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Note

KINETIC PARAMETERS OF THE NON-ISOTHERMAL DECOMPOSITION OF Cu(II) CHELATES OF *o*-HYDROXYCHALCONES

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Structural studies on several metal chelates of β-diketonates and *o*-hydroxycarbonyl compounds have been reviewed by Holm and O'Connor [1] Among the various *o*-hydroxycarbonyl compounds, *o*-hydroxychalcones form a distinct category which can form chelates, with metal ions with low-spin square-planar configuration These chelates are reluctant to form adducts and this has been attributed to the presence of extensive conjugation [2]. Chalcones were found to be physiologically and pharmacologically active They were also found to have germicidal [3], bactericidal [4] fungicidal [5] and carcinogenic activity [6] Several of the chalcones have been employed as useful analytical reagents

This communication describes the pyrolysis curves of Cu(II) chelates of 2′-hydroxy-, 2′,2-dihydroxy-, 2′-hydroxy-4-methoxy- and 2′-hydroxy-4-chlorochalcones and the evaluation of kinetic parameters employing the integral method using the Coats-Redfern equation [7]

$$\log\left[\frac{\ln\dfrac{W_\infty}{W_\infty - W}}{T^2}\right] = \log\left[\frac{ZR}{\phi E^\star}\left(1 - \frac{2RT}{E^\star}\right)\right] - \frac{E^\star}{2\ 303RT}$$

where W_∞ = mass loss at the completion of the reaction, W = mass loss at time t, Z = frequency factor, ϕ = linear rate of heating, and $E^\star$ = activation energy of the reaction

EXPERIMENTAL

ortho-Hydroxychalcones were prepared as described [8,9] The copper chelates were obtained by adding an alcoholic solution of chalcone to copper acetate solution in the presence of sodium acetate (pH 6–7 5) The precipitates were filtered, washed with 10% aqueous alcohol and dried in a vacuum desiccator over fused calcium chloride The thermograms were

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recorded using a Stanton thermobalance in ambient air and a rate of heating maintained at 6 K min^{-1} Weights of samples used were as follows· Cu-2′-hydroxychalcone, 89 0 mg, Cu-2′,2-dihydroxychalcone, 82 0 mg, Cu-2′-hydroxy-4-methoxychalcone, 95 9 mg, Cu-2′-hydroxy-4-chlorochalcone, 92 0 mg

RESULTS AND DISCUSSION

All the complexes are coloured powders which are insoluble in water The elemental analysis of the chelates showed copper to ligand ratios of 1 2 The complexes were found to be stable in air and non-hygroscopic All the complexes apart from Cu-2′,2-dihydroxychalcone are stable to about 200 ° C indicating that they are anhydrous In the case of Cu(II)-2′,2-dihydroxychalcone there is a constant weight level corresponding to the hydrated complex The complex loses water of hydration in the range 100–150 ° C The observed weight loss due to water is close to the calculated amount, the theoretical percentage of water for monohydrate is 3.6, the percentage found is 3 2 The final pyrolysis product in all complexes corresponds to the oxide stage The thermal stability data (Table 1) of the chelates reveal that the introduction of a –OH group or –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 –OH and –OCH_3 groups at positions 2 and 4 respectively was ascribed to the availability of higher electron density at the reactive centre The lower thermal stability of Cu-2′-hydroxy-4-chlorochalcone may be attributed to the electron withdrawing effect of a chlorine atom, leading to lower electron density at the reactive centre

The thermal decomposition of the chelates resembles the reaction A(s) → B(s) + C(g) Assuming the decomposition of Cu(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

TABLE 1

Thermal stabilities and residue percentage of complexes

Cu(II) complex of	Decomposition temp (° C)	Residue percentages		
		Theoretical		Experimental
		Metal	Oxide	
2′-Hydroxychalcone	220	12 7	14 9	15 7
2′2-Dihydroxychalcone	240	11 3	14 2	13 5
2′-Hydroxy-4-methoxychalcone	240	11 1	13 9	14 5
2′-Hydroxy-4-chlorochalcone	200	10 7	13 7	14 2

TABLE 2

Kinetic parameters of the non-isothermal decomposition of Cu(II) chelates of *o*-hydroxychalcones

Complex	Activation energy $E^\star$ (kcal mol^{-1})	Frequency factor Z (s^{-1})	Activation entropy $\Delta S^\star$ (e u)
Cu-2′-hydroxychalcone	5 632	0 0339	−57 160
Cu-2′,2-dihydroxychalcone	22 880	2464 3	−44 915
Cu-2′-hydroxy-4-methoxychalcone	13 312	3 242	−58 098
Cu-2′-hydroxy-4-chlorochalcone	15 253	28 226	−61 794

$-E^\star/2\ 3R$ from which the activation energy was calculated The value of Z was obtained from the intercept and the entropy of activation was obtained using the equation $\Delta S^\star = 2\ 3\ R\log(Zh/KT)$ where h is the Planck constant and k is the Boltzmann constant The negative values of $\Delta S^\star$ (Table 2) indicate that the activated complex has a more ordered structure than the reactants [10,11] and further the low values of Z indicate the reactions to proceed slowly [12]

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