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KINETIC PARAMETERS OF THERMAL DECOMPOSITION OF BIS(2-OH-1-NAPHTHALDOXIME) CHELATES USING FREEMAN–CARROLL EQUATION

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ABSTRACT

The activation energy, frequency factor, entropy of activation and free energy of activation for the non-isothermal decomposition of bis(2-OH-1-naphthaldoxime) chelates of copper, nickel, cobalt, manganese, zinc and palladium have been evaluated using the Freeman–Carroll equation. The trend of the kinetic parameters is different from that of the thermal stability order.

INTRODUCTION

The structural elucidation of complexes of bivalent cobalt, nickel and copper with *o*-hydroxycarbonyl compounds has shown that π delocalization plays an important role in deciding the nature of bonding, structure and stability [1–3]. Replacement of carbonyl oxygen by nitrogen in carbonyl compounds usually leads to increased ligand field strength as illustrated by Co(II) and Ni(II) complexes of salicylaldoxime and 2-hydroxy-1-naphthaldoxime [4,5]. However, a decrease in the ligand field strength accompanied by a change in the structure of the metal complexes has been observed [6], where extensive conjugation of coordinated C=N was present. Several of the oximes are biologically important and exhibit insecticidal, miticidal and nematocidal activities [7]. Some of the aldoximes linked to glucose moieties are effective as antidotes against organophosphorus poisoning [8].

2-Hydroxy-1-naphthaldoxime and its copper chelate inhibit germination of mungbean seedlings and also biosynthesis of water-soluble vitamins and pyridoxine [9].

This paper reports the determination of the kinetic parameters of the non-isothermal decomposition of divalent transition metal chelates of 2-hydroxy-1-naphthaldoxime based on the differential method using the Freeman–Carroll equation [10].

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EXPERIMENTAL

2-Hydroxy-1-naphthaldoxime was prepared from a pure sample of 2-hydroxy-1-naphthaldehyde (Fluka) following the usual procedure. Its copper, nickel, cobalt, manganese, zinc and palladium chelates were prepared according to the procedures described in an earlier paper [11]. A Stanton thermobalance model HT-SM with an accuracy of 1 mg was used for recording the TG curves. The samples were heated in a mullite crucible in static air and the heating rate was 6 K min^{-1}. The amounts of samples used were as follows: copper chelate, 100.4 mg; nickel chelate, 100.1 mg; cobalt chelate, 95.0 mg; manganese chelate, 86.3 mg; zinc chelate, 101.7 mg; palladium chelate, 85.8 mg.

RESULTS AND DISCUSSION

Elemental analyses and thermogravimetric studies indicate metal to ligand ratios of 1 : 2. All the chelates are stable in air and are non-hygroscopic. Furthermore the TG curves reveal that copper, nickel, palladium and zinc chelates are anhydrous, whereas manganese and cobalt are monohydrates. The observed percentage loss during the elimination of the water molecule is fairly close to the calculated amount. An examination of the TG curves of copper, nickel, palladium and zinc chelates indicates a sharp initial decomposition associated with a rapid loss in weight. In the case of manganese and cobalt chelates this is less marked. The extrapolation of the fairly linear portions of the pyrolysis curves to high and low temperatures, taking the point of intersection as the decomposition temperature, leads to the following order of thermal stability

$\mathrm{Co} > \mathrm{Pd} > \mathrm{Ni} > \mathrm{Mn} > \mathrm{Cu} > \mathrm{Zn}$

The residues remaining after the pyrolysis of the metal chelates correspond to the respective metallic oxides and, in the case of palladium chelate, to the metal itself. Mathematical analysis of the TG curves was carried out using the Freeman–Carroll equation which may be written in the form

$$\frac{\Delta \log(\mathrm{d}W/\mathrm{d}t)}{\Delta \log W_\mathrm{r}} = \frac{-(E^\star/2.303R)\ \Delta(\mathrm{T}^{-1})}{\Delta \log W_\mathrm{r}} + n$$

where $W_\mathrm{r} = W_\alpha - W$, W_α is the mass loss at the completion of reaction, W is the mass loss up to time t, T is the absolute temperature at time t, n is the order of reaction, R is the gas constant in calories and $E^\star$ is the energy of activation in Kcal mol^{-1}. W_r and T can be directly obtained from the TG traces. The temperature slopes $\mathrm{d}W/\mathrm{d}T$ were converted into time slopes

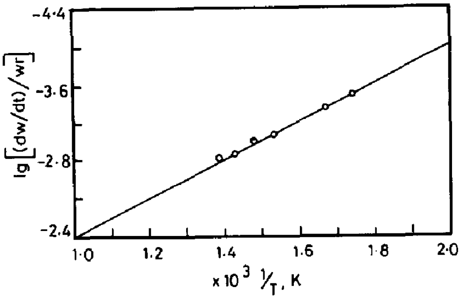

Fig. 1. Freeman–Carroll plot of copper chelate.

dW/dt, using the relation [12]

$$\frac{dW}{dt} = \frac{dW}{dT} \cdot \frac{dT}{dt} = \left(\frac{dW}{dt}\right)\phi$$

where ϕ is the heating rate. The usual first-order rate law expression

$$\frac{dW}{dt} = k(a - x)$$

can be written in the following form using the terms W and W_r

$$\frac{dW}{dt} = kW_r$$

Combining this with the Arrhenius equation

$$K = Z \exp(-E^{\star}/RT)$$

We obtain

$$\log\left(\frac{dW/dt}{W_r}\right) = -\frac{E^{\star}}{2.303RT} + \log Z$$

Plots of log[(dW/dt)/W_r] against T^{-1} were drawn. They gave straight lines in all cases (see Figs. 1–6) with slopes $-E^{\star}/2.303R$ from which $E^{\star}$

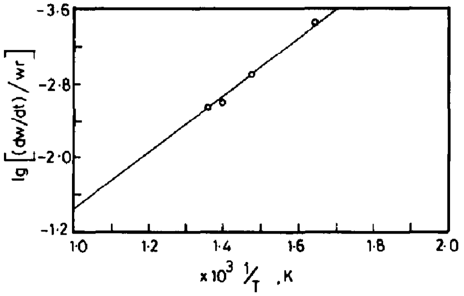

Fig. 2. Freeman–Carroll plot of nickel chelate.

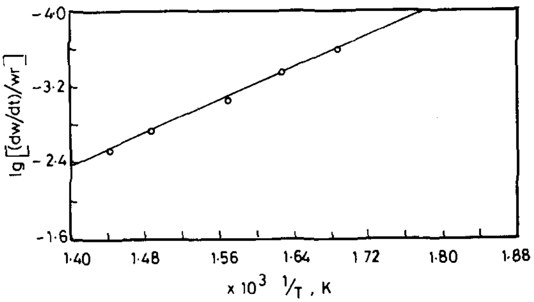

Fig. 3. Freeman–Carroll plot of cobalt chelate.

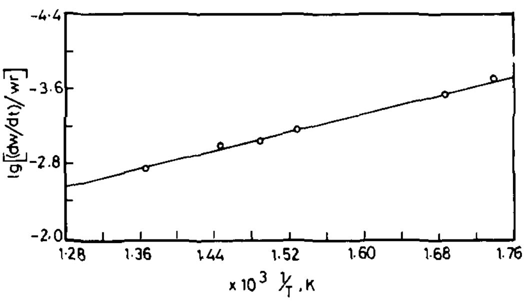

Fig. 4. Freeman–Carroll plot of manganese chelate.

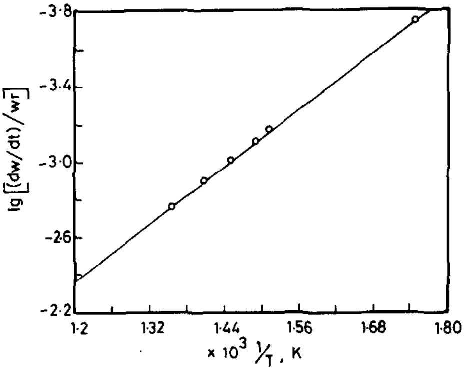

Fig. 5. Freeman–Carroll plot of zinc chelate.

values were obtained. Z was calculated from the above equation and the entropy of activation $\Delta S^\star$ was obtained from the relation [13]

$$\Delta S^\star = 2.303R \log(Zh/kT_S)$$

where k is the Boltzmann constant, h is the Planck constant and T_S is the peak temperature from DTG. The free energy of activation $G^\star$ was calcu-

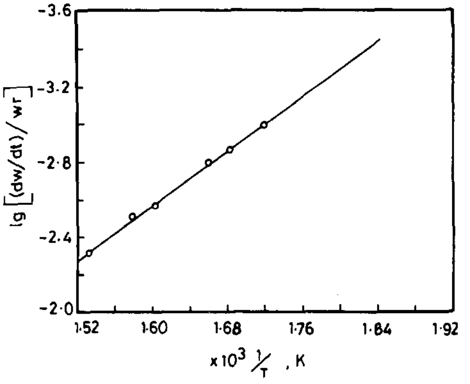

Fig. 6. Freeman–Carroll plot of palladium chelate.

lated using the following equation [14]

$$G^\star = E^\star - T_S\, \Delta S^\star$$

The kinetic parameters thus obtained are presented in Table 1. It can be seen from Table 1 that the activation energy values of the chelates increase in the order

Zn < Mn < Cu < Ni < Co < Pd

The negative values of the entropy of activation suggest that the activated complex has a more ordered structure than the reactants [15] and the low Z values indicate that the reactions are slower than normal [16]. The trend in

TABLE 1

Kinetic parameters of 2-OH-1-naphthaldoxime chelates

$E^\star$ (kcal mol^{-1})	Z (s^{-1})	Activation entropy $\Delta S^\star$ (e.u.)	Free energy of activation $G^\star$ (kcal mol^{-1})
$Cu(C_{11}H_8O_2N)_2 \rightarrow CuO +$ organic matter			
11.44	10.79	−55.31	46.44
$Ni(C_{11}H_8O_2N)_2 \rightarrow NiO +$ organic matter			
15.23	2.39×10^2	−49.15	46.35
$Co(C_{11}H_8O_2N)_2 \rightarrow Co_3O_4 +$ organic matter			
18.30	1.95×10^3	−44.10	47.98
$Mn(C_{11}H_8O_2N)_2 \rightarrow Mn_3O_4 +$ organic matter			
10.53	8.74	−55.60	43.49
$Zn(C_{11}H_8O_2N)_2 \rightarrow ZnO +$ organic matter			
10.52	5.49	−58.52	53.37
$Pd(C_{11}H_8O_2N)_2 \rightarrow Pd +$ organic matter			
18.35	10.46×10^3	−41.58	43.78

the kinetic parameters is different from the trend in thermal stability. This may be due to the fact that the decisive criteria in kinetics are often different from those which decide thermal stability.

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