*Thermochimica Acta*, 66 (1983) 347–350
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands



## Note

# KINETICS OF THE NON-ISOTHERMAL DECOMPOSITION OF SOME METAL DERIVATIVES OF 8-QUINOLINOL AND ITS DIHALO DERIVATIVES FROM DTG/DTA CURVES

S.S. SAWHNEY and A.K. BANSAL

*Department of Chemistry, D.A.V. (P.G.) College, Dehra Dun 248001 (India)*

(Received 7 January 1983)

Wendlandt [1] carried out thermogravimetric pyrolysis of 8-quinolinol and 5,7-dihalo-8-quinolinol chelates of scandium, thorium and uranium; Mittal et al. [2] investigated the kinetics of the thermal decomposition of metal chelates of diiodo-8-quinolinol with Ba(II), Mg(II) and Cd(II) using slope dependent methods [3–5] which were reviewed by Sawhney et al. [6] by non-slope dependent methods. [7]. Wendlandt and Horton [8] have reported the differential thermal analysis of some metal chelates of 8-quinolinol and substituted 8-quinolinols.

The purpose of the work described here was to estimate the kinetic parameters of the non-isothermal decomposition of $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$, $UO_2(C_9H_4Cl_2NO)_2 \cdot C_9H_4Cl_2NOH$, $UO_2(C_9H_4Br_2NO)_2 \cdot C_9H_4Br_2NOH$, $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$, $Th(C_9H_4Cl_2NO)_4 \cdot C_9H_4Cl_2NOH$ and $Th(C_9H_4Br_2NOH)_4 \cdot C_9H_4Br_2NOH$, pyrolysed on a torque balance 0–100 mg range (Vereenigde Draadfabrieben, Nijmegen, Holland), with a heating rate of $\sim 4.5°C\ min^{-1}$, using Dave and Chopra's [7] procedures (1) and (2)

$$k = \frac{dx/dt}{A - a} \text{ for } n = 1 \tag{1}$$

$$\frac{-E/2.303R(T^{-1})}{\log(A - a)} = -n + \frac{\log dx/dt}{\log A - a} \tag{2}$$

and $Cu(C_9H_6NO)_2 \cdot 2\,H_2O$, $Zn(C_9H_6NO)_2 \cdot 2\,H_2O$, $Mn(C_9H_6NO)_2 \cdot 2\,H_2O$, $Co(C_9H_6NO)_2 \cdot 2\,H_2O$, $Co(C_9H_6NO)_3 \cdot 1\,H_2O$, $Pb(C_9H_6NO)_2$, 1.5 $H_2O$, $UO_2(C_9H_6NO)_2$, and $Cd(C_9H_6NO)_2 \cdot 1\,H_2O$, the DTA curves of which were obtained on a Deltatherm (Technical Equipment Corp., Denver, CO) under controlled conditions of sample size, heating rate and furnace temperature, with the help of Borchardt and Daniels' plots [9] using the expression

$$k = \frac{\Delta T}{A - a}(n = 1) \tag{3}$$

where $\Delta T$ is the deviation from the base line, $A$ is the total area of the DTA curve, $a$ is the area at time $t$, and $n$ is the reaction order.

0040-6031/83/$03.00 

TABLE 1

Kinetic parameters for the non-isothermal decomposition of 8-quinolinol and dihalo-8-quinolinol complexes from DTG curves

| Method [a] | $n$ | $E$ (kcal mole$^{-1}$) | $Z$ |
|---|---|---|---|
| $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH \rightarrow UO_2(C_9H_6NO)_2 + C_9H_6NOH$ | | | |
| A | 1 | 42.10 | 126.0 |
| B | 00.71 | 109.82 | |
| $UO_2(C_9H_6NO)_2 \rightarrow U_3O_8 +$ organic matter | | | |
| A | 1 | 183.04 | 0.32 |
| B | 0.82 | 411.84 | |
| $UO_2(C_9H_4Cl_2NO)_2 \cdot C_9H_4Cl_2NOH \rightarrow U_3O_8 +$ organic matter | | | |
| A | 1 | 6.41 | 9.1 |
| B | 0.98 | 5.49 | |
| $UO_2(C_9H_4Br_2NO) \cdot C_9H_4Br_2NOH \rightarrow U_3O_8 +$ organic matter | | | |
| A | 1 | 4.58 | 7.9 |
| B | 0.58 | 3.66 | |
| $Th(C_9H_6NO)_4 \cdot C_9H_6NOH \rightarrow Th(C_9H_6NO)_4 + C_9H_6NOH$ | | | |
| A | 1 | 8.51 | 50.0 |
| B | 1.1 | 15.56 | |
| $Th(C_9H_6NO)_4 \rightarrow ThO_2 +$ organic matter | | | |
| A | 1 | 6.41 | 5.5 |
| B | 0.86 | 9.15 | |
| $Th(C_9H_4Cl_2NO)_4 \cdot C_9H_4Cl_2NOH \rightarrow ThO_2 +$ organic matter | | | |
| A | 1 | 6.86 | 9.1 |
| B | 1.14 | 9.15 | |
| $Th(C_9H_4Br_2NO)_4 \cdot C_9H_4Br_2NOH \rightarrow ThO_2 +$ organic matter | | | |
| A | 1 | 14.64 | 25.0 |
| B | 1.35 | 12.81 | |
| $Ba(C_9H_4I_2NO)_2 \rightarrow BaCO_3 +$ organic matter | | | |
| A | 1 | 5.72 | 3.16 |
| B | 0.64 | 5.49 | |
| C | 0.0 | 27.45 | |
| D | 1 | 28.76 | |
| E | 1 | 29.16 | |
| $Mg(C_9H_4I_2NO)_2 \rightarrow$ Mgo + organic matter | | | |
| A | 1 | 5.75 | 2.75 |
| B | 0.61 | 3.20 | |
| C | 0.0 | 18.06 | |
| D | 1 | 17.56 | $1.7 \times 10^{-2}$ |
| E | 1 | 17.60 | $1.58 \times 10^{-2}$ |
| $Cd(C_9H_4I_2NO)_2 \rightarrow CdO +$ organic matter | | | |
| A | 1 | 5.72 | 3.31 |
| B | 0.67 | 3.20 | |
| C | 0.0 | 29.16 | |
| D | 1 | 18.53 | $3.11 \times 10^{-2}$ |
| E | 1 | 18.45 | $2.0 \times 10^{-2}$ |

[a] A = Dave and Chopra's method [eqn. (1); B = Dave and Chopra's method [eqn. (2)]; C = Freeman and Carroll's method; D = Coats and Redfern's method; E = Horowitz and Metzger's method.

## EXPERIMENTAL

DTG curves were obtained from the TG curves due to Wendlandt [1]. For Borchardt and Daniels' plots, DTA curves recorded by Wendlandt and Horton [8] were directly used for the study.

## RESULTS AND DISCUSSION

### *DTG and kinetics*

$A$, $a$ and $dx/dt$ were determined from derivative thermogravimetric curves. values of log $k$ from the Dave and Chopra expression for the first-order reaction

$$k = \frac{dx/dt}{A - a}$$

TABLE 2

Kinetic parameters for the pyrolytic desolvation/decomposition of metal–8-quinolinol complexes from DTA curves for Borchardt and Daniels' plot

| $n$ | $E$ (kcal mole$^{-1}$) | $Z$ |
|---|---|---|
| $Co(C_9H_6NO)_3 \rightarrow Co_3O_4$ + organic matter | | |
| 1 | 76.27 | 1.90 |
| $Cd(C_9H_6NO)_2 \cdot 1\ H_2O \rightarrow Cd(C_9H_6NO)_2 + 1\ H_2O$ | | |
| 1 | 32.03 | 0.40 |
| $Pd(C_9H_6NO)_2 \cdot 1.5\ H_2O \rightarrow Pb(C_9H_6NO)_2 + 1.5\ H_2O$ | | |
| 1 | 18.30 | 0.33 |
| $Pb(C_9H_6NO)_2 \rightarrow PbO$ + organic matter | | |
| 1 | 140.80 | 19.95 |
| $Co(C_9H_6NO)_2 \cdot 2\ H_2O \rightarrow Co(C_9H_6NO)_2 + 2\ H_2O$ | | |
| 1 | 32.03 | 0.32 |
| $UO_2(C_9H_6NO)_2 \rightarrow U_3O_8$ – organic matter | | |
| 1 | 146.43 | 3.98 |
| $Mn(C_9H_6NO)_2 \cdot 2\ H_2O \rightarrow Mn(C_9H_6NO)_2 + 2\ H_2O$ | | |
| 1 | 36.61 | 1.26 |
| $Zn(C_9H_6NO)_2 \rightarrow ZnO$ + organic matter | | |
| 1 | 146.43 | 2.75 |
| $Cu(C_9H_6NO)_2 \cdot 2\ H_2O \rightarrow Cu(C_9H_6NO)_2 + 2\ H_2O$ | | |
| 1 | 27.73 | 0.72 |
| $Cu(C_9H_6NO)_2 \rightarrow CuO$ + organic matter | | |
| 1 | 67.79 | 2.75 |

corresponding to different temperatures were determined and plotted against the reciprocal of absolute temperature. The resulting linear plot for each reaction with $-E/2.303\ R$ and log $Z$ as the slope and intercept, respectively, gave the value of $E$ and $Z$. Use of eqn. (2) involved a plot of $T^{-1}/\log(A-a)$ vs. $\log(dx/dt)/\log(A-a)$; the slope and intercept being used for the values of $E$, $n$. Table 1 lists the kinetic parameters for the non-isothermal decomposition of $UO_2$(II) and thorium(IV) complexes of 8-quinolinol and dihalo-8-quinolinol due to Dave and Chopra's expression.

*DTA and kinetics*

The kinetic data on the pyrolytic decomposition of solvated copper, manganese, cobaltous, cobaltic, plumbous, cadium, and zinc quinolinolates and unsolvated uranyl quinolinolate (Table 2) were determined from Borchardt and Daniels' plots (log $k$ vs. $T^{-1}$) which were linear in nature, the slope ($-E/2.303\ R$) and the intercept (log $Z$) giving the values of $E$ and $Z$. The linearity of Borchardt and Daniels' plots in all the reactions shows that all the reactions under study follow first order kinetics.

Values of $n$, $E$, and $Z$ estimated by different procedures (Tables 1 and 2) almost agreed and further low values of $Z$ (collision number) led us to conclude that these reactions are slow processes.

REFERENCES

1 W.W. Wendlandt, Anal. Chem., 24 (4) (1956) 499.
2 A. Mittal, A.D. Kelkar and G.V. Golap, J. Indian Chem. Soc., 57 (1980) 517.
3 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
4 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
5 H.H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
6 S.S. Sawhney, R.M. Sati and A.K. Bansal, Thermochim. Acta, 49 (1981) 371.
7 N.G. Dave and S.K. Chopra, Z. Phys. Chem., N.F., 58 (5/6) (1966) 257.
8 W.W. Wendlandt and G.R. Horton, Anal. Chem., 34 (9) (1962) 1098.
9 H.J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.