Synthesis, characterization, thermal decomposition and kinetic parameters of Ni(II) and Cu(II) terephthalate-8Hq complexes

A P Mishra, V K Tiwari & R Singhai*

Department of Chemistry, Dr. H.S. Gour University, Sagar, 470003 (India)
E-mail: rashmitiwari@epra.com
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Ni(II)-8Hq terephthalate and Cu(II)-8Hq terephthalate complexes have been synthesised and characterized by elemental analysis, magnetic measurements, IR spectra and UV-Vis spectra. The complexes have also been analysed thermogravimetrically for the evaluation of their decomposition kinetic parameters. The thermal decomposition of the compounds occurs mainly in two steps. Kinetic parameters, (E*, Z and ΔS*) have been determined by using three different methods.

Terephthalates are known in industry for their polymeric, resistant and tolerant nature. Besides industrial and biological significance, mixed ligand chelates have their theoretical and chemical importance where we interpret the phenomena of ligand–ligand and metal–metal interaction in solution as well as in isolated solid state1,2. The preparation and thermal decomposition of metal terephthalates have been studied earlier3. Sharma et al.4 have prepared some complexes of metal terephthalates and their thermal studies have also been studied but very limited work on high temperature solid state behaviour of metal terephthalate complexes have been done. The present work describes the kinetic parameters (E*, Z, and ΔS*) of Ni(II) and Cu(II) chelates with 8-hydroxyquinoline. Such values are determined through TG and DTA curves using Coats–Redfern5, Piloyan-Novikova6 and Horowitz-Metzger7 methods.

Experimental

Metal terephthalate complexes have been prepared by the reaction of metal terephthalate of Ni(II) and Cu(II) with 8-hydroxyquinoline in 1:2 molar ratio in ethanol, slight amount of 0.1N HCl was added and the pH of the reaction mixture was adjusted to 4.5-5.5. The reaction mixture was then refluxed for about 7 h on a water bath. The refluxate was allowed to cool and stand for about 2h. The coloured precipitate thus obtained was filtered and washed three or four times with ethanol followed by ether. The product was dried first in a desicator over anhydrous CaCl₂ and after that in an electric oven at 70°C. The reagents used for the synthesis of the complexes were of analytical grade BDH Merck, Sisco and Loba.

Structural characterization was carried out by elemental analysis, infrared spectra, UV-Vis (dr.s.) spectra and magnetic measurements. The compounds were thermogravimetrically analysed for obtaining simultaneous DTA-TG curves Coats–Redfern5, Piloyan-Novikova6 and Horowitz-Metzger7 methods were employed for finding the kinetic parameters and mechanism (Fig. 1).

Elemental analysis, infrared spectra and UV-Vis (diffuse reflectance) spectra were recorded at CDRI Lucknow. The magnetic measurements were made by Gouy method. The thermograms were recorded at RSIC Nagpur, at a heating rate of 20K min⁻¹ in air atmosphere.

Results and discussion

The elemental analysis data (Table 1) reveal that compounds have the composition [Ni L₂(H₂O)₂ T] and H₂[Cu L₂ T]. A feeble solubility and slight solvolysis in common organic solvents precluded the measurement of conductance of these complexes4,8,9. Rather high decomposition temperature, practically insoluble behaviour towards solvents and to certain extents lowering magnetic moments values also suggest about the slight polymeric tendency of the complexes4,10,11.

For observing the phenomenon of complexation, the IR band positions of 8-hydroxyquinoline have been taken from the literature as a reference12,14. The strong band as a result of the vibration of pyridine ring nitrogen (C=N-) has been found to shift from 1580 cm⁻¹ (in 8-Hq) to 1560±10 cm⁻¹ (in complexes), suggesting its involvement in coordination. An intense band at around 1400 cm⁻¹ and another at around 1100 cm⁻¹ in 8-Hq have been assigned to phenolic-OH and C-O, respectively14,16. In the IR spectrum of Ni(II) complex, practically negligible change occurs in the band position of both the groups i.e. phenolic-OH and C-O. But in case of Cu(II) complex the phenolic –OH band disappears and a
positive shift of about 50 cm\(^{-1}\) appear also in vC-O. This indicates that the ligand 8-Hq behaves as a monodentate neutral coordinating species with Ni(II); while in Cu(II) complex, 8-Hq acts as an anionic bidentate ligand chelating through nitrogen and deprotonated phenolic group oxygen.\(^{12,16}\) The characteristic carboxylate bands due to terephthalate anion appears at 1640±10 and 1340±10 cm\(^{-1}\) in complex spectra with respect to their positions in ligand at 1680 and 1360 cm\(^{-1}\) (ref. 14-16). This observation works as an evidence for terephthalate's chelation with metal ion. A broad band at 3450 cm\(^{-1}\) and a medium sharp band at 770 cm\(^{-1}\) have respectively been assigned to stretching and rocking modes of coordinated water in Ni(II) complex. New bands at 470 and 390 cm\(^{-1}\) in nickel (II) complex and 400 and 500 cm\(^{-1}\) in copper (II) complex have respectively been assigned to vM-O and vM-N vibrations\(^{13,16}\).

In the reflectance spectrum of Ni (II) complex, three bands have been observed. A shoulder occurring at 11235 cm\(^{-1}\) may be assigned to the \(^{3}A_{2g} \to ^{3}T_{2g}(v_4)\) transition. The middle band \(v_2\) has splitted into two, perhaps due to spin-orbit coupling and distortion in regular symmetry\(^{17,18}\). Its band position around 16393 cm\(^{-1}\) to 17543 cm\(^{-1}\) has been attributed to \(^{3}A_{2g} \to ^{3}T_{1g}(v_4)\) transition. Relatively, a higher energy band at 24390 cm\(^{-1}\) has been ascribed to \(^{3}A_{2g}(F) \to ^{3}T_{1g}(P)\) transition. The ligand field parameters viz., 10Dq, B (Racah parameter), \(\beta\) (Nephelauxetic ratio), \(\beta^0\) (covalent character) and LFSE have been evaluated\(^{17,18}\) and their values are as 11235 cm\(^{-1}\), 606 cm\(^{-1}\), 0.56, 43.3 and 161.65 kJ/mol, respectively. Values of ligand field parameters\(^{17,18}\) reflects that the M-L bond is sufficiently strong bearing 43.8% covalency; which in turn suggest enough overlapping of metal orbitals with the ligand orbitals. Ligand behaves as moderately strong field ligand. The value of observed magnetic moment of this Ni(II) complex is 2.92 B.M. The reflectance spectrum of Cu(II) complex exhibits a broad band which appears rather bifurcated into two. The two band positions at 12345 and 15384 cm\(^{-1}\) may be because of the Jahn-Teller distortion, spin-orbit coupling and lowering of symmetry and hence have been considered belonging to transition \(^{2}E_g \to ^{2}T_{2g}\) (splitted). The value of 10 Dq and LFSE have been found\(^{17,18}\) to be 14371 cm\(^{-1}\) and

![Fig. 1—Piloyan-Novikova (P-N), Coats-Redfern (C-R) and Horowitz - Metzger (H-M) Plots of Ni(II) Complex [First decomposition stage]

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molecular Formula/ wt.</th>
<th>Colour</th>
<th>Found</th>
<th>Calc</th>
<th>Magnetic measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(II)</td>
<td>[Ni L(_2) (H(_2)O)(_2)] T</td>
<td>Yellowish</td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>L = C(_9)H(_7)NO</td>
<td>green</td>
<td>(56.10)</td>
<td>(4.05)</td>
<td>(5.49)</td>
</tr>
<tr>
<td></td>
<td>T = C(<em>6)H(</em>{12})O(_4)</td>
<td>&gt;340°C</td>
<td>548.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(II)</td>
<td>H(_2) [Cu L(_2) T]</td>
<td>Greenish</td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>L = C(_9)H(_6)NO</td>
<td>cream</td>
<td>(59.11)</td>
<td>(3.38)</td>
<td>(5.20)</td>
</tr>
<tr>
<td></td>
<td>T = C(<em>6)H(</em>{12})O(_4)</td>
<td>&gt;310°C</td>
<td>515.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
103.38 kJ/mol. The observed magnetic moment is 1.77 B.M.

Electronic spectral assignments\(^{17,18}\), ligand field data and magnetic moments favour the distorted octahedral stereoarrangement for both of the above complexes.\(^{17,18}\)

**Thermal decomposition**

(a) Ni(II) 8-Hq terephthalate complex - A careful analysis of thermogram of Ni(II) 8-Hq terephthalate complex indicates that complex compound is stable up to 100°C, an elimination of two coordinated molecules of water has been observed on progression up to temperature 150°C (Remaining weight% obs./cal. 92.92/92.66). Almost negligible weight loss occurs between the temperature range 150-250°C indicating the complexes having two coordinated molecules of water which in turn reflects as a horizontal from the pyrolysis curve. Above 250°C, a gradual weight loss continues up to 310°C indicating the decomposition of the ligand moiety; however a very small fraction of the chelated ligand i.e. two nitrogens, two oxygens and four carbon atoms remain attached with metal ion at this temperature (Remaining weight%, obs./cal. 58.00/60.2). No change in weight appears between the temperature 130°C to 430°C, but after 430°C, a quick loss in weight occurs, which is reflected as an inflection in the curve between the temperature region 430°C to 450°C. A horizontal zone beyond 450°C suggest about the ultimate product which in oxygenated atmosphere, is an oxide of nickel (Remaining weight %, obs./cal. 14.00/13.58).

(b) Cu(II) 8-Hq terephthalate complex — The thermogram of the complex shows no weight loss up to 215°C indicating the absence of any lattice or coordinated water in the complex. A gradual increase in temperature above 215°C is accompanied by loss in weight up to 300°C, which indicates the decomposition of coordinated ligand, but incomplete. Some directly chelated atoms (a ligand moiety) still remains associated with central metal (Remaining weight %, obs./calc. 63.00/64.8). Above 340°C a deep inflection in the curve occurs which ranges upto 360°C. The loss in weight in the region corresponded mainly with the degradation of terephthalate unit. A further increase in temperature above 360°C witnesses no loss in weight and this constant weight region is due to copper oxide which appears as a final pyrolysis product (Remaining weight %, obs./cal. 16.00/15.35).

**Kinetics of decomposition**

The fractional weight loss(\(\alpha\)) and the corresponding \((1-\alpha)^n\) have been calculated from TG curves at different temperatures, where 'n' depends upon the reaction model and \(\alpha = (w_i-w_f) / (w_0-w_f)\). The \(T\) vs \((1-\alpha)\) curves constructed on the basis of TG data for all the complexes, are more or less of the same pattern. The curves begin with an acceleratory period without any apparent induction period, thus indicating that no surface nucleation on branching occurs before the start of these steps\(^{9,20}\). The decomposition reaction of the complexes was subjected to non-isothermal kinetic studies and the weighted least square method was used for obtaining best fit for linear plots by applying the data to various equations\(^5\) and thus the kinetic parameters viz., energy of activation \((E^*)\), frequency factor \(Z\) and entropy of activation \((\Delta S^*)\) were evaluated from plots. The value of frequency factor was evaluated using Eq. (1) for C-R\(^2\) and P-N\(^6\) methods, while the value of \(Z\) in case of H-M\(^7\) method was calculated using Eq. (2). The entropy of activation \((\Delta S^*)\) was calculated by employing Eq. (3).

\[
\text{Intercept} = \log \frac{Z}{\beta E} \quad \ldots (1)
\]

\[
Z = \frac{E^*}{RT_m} \beta \exp \left(\frac{E^*}{RT_m}\right) \quad \ldots (2)
\]

or \(\Delta S^* = 2.303 R \log Z / K T \quad \ldots (3)
\]

where K represents Boltzman constant, h the Planck’s constant, \(\beta\) rate of heating, \(R\) molar gas constant and \(T_m\) peak temperature. The values of \(E^*\), \(Z\), \(\Delta S^*\) are given in Table. The mechanism involved in decomposition is random nucleation and apparent order of reaction is one.

The value of thermal kinetic parameters (Table 2) obtained by C-R\(^2\) and P-N\(^6\) methods are quite consistent while values by H-M\(^7\) method differs noticeably (Fig. 1). Therefore C-R and P-N methods may be considered more suitable for assessing the parameters. Generally, values of \(Z\) increases with decrease in \(E^*\) and the higher value of activation energy suggests the higher stability,\(^{21}\) but there lies some more inherent physical and chemical factors which may cause a change or deviation in this trend\(^{9,22}\). Higher values of \(E^*\) (activation energy) and lower values of \(Z\) (frequency factor) favours the reaction to proceed slower than normal. In present
studied, the numerical values of activation energy $E^*$, frequency factor ($Z$) and entropy of activation altogether indicates about the smoothness of the feasibility and reaction rate of the initial reactants and intermediate stage compounds. The negative values for entropy of activation indicates that the activated complex has a more ordered or more rigid structure than the reactants or intermediate (activated complex) and the reactions are slower than normal.

Quantitatively, slight change in the entropies $S^*$ of the compounds (than $E^*$) can set a reaction governing factor at.

Such kinetic parameters can necessarily be treated as reaction course governing under particular conditions, but their particular physical significance and intrinsic behaviour become generalised with the change in conditions. The order of stability on thermal decomposition temperature and the energy of activation is almost similar or different for two decomposition steps. The variation in the trend might be interpreted to be on account of some intermolecular interactions (structural as well as electronic) occurring therein, besides several experimental factors.

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References
