

A Non-Isothermal Decomposition and Kinetic Studies of Some Copper-Cyanoferrates

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Abstract. The compounds, Copper-hexacyanoferrate (II), Copper-hexacyanoferrate (III) and Copper-nitrosopentacyanoferrate (II) have been studied by TG method. The non-isothermal degradation of the compounds was done at a uniform heating rate of 10K min^{-1} in air and the simultaneous DTA and TG curves were recorded. The thermal decomposition of the compounds occur mainly in two steps. The intermediates formed during decomposition usually undergo further decomposition without remaining stable over a considerable range of temperature. The TG data of relevant steps of thermal degradation have been analysed for the study of solid state kinetics. Kinetic parameters viz. energy of activation, frequency factor and entropy of activation were determined by Coats-Redfern, Piloyan-Novikova and Horowitz-Metzger methods. The order of stability of compounds is found to be Copper -HCF (III) > -NPCF (II) > -HCF (II).

1. Introduction

The cyano compounds of transition elements have been receiving attention for a long time owing to their physico-chemical and bio-chemical significance. The high temperature thermal studies of transition metal cyanoferrates in air or oxygen have been demonstrated to be advantageous for the preparation of orthoferrites and other oxides of unique magnetic and catalytic properties¹⁻³. The highly exothermic decomposition nature of cyanoferrates is helpful in deciding them as explosives⁴. The electrochemical behaviour of cyanoferrates has been studied in detail in past decades but very limited work has been done on high temperature solid-state behaviour of metal cyanoferrates⁵⁻⁸. Ludwig et al have discussed some applications of thermal analysis to the coordination chemistry⁹⁻¹⁰. This paper describes the non-isothermal degradation behaviour, mechanism of decomposition and kinetic parameters of copper ferrocyanide, -ferricyanide and - nitroprusside.

2. Experimental

A double decomposition of copper(II) sulphate and potassium ferrocyanide/ferricyanide/nitroprusside (AR grade), yield precipitates; which were washed thoroughly with distilled water and dried (at 50°C). These were used for the

purpose of the analyses. Structural characterization was carried out by IR and elemental analysis.

The compounds were thermogravimetrically analysed by a Shimadzu- DT-30. Thermal Analyser (Japan) for obtaining simultaneous DTA-TG curves. Heating rate was kept at 10K min^{-1} , in air atmosphere. Coats- Redfern¹¹, Piloyan-Novikova¹², Horowitz-Metzger methods¹³ were employed for deducing thermodynamic and kinetic parameters¹⁴.

3. Results and Discussion

Elemental analysis data reveal that compounds have the composition $\text{Cu}_2[\text{Fe}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$, $\text{K Cu}[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ and $\text{Cu}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 3\text{H}_2\text{O}$.

IR spectra of compounds¹⁵ show a strong and broad band at about 3400 cm^{-1} and a medium, and sharp band at 1610 cm^{-1} due to stretching and bending vibration of -OH group of water respectively. Characteristic ir frequencies due to $\nu_{(\text{CN})}$, $\nu_{(\text{Fe-CN})}$, $\nu_{(\text{Fe-C})}$, and $\nu_{(\text{M-O})}$, have been observed at 2080 ± 30 , 580 ± 20 , $430\text{-}510\text{ cm}^{-1}$ and $460\text{-}540\text{ cm}^{-1}$ respectively. In copper nitroprusside, a strong and sharp band appears at about 1960 cm^{-1} which is due to nitrosyl group.

The TG analyses of all the three compounds have been carried out, but for the reason of economy of space, the data and important plots for only one representative case are shown here (Fig 1-6).

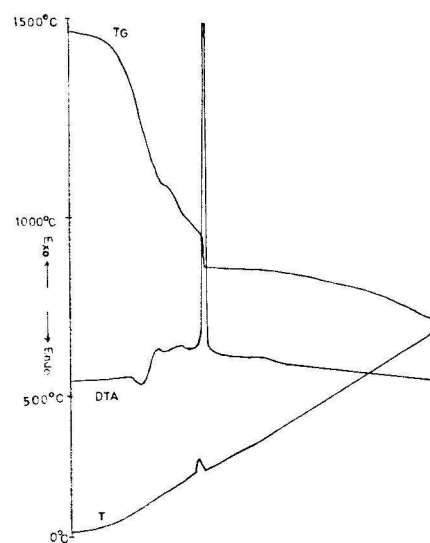


Fig. 1. TG-DTA curves of Cu-Hexacyanoferrate(II)

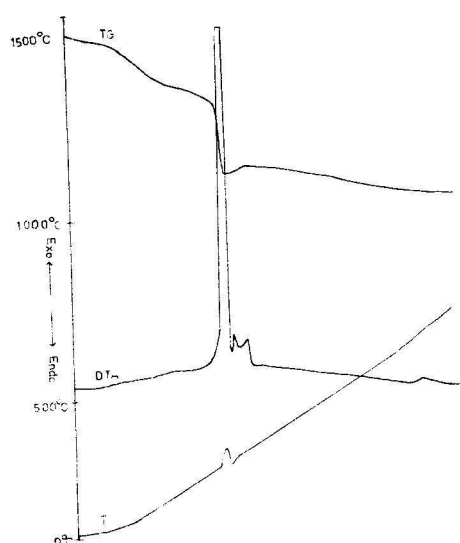


Fig. 2. TG-DTA curves of Cu-hexacyanoferrate (III)

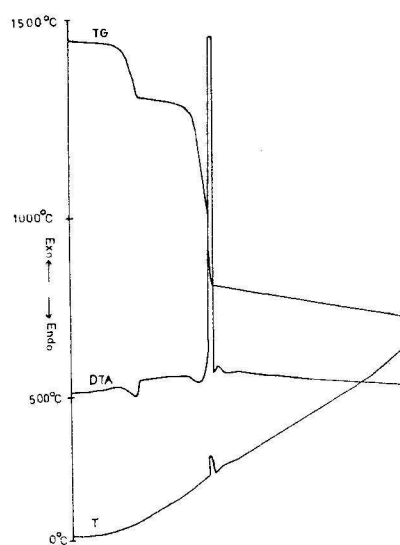


Fig. 3. TG-DTA curves of Cu-Nitrosopentacyanoferrate (II)

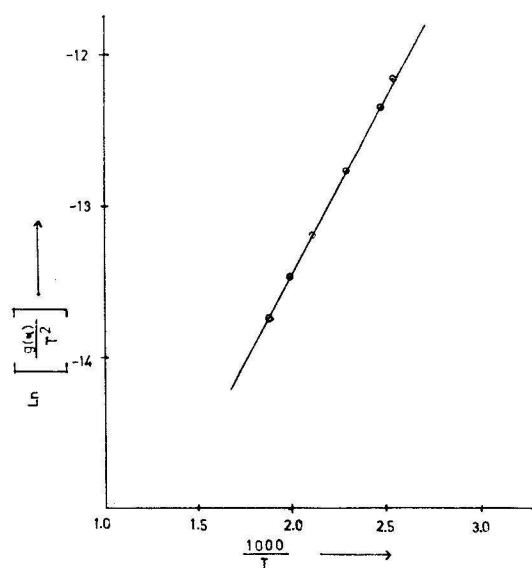


Fig. 4. Coats-Redfern plot of [Cu-hexacyanoferrate (II)]

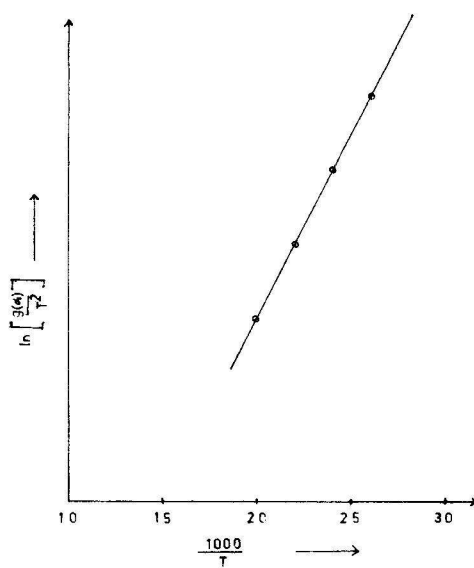


Fig. 5. Piloyan-Novikova plot of [Cu-hexacyanoferrate (II)]

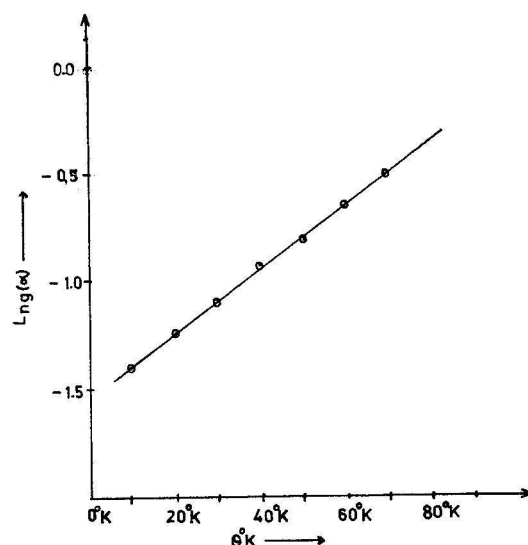


Fig. 6. Horowitz-Metzger plot of [Cu-hexacyanoferrate (II)]

(i) Thermal Decomposition :

(a) Copper-hexacyanoferrate (II) : The thermogram (TG-DTA) of the hydrated compound shows that dehydration occurs between 328 K to 393 K. A weak endotherm at about 373 K indicates the water molecules in lattice¹⁶ (wt. loss, observed 24.0%; cal. 24.2%). The thermal decomposition of the dehydrated compound starts at 403K and a regular and speedy loss in weight continues upto 538K which corresponds with the loss of four -CN in one step (wt. loss 48.5%, cal. 47.5%). A sharp and deep exotherm appears at 413K. The thermogram exhibits almost a horizontal (no wt. loss) between 548-648K. The residue starts decomposing further after 648K, and the weight loss during 648-923K, corresponds to complete rupture of iron cyanide. A mixture of ferrites, oxides and carbides may be inferred as pyrolysis products (1-9, 17).

(b) Copper hexacyanoferrate (III) : On non-isothermal pyrolysis, the compound eliminates the associated water-molecules between 333-423K (wt. loss, obs. 10.1%, cal. 10.9%). A slow decomposition of the dehydrated compound starts at 463 K which becomes fast between the temperature 533-553 K. The loss in weight at this point corresponds with the loss of two cyanides (wt. loss, obs. 26.5%, cal. 25.2%). One sharp and large and other small exotherm appears at 533 K and 553 K respectively. Further, a slow decomposition of the remaining residue starts at 663 K,

indicating complete rupture of the compound giving end products which may be a mixture of iron carbide, ferrite and metal oxides beyond 923K^{1-9,17}.

(c) Copper nitrosopentacyanoferrate (II) : The compound dehydrates upto 383 K. A loss in weight is almost negligible between the temperature 383-453K. Further, the process of thermal degradation starts which become fast between temperature 483-503K. The weight loss in this region corresponds to elimination of one - NO and three -CN groups (wt. loss, obs. 48.0%; cal. 46.5%). The remaining residue starts decomposing again at 573 K, and the resulting pyrolysis products after 923K may be the ferrites oxides and carbides^{1-9,17}.

In general, the water of hydration may be considered as either crystal or coordinated water. According to Nikolaev et al¹⁶, water eliminated below 423 K can be considered as crystal water. In the present study, the removal of water from the compounds is complete before 423K. The transformations in the internal structure, composition and oxidation states of metal ions in intermediates/products beyond 673K appear complex. It is suggested that a mixture of metal carbides, ferrites and oxides may be the products between the temperature range 673-923 K, depending on the specific case. Beyond 923 K, oxides of copper and iron may be formed as end products in oxygenated atmosphere^{1-9,17}. The order of thermal stability on the basis of first decomposition temperature is found to be : Copper hexacyanoferrate (III) > - nitrosopentacyanoferrate (II) > - hexacyanoferrate (II).

The decomposition products of all the three compounds at different steps were confirmed from their analyses and i. r. spectrum. The i. r. spectra of the compounds were recorded at four stages of thermal degradation i.e. hydrated, dehydrated, decomposition stage first and the final product. It shows the characteristic bands¹⁵ for hydrated cyanocompound at $\nu_{(\text{OH})}$ 3410 $\pm$ 20, $\delta_{(\text{OH})}$ 1610 $\pm$ 10, $\nu_{(\text{CN})}$ 2085 $\pm$ 30, dehydrated compound $\nu_{(\text{CN})}$ 2085 $\pm$ 20 (absence of H₂O bands); compound at decomposition stage first $\nu_{(\text{CN})}$ 2090 $\pm$ 20, $\delta_{(\text{M-CN})}$ 575 $\pm$ 20; and for final product $\nu_{(\text{M-C})}$ 430-510 cm⁻¹, $\nu_{(\text{M-O})}$ 450-540 cm⁻¹ (lacking -CN bands), respectively. These spectral findings support the above mechanistic conclusion.

(ii) Kinetics of Decomposition :

The fractional weight loss (α) and the corresponding $(1 - \alpha)^n$ were calculated from TG curves at different temperatures, where n depends upon the reaction model and $\alpha = (W_t - W_f) / (W_0 - W_f)$. The $\alpha - T(K)$ curves (Figs not shown) begin with an acceleratory period without any apparent induction period thus indicating that no surface nucleating or branching occurs before the start of these steps^{14,18,19}.

The decomposition reactions of the anhydrous (dehydration step was excluded) were subjected to non-isothermal kinetic studies and the weighted least squares method (LSM) was used for obtaining best fit linear plots by applying the data to various equations and thus the kinetic parameters were evaluated^{14,19,20}. Three different equations were employed for nonisothermal kinetic studies.

The values of the slope, intercept and energy of activation were obtained from the plots. The value of Z was evaluated using equation (1), for piloyan -Novikova and Coats-Redfern while equation (2) was used for Horowitz-Metzger. The entropy of activation (ΔS^*) was calculated employing equation (3).

$$(1) \quad \text{Intercept} = \log \frac{ZR}{\beta E}$$

$$(2) \quad Z = \frac{E}{RTm} \beta \exp. (E/RTm^2)$$

$$(3) \quad Z = \frac{KTm}{h} \exp. \left(\frac{\Delta S^*}{R} \right)$$

Where k is the Boltzmann constant and h the Planck constant, β rate of heating, R the gas constant and Tm is the peak temperature. The values of $E, Z, \Delta S^*$ are given in Table No. 1. The mechanism involved in decomposition is random nucleation with apparent order of reaction one.

The values of parameters obtained by C-R and P-N methods are quite consistent while those obtained by H-M method differ. The higher value of activation energy suggests the higher stability, but some more inherent physical and chemical factors which may cause a change or deviation in this trend. In these cyano compounds the order of stability, on the basis of first decomposition temperature and activation energy is the same. The negative values for entropy of activation indicate that the activated complex has a more ordered structure than the reactants, and the reactions are slower than normal. This is further supported by relatively low Z values. Quantitatively, slight change in the entropy values of the compounds (than E^*) can not be set a reaction governing factor^{14, 21-24}.

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 conditions²⁵.

Table I. Thermal Data (Kinetic Parameters)

Compound	Equation or Method	ΔE^* KJ mol ⁻¹	Z S ⁻¹	ΔS^* J K mol ⁻¹
Cu-HCF(II)	C-R	21.84	2.052×10^2	-102.54
	P-N	22.68	2.134×10^2	-102.37
	H-M	14.78	1.374×10^2	-104.22
Cu-HCF(III)	C-R	49.98	3.422×10^2	-100.75
	P-N	51.66	3.542×10^2	-101.60
	H-M	38.65	2.622×10^2	-102.87
Cu-NPCF(II)	C-R	45.61	3.455×10^2	-101.30
	P-N	47.33	3.581×10^2	-101.14
	H-M	30.63	2.286×10^2	-103.04

C-R, Coats Redfern; P-N, Piloyan-Novikova; H-M, Horowitz Metzger.

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