Thermal decomposition kinetics of Zn\n chelates of substituted chalcones

K. G. Mallikarjun

Department of Chemistry, Jawahar Navodaya Vidyalaya, Peddapuram-533 437, India
E-mail: mallikarjunkg@yahoo.co.in  Fax: 91-8852-243363

Manuscript received 23 April 2004, revised 5 July 2005, accepted 5 August 2005

The thermal decomposition of Zn\n complexes of 3-(phenyl)-1-(2'-hydroxynaphthyl)-2-propen-1-one (PHPO), 3-(4-chlorophenyl)-1-(2'-hydroxynaphthyl)-2-propen-1-one (CPHPO), 3-(4-methoxyphenyl)-1-(2'-hydroxynaphthyl)-2-propen-1-one (MPHPO), 3-(3,4-dimethoxyphenyl)-1-(2'-hydroxynaphthyl)-2-propen-1-one (DMPHPO) was studied by thermogravimetry. Mathematical analysis of the data has allowed us to determine various parameters using Freeman-Carroll equation, the integral method using the Coats-Redfern equation and the approximation method using the Horowitz-Metzger equation. The trend of the kinetic parameters was found to be different from that of the thermal stability order. The low values of $Z$ suggest the slow nature of the reaction.

In continuation of our earlier work\(^1\) on thermal decomposition kinetics of metal chelates, the present investigation deals the thermal stability of the zinc chelates of 3-(phenyl)-1-(2'-hydroxynaphthyl)-2-propen-1-one (PHPO), 3-(4-chlorophenyl)-1-(2'-hydroxynaphthyl)-2-propen-1-one (CPHPO), 3-(4-methoxyphenyl)-1-(2'-hydroxynaphthyl)-2-propen-1-one (MPHPO), 3-(3,4-dimethoxyphenyl)-1-(2'-hydroxynaphthyl)-2-propen-1-one (DMPHPO) and evaluation of kinetic parameters employing the differential Freeman-Carroll equation, the integral method using the Coats-Redfern equation and the approximation method using the Horowitz-Metzger equation\(^2\).

Results and discussion

All the complexes are coloured powders which are insoluble in water. The elemental analysis of the chelates showed zinc to ligand ratios of 1:2. The complexes were found to be stable in air and non-hygrosopic. The final pyrolysis product of all the complexes corresponds to ZnO. The thermal stability data (Table 1) of the chelates reveal that the introduction of a -OCH\(_3\) group increases the thermal stability, whereas introduction of a chlorine atom decreases the thermal stability. The enhancement thermal stability by the presence of electron releasing -OCH\(_3\) groups at position 3 and 4 was ascribed to the availability of higher electron density at the reactive centre. The lower thermal stability of CPHPO may be attributed to the electron withdrawing effect of a chlorine atom, leading to lower electron density at the reactive centre. The relative thermal stability of the chelates is $\text{Zn(CPHPO)}_2 < \text{Zn(PHPO)}_2 < \text{Zn(MPHPO)}_2 < \text{Zn(DMPHPO)}_2$. Mathematical analysis of the TG curves was carried out using the differential Freeman-Carroll equation, the integral method using the Coats-Redfern equation and the approximation method using the Horowitz-Metzger equation.

Freeman-Carroll equation:

Freeman-Carroll equation which may be written in the form.

$$\frac{\Delta \log (dW/dt)}{\Delta \log W_r} = \frac{-\left(\frac{E^*}{2.303 R} \frac{\Delta (T^{-1})}{\Delta \log W_r}\right)}{n} + \frac{1}{n}$$

where $W_r = W_{\infty} - W$, $W_{\infty}$ 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 $E^*$ is the energy of activation in kcal mol\(^{-1}\). $W_r$ and $T$ can be directly obtained from the TG traces. The temperature slopes $dW/dT$ were converted into time slopes $dW/dt$, using the relation

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

where $\phi$ 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

$$K = Z \exp \left(-\frac{E^*}{RT}\right)$$
We obtain

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

Plot of log [(dW/dt)/W_r] against 1/T were drawn. They gave straight lines in all cases with slopes \(-E^*/2.303R\) from which \(E^*\) values were obtained. \(Z\) was calculated from the above equation and the entropy of activation \(\Delta S^*\) was obtained from the relation

\[
\Delta S^* = 2.330RT \log (Z/hkT_s)
\]

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 \(G^*\) was calculated using the following equation

\[
G^* = E^* - T_s \Delta S^*
\]

\(K_r = Z \exp (-E^*/RT_s)\)

Coats-Redfern equation:

\[
\log \left( \frac{W_{\infty} - W}{2.303 RT} \right) \log \left( \frac{W_{\infty}}{W} \right) = \log \left[ \frac{Z}{\phi E^*} \left( 1 - \frac{2RT}{E^*} \right) \right] - \frac{E^*}{2.303 RT}
\]

where \(W_{\infty}\) = mass loss at the completion of the reaction, \(W =\) mass loss at time \(t\), \(Z =\) frequency factor, \(\phi =\) linear rate of heating and \(E^* = \) activation energy of the reaction.

Assuming the decomposition of Zn^{II} chalcone chelates to follow first order kinetics \((n = 1)\) a plot of log \(\{\ln[(W_{\infty}/(W_{\infty} - W))/T^2]\}\) against \(1/T\) was drawn which gave straight lines in all cases with a slope of \(-E^*/2.303R\) from which the activation energy was calculated.

**Horowitz-Metzger equation:**

\[
\log \frac{W_{\infty}}{W_r} = \frac{E^*}{2.303 RT_s^2} - \log 2.303
\]

where, \(W_{\infty}\) = mass loss at the completion of the reaction, \(W_r = W_{\infty} - W, W =\) mass loss at time \(t\), \(T_s =\) peak temperature, \(R =\) gas constant.

A plot of log \(\log W_{\infty}/W_r\) against \(\theta\) was drawn which gave straight lines in all the cases with the slope \(-E^*/2.303RT_s^2\) from which \(E^*\) values were obtained.

**Decomposition kinetics:**

The analysis of data using the Freeman-Carroll equation gives the order of the decomposition reaction near unity for these complexes. The values of activation energy \(E^*\) obtained by all three methods for the zinc chelates are given in Table 2. The values of \(E^*\) and \(Z\) increase in the order Zn(PHPO)\(_2\) < Zn(CPHPO)\(_2\) < Zn(MPHPO)\(_2\) < Zn(DMPHPO)\(_2\).
The kinetic parameters show a somewhat different trend from that of thermal stability. This is due to the fact that the decisive criteria in kinetics are often quite different from those which decide thermal stability.

**Experimental**

The chalcones were prepared by the condensation of 2-hydroxy-1-acetonaphthone with benzaldehyde, chlorobenzaldehyde, methoxybenzaldehyde and dimethoxybenzaldehyde employing the Claisen-Schmidt condensation reported earlier. The zinc complexes of chalcones were prepared by refluxing a toluene solution of zinc acetate and the ligand in 1:2 molar ratio, in the presence of sodium acetate (pH 6–7) for 12 hours. The precipitates were filtered, washed with toluene and dried in a vacuum desiccator over fused calcium chloride. The purity of the sample was checked by elemental analysis. The thermograms were recorded using a Perkin-Elmer TGS-2 thermo balance in ambient air and at a heating rate of 6 K min⁻¹.

Typical TG curves are presented in Fig. 1 and Freeman-Carroll Plots in Fig. 2.

**References**

1. R. S. Naidu, R. Ruby, E. N. Rao and K. G. Mallikarjun, *Bull. Pure Appl. Sci.*, 1987, 60, 1; R. S. Naidu, E. N. Rao, R. Ruby and K. G. Mallikarjun, *Thermochim. Acta.*, 1988, 131, 299; 1989, 140, 97; *J. Indian Council Chem.*, 1988, 3, 41: *Acta Chim. Acad. Sci. Hung.*, 1990, 127, 385; K. G. Mallikarjun and R. Seshadri Naidu, *Thermochimica Acta*, 1992, 206, 273; K. G. Mallikarjun, *e-Journal of Chemistry*, 2004, 01(02), 105.

2. E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 1958, 62, 394; A. W. Coats and J. P. Redfern, *Nature*, 1964, 200, 68; H. H. Horowitz and G. Metzger, *Anal. Chem.*, 1963, 35, 1464.

3. P. V. Khadikar, S. M. Ali and B. Heda, *Thermochim. Acta*, 1984, 82, 253.

4. J. Chacko and G. Parameswaran, *J. Therm. Anal.*, 1984, 29, 3.

5. S. S. Misra and Dinakar, *J. Indian Chem. Soc.*, 1972, 49, 6.