addition of 20 mL water afforded a yellow precipitate, which was recrystallized from methanol containing a few drops of concentrated H_2SO_4 . The crude product was purified by column chromatography using 5 % methanol in toluene.

Synthesis of Phth-1

1 mmol of phthiocol (0.188 g) was dissolved in 15 mL anhydrous methanol. Na metal 1 mmol (0.230 g) was dissolved in 10 mL of anhydrous methanol. The two solutions were mixed under N_2 atmosphere with constant stirring for 20 min at 4 °C. Precipitated product was filtered and washed with diethyl ether and dried under vacuum.

Synthesis of Phth-2 and Phth-5

1 mmol of phthiocol (0.188 g) was dissolved in 15 mL anhydrous methanol. Alkali and alkali metal salts, viz 1 mmol CH₃COONa for Phth-2 (0.820 g), NaOH (0.400 g) for Phth-3, KOH (0.560 g) for Phth-4, K_2CO_3 (0.690 g) for Phth-5 each was dissolved in 10 mL of anhydrous methanol. The ligand and metal solutions were mixed with constant stirring over a period 20 min at room temperature (26 °C). Precipitated products were filtered and washed with diethyl ether and dried under vacuum.

Results and discussion

The synthesis of Phth-1 was carried out under N_2 atmosphere, and the temperature was kept constant at 4 °C, while the synthesis of all other complexes (Phth-2 to Phth-5) was carried out at room temperature (26 °C). The mole ratio of phthiocol to either 'Na', or alkali, or alkali metal salts was kept constant as 1:1 in synthesis of complexes. The products obtained are as hydrated complexes [11, 12]. Phth-1 is expected to form as anion radical complex or neutral radical complex of Na⁺ as the reduction is directly done by 'Na' metal (Table 1).

Concentration of alkali metal ions in all complexes, viz Na⁺ and K⁺ (wherever necessary) was determined by flame photometry (Table 2). The cation-to-anion ratio was found to be 1:1 in all complexes, while in Phth-4, it was observed as 2:1. The metal–ligand ratio in Phth-4 was confirmed after repetitive synthesis and characterization by elemental analysis (Supplementary material). The presence of additional K⁺ ion in Phth-4 may be probably due to coordination of ligand in monoanionic naphthosemiquinone radical form (form II in Scheme 1). The increase in concentration of Potassium ions in Phth-4 was also confirmed by flame photometric analysis. Weak triplet signal was observed $\sim g = 4$ in EPR of Phth-4, which confirms the coordination of phthiocol ligand in naphthosemiquinone form (form II in Scheme 1).

Comp	Color	UV-Vis bands/nm	Yield/%	Composition	Elemental analysis found/Calc. %		
					M. wt/g	С %	Н %
Phth	Yellow	287, 330, 388, 479	84	$C_{11}H_8O_3$	188.00	_	_
Phth-1	Red	286, 329, 481	83	C ₁₁ H ₇ O ₃ Na	210.16	62.51/62.86	04.48/03.35
Phth-2	Red	296, 329, 483	52	C11H9O4Na	228.16	57.27/57.90	04.31/03.09
Phth-3	Red	292, 329, 483	82	C ₁₁ H ₉ O ₄ Na	228.16	53.85/53.66	04.36/04.50
Phth-4	Red	295, 324, 479	73	C ₁₁ H ₁₂ O _{5.5} K ₂	310.41	42.82/42.56	03.86/03.89
Phth-5	Red	293, 331, 483	75	$C_{11}H_{13}O_6K_3$	358.51	36.53/36.85	02.53/03.36

Table 1 Elemental analysis and UV-Vis spectroscopy data for Phth-1 to Phth-5

Table 2 Observed Na⁺ value in ppm by flame photometry for Phth-1 to Phth-5

S. No.	Expected Na ⁺ , K ⁺	Phth-1	Phth-2	Phth-3	Phth-4	Phth-5
1	100	100.66	100.41	100.95	101.68	99.41
2	80	82.61	80.31	80.00	88.01	81.26
3	60	62.35	60.00	64.00	71.96	60.70
4	40	40.80	40.12	40.04	53.40	41.67
5	20	26.00	20.09	23.83	26.50	22.00

FT-IR studies

The v_{OH} stretching vibrations in solid state of free phthiocol ligand (Fig. 1) were observed at ~3371 cm⁻¹, whereas it was observed at 3471 cm⁻¹ in CCl₄ [15]. This



Fig. 1 FT-IR spectra of phthiocol and Phth-1 to Phth-5

band was observed as an overlap of v_{OH} and v_{C-H} vibrations in complexes Phth-3, Phth-4, and Phth-5, as the nature of this band was very broad between ~ 3700 and 2500 cm⁻¹. This may be due to the presence of hydrogenbonded water molecules in the coordination sphere or the hydrated water molecules in these complexes. A sharp band observed at ~ 1660 cm⁻¹ (Fig. 1; Table 3) in free phthiocol ligand, which was assigned to $v_{C=O}$ stretching vibrations; this vibrations were observed at 1662 and 1655 cm⁻¹ in CCl₄ [15]. The peak position of $v_{C=O}$ band shifts ~ 20 cm⁻¹ toward higher frequencies in Phth-1 to Phth-4 (Table 3), suggestive of metal to ligand $(M \rightarrow L)$ charge transfer.

The signatures of naphthosemiquinone coordination of the phthiocol ligand in all complexes can be evaluated by FT-IR spectroscopy. Mac et al. [16] studied quenching of triplet state of menadione (2-methyl-1,4-naphthoquinone; MeNQ) by amines. A triplet state of MeNQ (Scheme 2) was formed by flash photolysis, which shows FT-IR band at 1503 cm⁻¹, and was assigned to menadione radical anion (MeNQ⁻). This band was shifted to 1513 cm⁻¹ by addition of LiClO₄ salt; lithium ion does not bind to menadione; however, it gets associated with MNQ⁻⁻ radical anion and thus the vibrational frequencies shifted from 1503 to 1513 cm⁻¹. The band at 1536 cm⁻¹ was assigned to ketyl radical (MeNQH⁻) (Scheme 2). In FT-IR spectra of Phth-1 to Phth-5, a sharp band was observed at ~1521 \pm 2 cm⁻¹ (NSO^{-.}); this band may be assigned to NSQ^{-.} radical anion (Scheme 1) or to the coordinated $v_{C=O}$ vibrations of phthiocol ligand. Association of neighboring radical anions would generate a triplet state in solid

Table 3 Important FT-IR frequencies of phthiocol ligand and Phth-1 to Phth-5 complexes

Phthiocol	Phth-1	Phth-2	Phth-3	Phth-4	Phth-5
1660(s)	1672(s), 1641(s)	1678(s)	1668(s)	1670(s)	1653(sh)
1591(s)	1595(s), 1545(sh), 1519(s)	1575(br), 1519(sh)	1585(s), 1523(s)	1589(s), 1521(s)	1593(br), 1550(br)
1392(s)	1390(s)	1383(s)	1390(s)	1392(s)	1386(sh)
1276(s)	1280(s)	1265(br)	1280(s)	1280(s)	1276(br)
1211(s)	1222(sh)	1219(sh)	1230(sh)	1230(s)	1233(sh)
833(s)	835(sh)	835(s)	846(s)	844(sh)	848(s)
727(s)	727(s)	707(s)	731(s)	734(s)	734(s)
684(s),	617(s)	651(s)	621(s)	682(s),	671(s)
634(sh)				621(s)	

s sharp, sh shoulder, br broad



state. Radical signatures in all complexes were supported by EPR spectroscopy.

Paranaphthoquinone (p-NQ) vibration (1276 cm⁻¹) of free phthiocol ligand was shifted (~5 cm⁻¹) toward higher frequencies in Phth-1 and Phth-3 to Phth-5. v_{C-O} vibrations of free phthiocol ligand (1211 cm⁻¹) was shifted to 1225 ± 5 cm⁻¹ higher frequencies in all complexes, and δ_{CH3} vibration (1178 cm⁻¹) was shifted ~1130 ± 10 cm⁻¹ to lower frequencies in all complexes.

¹H NMR spectra

There were *six* resonance peaks expected for free phthiocol ligand and *five* peaks for alkali metal complexes Phth-1 to Phth-5, a singlet due to -OH and $-CH_3$, doublet due to C(5)H and C(8)H, and triplets due to C(6)H and C(7)H (Scheme 1). Phth-1 to Phth-5 show upfield shift in proton resonance of C(5) to C(8) protons as well as in δ C(3)–CH₃ as compared to phthiocol free ligand. A sharp singlet of C(2)OH in phthiocol free ligand at $\delta = \sim 10.9$ was absent in all complexes (Table 4).

Electronic spectral studies

UV–Vis spectra of free phthiocol ligand and Phth-1 to Phth-5 were recorded between 275 and 800 nm in methanol (Fig. 2). There were mainly three bands observed in methanol for all complexes as well as in free phthiocol ligand. Two bands in UV region were centered at ~327 nm for free phthiocol and these bands were assigned to $\pi \rightarrow \pi^*$ transition of quinonoid and benzenoid rings, respectively [17–19]. There was hypsochromic shift observed due to band at ~329 nm in Phth-1 to Phth-5. A single broad band was observed in all complexes as well as in free phthiocol ligand in visible region. This band is assigned with charge transfer transition.

TG studies of Phth-1 to Phth-5

The curve of free phthiocol ligand and all alkali metal complexes: Phth-1 to Phth-5 are shown in Fig. 3, and thermodynamic data are represented in Table 5.

The mass losses in all complexes start from ~ 30 to ~ 100 °C in TG studies, which accounts for loss of adsorbed water molecules [11, 12, 20]. The nature of TG curves varies in all complexes (Fig. 3).

The complexes Phth-1, Phth-3, and Phth-4 showed a pyrolytic decomposition involving four steps, whereas Phth-2 showed three steps and Phth-5 showed five steps in their pyrolytic decomposition. Step I in all complexes led to the loss of adsorbed water molecules, as this loss was observed at a temperature below 100 $^{\circ}$ C.

The step III and step IV in Phth-1 and Phth-4 led to decomposition of phthiocol anion, whereas in Phth-2 and

Comp. name	δ C(5)H(d)/J(Hz)	δ C(6)H(t)/J(Hz)	δ C(7)H(t)/J(Hz)	δ C(8)H(d)/J(Hz)	δ C(3)H(s)/J(Hz)	δ C(2)OH(s)/J(Hz)
Phthiocol	7.969/6.3	7.821/6.1	7.778/6.3	7.989/5.4	1.956	10.900
Phth-1	7.833/7.5	7.593/7.3	7.695/7.2	7.886/7.2	1.845	-
Phth-2	7.842/7.8	7.760/7.6	7.584/7.5	7.915/7.5	1.965	_
Phth-3	7.701/7.5	7.442/7.5	7.587/7.2	7.817/7.5	1.766	_
Phth-4	7.699/7.2	7.581/7.3	7.439/7.3	7.817/7.2	1.764	_
Phth-5	7.854/7.2	7.764/7.3	7.589/7.3	7.921/8.4	1.967	-

Table 4 Chemical shift δ /ppm in phthiocol and Phth-1 to Phth-5



Fig. 2 UV–Vis spectra of phthiocol and Phth-1 to Phth-5; methanol concentration used was $1 \times 10^{-4} \ M$

Phth-3, phthiocol anion decomposed in step II to step IV. The % mass loss of phthiocol anion in Phth-1 to Phth-5 varied as it was almost 85:15 in Phth-1 and Phth-2, 56:44 in Phth-4, and 44:56 in Phth-3 and Phth-5. Thus, decomposition mechanism varied in all complexes. The respective metal oxide, viz $\frac{1}{2}$ Na₂O or $\frac{1}{2}$ K₂O was formed after complete pyrolytic decomposition of Phth-1 to Phth-3, Phth-5, and K₂O for Phth-4.

The decomposition temperatures in all complexes were found to be on the higher side as compared to that of the free phthiocol ligand; thus, all the complexes were thermodynamically more stable as compared to the free phthiocol ligand. As an organic moiety, there was 100 % loss in mass observed in the curve of free phthiocol ligand.

DSC studies

DSC curves were recorded in the temperature range of 30-300 °C. There was a single endothermic peak observed due to melting point of free phthiocol ligand at ~173 °C in DSC curve (Fig. 4a). There were two (Phth-2 and Phth-5) and three (Phth-3) endothermic peaks observed in the temperature range ~100-270 °C (figures in Supplementary



Fig. 3 TG curves of Phth-1 to Phth-5

material). DSC curve of Phth-4 showed four endothermic peaks in temperature range $\sim 100-163$ °C (Fig. 4b).

GC-MS studies of phthiocol and Phth-1 to Phth-5

Similar fragmentation pattern was observed in GC-MS spectra for all complexes. The representative GC-MS

Table 5	Thermogravimetric	data for	Phth-1	to Phth-5
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Sr. No.	Mol. formula, Mol. wt./g	Step no.	Temp. range/°C	Mass loss/%	Probable composition of group lost	Residue/%
Phth-1	PhthNa.H ₂ O*, 228.17	Ι	035–039	05.02/05.92**	0.75 H ₂ O↑	PhthNa.0.25H ₂ O
		II	135–145	02.67/01.97	0.25 H ₂ O↑	PhthNa
		III	275-610	65.98/66.75	0.85 Phth↑	PhthNa _{0.15}
		IV	780-820	07.54/11.78	0.15 Phth↑	(Na ₂ O) _{0.5}
						18.79/13.58
Phth-2	PhthNa.H ₂ O, 228.17	Ι	094–099	07.05/07.89	$H_2O\uparrow$	PhthNa.
		II	315-524	63.53/66.76	0.85 Phth↑	PhthNa _{0.15}
		III	655-800	11.77/11.77	0.15 Phth [†]	(Na ₂ O) _{0.5}
						17.65/13.58
Phth-3	PhthNa.H ₂ O, 228.17	Ι	027-032	06.06/07.89	$H_2O\uparrow$	PhthNa.
		II	086-112	09.51/11.77	0.15 Phth↑	PhthNa _{0.85}
		III	131–790	23.43/22.78	0.29 Phth [†]	PhthNa _{0.56}
		IV	807-850	42.42/43.98	0.56 Phth [†]	(Na ₂ O) _{0.5}
						18.58/13.58
Phth-4	PhthK ₂ .2H ₂ O, 301.40	Ι	037-112	08.27/05.97	$H_2O\uparrow$	PhthK ₂ .H ₂ O
		II	148-202	14.85/05.97	$H_2O\uparrow$	PhthK ₂
		III	236-415	11.18/15.34	0.27 Phth [†]	Phth _{0.73} K ₂
		IV	447-892	31.31/41.47	0.73 Phth↑	(K ₂ O)
						34.39/31.25
Phth-5	PhthK.2.5H ₂ O, 271.31	Ι	027-029	03.16/03.31	$0.5 \text{ H}_2\text{O}^{\uparrow}$	PhthK.2H ₂ O
		II	076-110	06.22/06.63	$H_2O\uparrow$	PhthK.H ₂ O
		III	172-201	06.36/06.63	$H_2O\uparrow$	PhthK
		IV	239–520	26.19/29.08	0.44 Phth↑	PhthK _{0.56}
		V	600–750	38.71/37.00	0.56 Phth [†]	(K ₂ O) _{0.5} 19.36/17.35

* Phth Phthiocol ligand [2-oxido-3-methyl-1,4-naphthoquinone]

** Figures indicate calculated mass loss

Table 6 Value of gyromagnetic ratio 'g' Phth-1 to Phth-5

Sr. No.	$g_{\rm iso}~(298~{\rm K})$	$g_{\rm iso}~(133~{\rm K})$	$g_{\rm iso}(133 {\rm K})$ in Methanol
Phth-1	2.0552	4.2519	4.2519
Phth-2	Broad signal	1.9713	Broad signal
Phth-3	2.0072	2.0140	_*
Phth-4	Broad signal	4.2799	_
Phth-5	2.0078	-	_

* Not recorded

spectrum of free phthiocol ligand was shown in Fig. 5. Three decomposition pathways are proposed based on fragmentation patterns observed in GC–MS of phthiocol complexes and are shown in Scheme 3. Molecular mass formed after decomposition was compared with the % mass loss in TG studies. Decomposition occurred via

radical mechanism in all complexes. The decomposition mechanisms were proposed for free phthiocol ligand and complexes, Phth-1 to Phth-5. Fragmentation peaks were correspond to loss of 'CO and $-O-C' = CH^-$ groups.

EPR studies

EPR spectra of the radical anion of vitamin K3 have been studied in various solvents [21–31]. Hyperfine coupling constants of protons of methyl group of vitamin K3 are solvent dependent [25, 31]. In general, the spin density distribution in quinone chemistry is influenced by solvents via quinonoid oxygens and the total spin density remains unchanged in the quinonoid ring. NaOH, KOH, and KF in solvents (0.1 NaOH, methanol/water, ethanol/water, ethanol (abs), methanol, DMSO, THF) were also used to generate the anionic radicals of menadione (MNQ⁻⁻). The gyromagnetic ratio 'g' observed in the presence of above salts in various solvent is 2.00045 ± 0.00002 . It is also known that hydroquinone reacts with potassium fluoride



Fig. 4 DSC (Heating) curves of a phthiocol and b Phth-4

(KF) in methanolic solutions producing the dipotassium salt. A disproportionate reaction of the dinegative anion and the neutral substance would produce radical anions.

$$MNQ^{2-} + MNQ \rightleftharpoons 2MNQ^{-}$$

The powder spectra of menadione with 'KF' salt show potassium (I = 3/2) hyperfine with hyperfine coupling constant of 0.0166 mT. A salt of menadione cation radical will be formed as shown in the following reaction,

$$MNQ^{--} + K^+ \rightleftharpoons MNQK^-$$

 $MNOK^+ + K^+ \rightleftharpoons MNOK^+_2$

This salt shows EPR spectrum of axial symmetry.

In this investigation 1:1 M ratio of phthiocol with sodium, alkali and alkali metal salts were used to synthesize Phth-1 to Phth-5 complexes. With this proportion, only the hydroxyl group was deprotonated, and if the radicals are formed by this mechanism, they will be neutral radicals.

 $2Phth^{-} + 2Phth \rightleftharpoons 2Phth^{-}$

2 Phth⁻⁻ + 2 K^+ / 2Na⁺ \Rightarrow 2Phth⁻K / 2Phth⁻Na

A single line was observed at room temperature at $\sim g = 2.0552$ (at 298 K in Fig. 6, Table 6), whereas weak signal is observed at $\sim g = 4$ in polycrystalline powder or methanol solution (at 133 K in Fig. 7), X-band EPR spectra of Phth-1. It is reported that naphthoquinones could form polymeric structures through hydrogen bonding [30]. The radical spins of the neighboring molecules could interact with each other to form triplet state in Phth-1 as evidenced at 133 K. The weak signals observed for Phth-1 and Phth-4 (Supplementary information) at $g = \sim 4$ are indicative of ion pairs formation of the molecules and triplet state.



Fig. 5 GC-MS spectra of phthiocol ligand



Scheme 3 Proposed decomposition mechanism of phthiocol and Phth-1 to Phth-5



Fig. 6 Polycrystalline powder, X- band EPR spectra of Phth-1 at 298 K (field set: 3000 G, scan range: 2000 G, time constant: 0.63 s, scan time: 4 min, modulation amplitude: \times 2 G, modulation frequency: 100 kHz, receiver gain: $1.6 \times 10^3 \times 10$, microwave power: 5 mW, temperature: 298 K, microwave frequency: 9.1 GHz)



Fig. 7 X-band EPR spectra of Phth-1 in methanol at 133 K (field set: 4000 G, scan range: 2000 G, time constant: 0.63 s, scan time: 4 min., modulation amplitude: $\times 2$ G, modulation frequency: 100 kHz, receiver gain: $1.6 \times 10^3 \times 10$, microwave power: 5 mW, temperature: 133 K, microwave frequency: 9.1 GHz)

Conclusions

The reactions of 2-hydroxy-3-methyl-1,4-naphthoquinone with sodium (Phth-1), alkali (NaOH (Phth-3) and KOH(Phth-4)), and alkali metal salts such as CH_3COONa (Phth-2) and K_2CO_3 (Phth-5) were studied in this paper. The products were characterized by various analytical techniques, namely elemental analysis, FT-IR, ¹H NMR, non-isothermal thermogravimetric studies (TG), and DSC studies. The radical signatures of the phthiocol ligand in complexes were evaluated by EPR studies. 100 % reduction was observed to phthiocol ligand in Phth-1. The solutions of CH₃COONa, NaOH, KOH, and K₂CO₃ in methanol are basic, and hence, it will facilitate the

reduction of the phthiocol ligand in all complexes. This reduction may be most probably due to disproportion reaction of 'catechol' form (form III, Scheme 1) and the fully oxidized naphthoquinone (NQ) form of the ligand (form I, Scheme 1). Half field triplet signal was observed in polycrystalline powder EPR spectra of Phth-1, Phth-2, and Phth-5. A triplet state may be generated by the interaction between radical spins of the neighboring coordinated naphthosemiquinone form phthiocol ligands. Thus, EPR studies also revealed the polymeric nature of these complexes.

Pyrolytic decomposition of all compounds was studied by non-isothermal TG studies in air atmosphere. Pyrolytic decomposition of phthiocol ligand in all complexes was observed to involve two or more steps. Residue formed after complete decomposition of complexes is observed to be $\frac{1}{2}$ Na₂O in Phth-1 to Phth-3, K₂O in Phth-4, and $\frac{1}{2}$ K₂O Phth-5. Based on GC–MS and TG studies, three decomposition mechanisms were proposed for all complexes.

Alkali KOH and NaOH, and alkali metal salts such as Na_2CO_3 , K_2CO_3 , and CH_3COONa are used to synthesize hydroxynaphthoquinone derivatives. Intrinsic radicals are observed in polycrystalline powder form of these derivatives, for example, in synthesis of naphthoquinone oximes [32]. The present investigation concludes that alkali metal complexes of hydroxy naphthoquinones may form as intermediates of such reactions.

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