Complexation and Thermogravimetric Analysis of Platinum (IV) Choloride with Nitrogen and Sulphur containing Ligand Thiopicolinanilide (TPA)

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ABSTRACT

The technique of thermogravimetric analysis involves change in weight of a system under examination with increase in temperature at predetermined and preferably at a linear rate study the solid reaction. In the present with the physico-chemical data on kinetic parameters i.e. apparent activation energy ,frequency factor, activation entropy and the order of reaction of Platinum complex with Nitrogen and Sulphur containing ligand Thiopicolinanilide(TPA) have been evaluated from their thermogravimetric curves which have been recorded on an electrobalance with auto recorder. Freeman and Carroll first of all introduced the widely used differential method for determination of kinetic parameters from the thermogravimetric curves.The exponential integral method used by Coats-Redfern for determination of chemical parameters of Platinum complex.

KEY WORDS

Thermogravimetric Analysis (TGA), Differential and Integral Method, Platinum Complex, Thiopicolinanilide (TPA)

INTRODUCTION

There are several factors associated with the complexation of central metal atom ligand like different solvent and solid conditions make the study of stability of metallic complexes more complicated. Chemical parameters of complexes have been determined with the help of thermogravimetric analysis. The technique of thermogravimetric analysis involves change in weight of a system under examination with increase of temperature at a predetermined preferably at a linear rate to study the kinetic reaction. A number of non-isothermal methods has been proposed to determining kinetic parameters from thermogravimetric fall in to two distinct approaches. The two approaches are differential and integral method. It would be important to eliminate the variability of the expected parameters as thermogravimetry is a continuous non –isothermal method which has many advantage over isothermal method there advantage are that a single experimental curve is sufficient to obtain estimate of the apparent heat of activation and that kinetics can be proved over entire temperature range in a continuous manner without any gaps. The Freeman-Carroll,Coats-Redfern,Karkhnawala-Dharwadkar and Doyle's procedure modified by Zsako used differential method for determination of kinetic parameters from the thermogravimetric curves the method is based on this equation------

$$\frac{d\alpha}{dt} = -\binom{Z}{\alpha}.e^{-E/RT}.f(\alpha)$$

Where $\frac{d\alpha}{dt}$ =Rate of Sample loss per degree

Z = Arrhenius pre-exponential factor

$\alpha = \frac{dT}{dt}$, linear heating rate

E = Activation Energy

R = Gas Constant

T = Absolute Temperature

$f(\alpha)$ = Function of weight loss

α = Fractional weight of the material acted as a function of the metal weight loss

PREPARAION OF PLATINUM COMPLEXES AND ITS THERMOGRAVIMETRIC ANALYSIS

About 0.30 gram of Platinum (IV) Chloride was dissolved in ethanol and slowly added to alcoholic solution of ligand. The colour was changed and followed by the a red precipitation of the compound. The precipitate obtained was filtered, washed several times with hot alcohol and dried.

The Platinum content of the complex was estimated by the standard procedures on decomposition of the complex. The weighed amount of the Platinum complex was decomposed with a mixture of nitric acid and per chloric acid in a conical flask. The resulting mass was boiled with hydrochloric acid in 25ml to obtained clear solution.

The Platinum was precipitated by adding alcoholic dimethyl glyoxime to the slightly acidic Platinum chloride solution. The characteristic precipitate of $Pt(C_4H_7O_2N_2)_2$ obtained was filtered through pre-weighed sintered glass crucible ,washed and then dried at 110^0-120^0C.The amount was multiplied with the factor 0.31606 for Platinum content.

INSTRUMENTAL TECHNIQUES

An Electrobalance Stanton Red Craft (TG) Balance model 750 with a recorder, operating on 1.0mv full scale for obtaining thermograms ie.temperature vs loss in weight curves was used. A chrome lalumel thermocouple placed 3-4mm below the sample holder, the platinum boat 2mm diameter was used for recording the sample temperature. A 10^0C per minute heating rate was employed for recording the pyrolysis curves.

Table – 01

Elemental Analysis of Compound

Compound	Molecular Formula	% of Carbon		% of Nitrogen		% of Hydrogen		% of Sulphur		% of Metal	
		Expt	Obsv	Expt	Obsv	Expt	Obsv.	Expt	Obsv	Expt	Obsv
Ligand	$C_{12}H_{10}N_2S$	67.28	67.23	13.08	13.11	4.67	4.68	14.95	14.92	NIL	NIL
Platinum	$PtL_2.2H_2O$	43.96	44.01	8.54	8.57	3.05	3.10	9.77	9.91	29.77	29.72

Table – 02

Colour and Solubility of the Platinum Complex

Complex	Colour	Solubility
$PtL_2.2H_2O$	Brick Red	Meth,Eth,Etr,Acet,N-N Mef

Symbol – Meth – Methyl Alcohol,Eth – Ethyl Alcohol ,Etr – Ether,Acct - Acetone,N-N.Mef – N-N. Methyl formamide

RESULTS AND DISCUSSION

Freeman-Carroll was primarily employed to evaluate the order of reaction and energy of activation from the data tabulated in table- 03 for the third stage of decomposition. The order of reaction and activation energy from

the linear plot between $\frac{\Delta log dw/dt}{\Delta log Wr}$ and $\Delta T^{-1} \times 10^3 / log Wr$ was observed to be 2.0 and 28.0 kcal per mole respectively.

In the method of Coats – Redfern $logf(\alpha)/T^2$was calculated for first, second and third order of reaction Table – 04 and plot of $logf(\alpha)/T^2$ and $\Delta T^{-1} \times 10^3$ was obtained for each presumed order of reaction. The linear plot was found for second order.

The values shown table-04 was used to calculate B_0, B1and B_2 for different activation energy. The values of Bi and B obtained were used to evaluate $'\delta'$values which ultimately resulted $'\delta'$ minimum values of δ=0.1054 corresponding to energy of activation energy equal to 28.1 kcal per mole.

Table – 03

Freeman – Carroll Calculations

S.No	Temp(^{0}C)	W(mg)	$\Delta log \frac{dw}{dt} / \Delta log W_r$	$\Delta T^{-1} \times 10^3 / \Delta log W_r$
01	250	6.28	-6.77	0.48
02	260	6.00	+1.37	0.33
03	270	5.68	+1.39	0.35
04	280	5.45	-0.28	0.37
05	290	5.28	+2.24	0.27
06	300	5.10	-1.00	0.37
07	310	5.00	-0.64	0.14
08	320	4.88	-	-
09	330	4.50	-	-

Table -04

Coats-Redfern Calculation

S.No	$T^{-1} \times 10^3$	$\log \frac{f(\alpha)}{T^2}$ for b=2	$\log \frac{f(\alpha)}{T^2}$ for b=3	$\log \frac{f(\alpha)}{T^2}$ for b=4
01	1.9120	-6.3170	-6.2870	-6.2560
02	1.8761	-6.0245	-5.9585	-5.8886
03	1.8414	-5.8415	-5.7266	-5.6014
04	1.8082	-5.7516	-5.5994	-5.4225
05	1.7760	-5.7080	-5.5150	-5.2900
06	1.7453	-5.6664	-5.4273	-5.1332
07	1.7151	-5.6523	-5.3823	-5.10404
08	1.6864	-5.6351	-5.3201	-5.9041
09	1.5624	-5.5948	-5.1203	-5.9621

Table – 05

Sample Weight and $log\ g(\alpha)$ Values

Initial Weight at 240 Celsius degree =6.42 mg

Final Weight at 240 Celsius degree =4.30 mg

S.No	Temp(^{0}C)	W(mg)	$log\ \alpha$	$log(ln\frac{\alpha}{1-\alpha})$	$log(\frac{\alpha}{1-\alpha})$
01	250	6.28	-0.880	-0.850	-0.819
02	260	6.00	-0.505	-0.505	-0.435
03	270	5.68	-0.372	-0.256	-0.132
04	280	5.45	-0.270	-0.114	+0.0163
05	290	5.28	-0.207	-0.014	+0.211
06	300	5.10	-0.150	+0.089	+0.383
07	310	5.00	-0.121	+0.149	+0.491
08	320	4.88	-0.089	+0.226	+0.642
09	330	4.50	-0.012	+0.316	+0.816

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