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Solid State Kinetics of Palladium-N-(2-benzothiazolyl)-Thiourea Complex from T.G. Analysis

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Palladium chloride forms a 1 : 2 complex with N-(2-benzothiazolyl)-thiourea. It undergoes a four steps decomposition. The complex decomposes regularly without any distinguishable rest with random nucleation mechanism. Kinetic parameters like apparent activation energy, frequency factor, activation entropy and apparent order of reaction have been determined employing the graphical method of Freeman and Carroll and Doyle method as modified by Zsako introducing standard deviations in the calculation.

INTRODUCTION

It is often difficult to choose a suitable equation to describe the kinetics of thermal decomposition reactions, specially of a complex where rate is governed by one or more rate determining processes. The process takes place in several stages such as the chemical action, breaking of bonds, destruction of the initial crystal lattice, formation of the crystal lattice of the solid product consisting of the formation of crystallization centres and the growth of these centres and adsorption, desorption of the gaseous product, diffusion of gas and heat transfer.[1]

The basis of the calculations of the kinetic data from a T.G. curve is based on the formal kinetic equation $-\frac{dx}{dt} = Kx^n$ where x is the amount of the sample undergoing reaction, n is the order of reaction and K is specific rate constant and the latter's dependence on temperature is expressed as $K = Ae^{-E/RT}$.[1]

In this paper kinetics of thermal decomposition of the 1 : 2 (metal-ligand) complex of palladium with N-(2-benzothiazolyl)-thiourea has been investigated and the kinetic parameters computed using Doyle's[2] method as modified by Zsako[3] and Freeman and Carroll's[4] method.

EXPERIMENTAL

An electrobalance "Stanton-Red Craft TG 750" with an automatic recorder operating on 1 mv full scale for recording the thermogram *i.e.* temperature *vs.* loss

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in weight was used. The heating rate 10°C per minute with chart speed 120 mm/h and water flow rate 10 L/h were maintained while obtaining the thermogram.

Preparation of sample: Ligand N-(2-benzothiazolyl)-thiourea (L) was prepared by described method[5]. The orange coloured complex of PdL_2Cl_2 was obtained by mixing 1 : 2 molar proportion $PdCl_2$ solution in dil. HCl and hot ethanolic solution of ligand (L).

RESULTS AND DISCUSSION

Elemental analysis data reveal that the complex contains Pd, 17.52; C, 32.01; N, 14.67; S, 21.85; H, 2.52%. PdL_2Cl_2 requires Pd, 17.87; C, 32.24; N, 14.10; S, 21.49; H, 2.35%.

The thermogram exhibits four stages of transformations of the compound. A gradual loss of weight on heating the complex is initially observed upto 220°C. Both the chloride ions are expelled at the temperature when PdL_2 is formed. A clear inflexion at 220°C on TG curve suggests further decompostion of the compound leading to Pd_3L_4, an unstable intermediate at 340°C which changes to PdL on further heating at 430°C. The compound PdL suffers rapid loss in weight, ensembling to PdO at 520°C which is quite stable up to 800°C.

The kinetics of the second step decomposition had been studied by non-isothermal method using the Freeman and Carroll method. Activation energy and order of reaction were determined noting the existing weight of the complex at equal temperature intervals *i.e.* 10°C. A linear plot is obtained when $\log -\frac{dW}{dt} / \log W_r$ *vs.* $T^{-1}/\log W_r$ was plotted. Here $W_r = W_c - W$; $W_c =$ weight loss at completion of reaction; W = total weight loss up to time. The time intercepted at 1.25 and gave slope 3.973. These values in turn are suggestive of order of reaction 1.25 and the activation energy 18.30 kcal/mole using Ea = slope × 2.303R.

These values were compared with the method of Doyle[2] as modified by Zsako[3]. Doyle's equations is

$$g(\alpha) = \frac{ZE}{Rq} p(x)$$

where Z is frequency factor, E the activation energy, R the gas constant, q the heating rate and $p(x) = -\int_{\infty}^{x} \frac{e^{-u}}{u^2} du$ have been calculated and tabulated by Doyle[2] for x values.

Using the above equation

$$\log \frac{ZE}{Rq} = \log g(\alpha) - \log p(x) = B \qquad (1)$$

where B depends upon the nature of the compound studied and upon the heating rate, but not upon temperature.

The log g(α) values are calculated for different temperatures covering the range 493 to 613 K for the assumed order of reaction as b = 0, 1 and 2 after calculating the α values for each temperature with relation

$$\alpha = \frac{W_0 - W}{W_0 - W_t}$$

where, W, W_0 and W_t are the actual, initial and final weights of the sample respectively.

For $b = 0$, $g_0(\alpha) = \alpha$; $b = 1$, $g_1(\alpha) = -\ln(1-\alpha)$ and $b = 2$, $g_2(\alpha) = \frac{\alpha}{1-\alpha}$.

The values of B_0, B_1 and B_2 have been calculated in the present case from equation (1) with the help of the data $g(\alpha)$ and $-\log p(x)$ at different temperatures. B_0, B_1 and B_2 are the constants of difference $\log(\alpha) - \log p(x)$ for zero, first and second order reaction respectively which provide information to suggest a quantitative method of determining the apparent activation energy consistent with a given function $g(\alpha)$.

$$b = 0; \quad B_0 = \log \alpha - \log p(x)$$

$$b = 1; \quad B_1 = \log\left(\ln \frac{1}{1-\alpha}\right) - \log p(x)$$

$$b = 2; \quad B_2 = \log\left(\frac{\alpha}{1-\alpha}\right) - \log p(x)$$

The values of $g(\alpha)$ are given below in Table-1.

TABLE-1

S. No.	Temp. (°C)	Weight (%)	α	$\log \alpha$	$\log\left(\ln \frac{1}{1-\alpha}\right)$	$\log \frac{\alpha}{1-\alpha}$
1.	230	86.0	0.08547	-1.06818	-1.04892	-1.02938
2.	240	83.4	0.19658	-0.70645	-0.65979	-0.61140
3.	250	80.0	0.34188	-0.46612	-0.37844	-0.28443
4.	260	76.0	0.51282	-0.29003	-0.14319	0.02227
5.	270	74.0	0.59829	-0.22308	-0.03999	0.17300
6.	280	71.4	0.70940	-0.14910	0.09195	0.38759
7.	290	70.1	0.76495	-0.11636	0.16076	0.51249
8.	300	69.0	0.81196	-0.09046	0.22301	0.63530
9.	310	68.0	0.85470	-0.06818	0.28523	0.76955
10.	320	65.2	0.94017	-0.02679	0.44967	1.19629
11.	330	64.6	0.97435	-0.01128	0.56390	1.57978

Initial weight at 220°C = 88.0%, Final weight at 340°C = 64.6%

In each case of B_0, B_1 and B_2 the arithmetical mean and δ (standard deviation) was obtained using

$$\delta = \sqrt{\frac{(B_i - \bar{B})^2}{r}}$$

The values of δ and E corresponding to B_0, B_1 and B_2 are given in Table-2.

TABLE-2

B_0		B_1		B_2	
E_a kcal/mol	δ_0	E_a kcal/mole	δ_1	K kcal/mole	δ_2
—	—	16	0.12275	28	0.12684
12	0.14119	18	0.11624	30	0.12198
14	0.15876	20	0.12922	32	0.13499

This indicates that δ are least if first order reaction is accepted corresponding to E = 18 kcal/mole.

The frequency factor Z was calculated using the equation

$$\log_2 = \overline{B} + \log Rq - \log E$$

and found to be $6.8429 \times 10^4 \text{ sec}^{-1}$.

The apparent entropy of activation was calculated out to be −157.19688 eu on solving the equation

$$\Delta S^{\#} = E \ln \frac{Zh}{KT}$$

where T stands for the temperature 534 K at which the reaction is half completed.

The value for E with order of reaction b = 1 by Freeman-Carroll and Zsako are 18.30 kcal/mole and 18 kcal/mole respectively. These values are in good agreement with each other. As standard deviation δ is a measure of precision between the experimental data and presumed kinetic equation, these values can be considered more reliable and thus may be utilised in the study of solid state reaction mechanism.

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