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Kinetic parameters from thermogravimetric analysis of Mn(II) complex with 5-amino-1,2,3,4-thiatriazole.

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ABSTRACT
Mn(II) acetate forms 1:2 complex with 5-amino-1,2,3,4-thiatriazole. It undergoes two steps decomposition. Kinetic parameters like apparent activation energy, frequency factor, activation entropy and order of reaction have been determined employing the graphical method of Freeman-Carroll and Doyle method as modified by Zsako introducing standard deviation in the calculation.

Keywords: solid state kinetics, thermogravimetric analysis, 5-amino-1,2,3,4-thiatriazole.

INTRODUCTION

Thermogravimetric analysis is a continuous non-isothermal method which has many advantages over currently used isothermal methods. Thermal analysis technique is becoming useful tool in different field of study such as chemical science, polymer science, biological science, medical science[1-8]. Transition metal complexes have been used as antifungal[9], antibacterial[10], antitumour[11], antiviral[12], hypotensive[13]. The thermal kinetics and decomposition products of the complex are apparently of significance in understanding the biochemistry of the compound.

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

In this paper kinetics of thermal decomposition of complex of Mn(II) with 5-amino-1,2,3,4-thiatriazole has been investigated and the kinetic parameters computed using graphical method of Freeman-Carroll[14] and Doyles[15]method as modified by Zsako[16].

MATERIALS AND METHODS

Ligand 5-amino-1,2,3,4-thiatriazole is prepared by the diazotization of thiosemicarbazide. To an ice cold solution of 20gram of thiosemicarbazide in 95 ml of 2.2N HCl, 150ml ice cold $NaNO_2$ solution (14.7 gram $NaNO_2$) was added in 50 ml portion. The product was collected washed with ice cold water, recrystallised with methyl alcohol and dried in vacuum. The colorless needle shaped crystal had melting point of 136°C with slight explosion. Complex was prepared by refluxing ligand solution in ethanol and Mn(II) acetate in hot ethanol. A brick red precipitate obtained was filtered, washed with ethanol and dried over anhydrous $CaCl_2$ in desiccators. Thermogram was recorded by "NETZSCH" simultaneous thermal analyzer STA-409 recorder.

RESULTS AND DISCUSSION

Second stage decomposition of complex was selected to study the kinetic parameters. The T.G. curve and data thus obtained has been used to calculate order of reaction, activation energy using Freeman and Carroll method. The existing weight of complex at equal temperature interval i.e. 10°C was noted. A linear plot was obtained when $\Delta\log dw/dt/\Delta\log w_r$ versus $\Delta\log T^{-1}x10^{-3}/\Delta \log w_r$ was plotted. Where $w_r=w_c-w_t$, w_c = weight loss at completion of the reaction. W_t= total weight loss up to time t. The line intercepted at 1.10. The values in turn are suggestive of order of reaction1.0 and activation energy19.87397 kcal/mol using E_a=slope 2.303R.

Table I
Data obtained by Freeman and Carroll method for the complex:-
$[Mn(5\text{-}ATTZ)(CH_3COO)_2]$

Serial no	Temperature	Weight left	$\frac{\Delta\log(dw/dt)}{\Delta\log dw_r}$	$\frac{\Delta\log T^{-1}x10^{-3}}{\Delta\log w_r}$
1	190	2.92	-17.11139	3.67683
2	200	2.87	0.000000	2.23063
3	210	2.79	-9.16306	1.96441
4	220	2.69	-3.27894	0.09016
5	230	2.55	-3.24164	0.89466
6	240	2.37	-1.65829	0.58875
7	250	2.27	6.16709	0.90064
8	260	2.21	8.25571	1.33484
9	270	2.12	-4.02873	1.03117
10	280	1.97	-2.63101	0.75314
11	290	1.74	-1.07304	0.43334
12	300	1.45	-0.24152	0.07437

Initial weight at 170°C = 3.00mg
Final weight at 310°C = 1.27mg

These values were compared with the method of Doyle as modified by Zsako. Doyle's equation is

$$F(\alpha) = ZE/Rq\ p(x)$$

W here Z is frequency factor, E is the activation energy, R is the gas constant, q is the heating rate and

$p(x)= -\int_{\infty}^{x} e^{-u}/u^2\,du$ have been calculated within limit ∞ to x and tabulated by Doyle's for x values using the above equation .Log ZE/Rq = log F(α)- log p(x) =B where B depends upon the nature of the compound studied and upon the heating rate.

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

$$\alpha = w_0 - w_t / w_0 - w_f$$

Here w_0 ,w_t and w_f are the initial, actual, and final weights of the sample respectively.

The value of $\overline{B}_0$,$\overline{B}_1$ and$\overline{B}_2$ have been calculated in the present case from the equation above with the help of the data F(α) and –log p(x) for zero, first and second order of reaction respectively.

b=0; B_0= log (α) – log p(x)

b=1 B_1= log (ln1/1-α) – log p(x)

b=2; B_2= log (α/1-α) – log p(x)

Table II

Data of log F(α) values for the complex [Mn(5-ATTZ)($CH_3COO)_2$]

Calculation at different temperature

Serial no	Temperature(^{0}C)	Weight left	α=w_0-w_t/w_0-w_t	Logα	log(ln1/1-α)	log(α/1-α)
1	180	2.97	0.01734	-1.76092	-1.75713	-1.75333
2	190	2.92	0.04624	-1.33496	-1.32472	-1.31439
3	200	2.87	0.07514	-1.12410	-1.10725	-1.09018
4	210	2.79	0.12139	-0.91583	-0.88803	-0.85962
5	220	2.69	0.17919	-0.74668	-0.70451	-0.66093
6	230	2.55	0.26012	-0.58483	-0.52106	-0.45400
7	240	2.37	0.36416	-0.43871	-0.34408	-0.24205
8	250	2.27	0.42197	-0.37472	-0.26112	-0.13668
9	260	2.21	0.45665	-0.34042	-0.21467	-0.07550
10	270	2.12	0.50867	-0.29356	-0.14835	0.01506
11	280	1.97	0.59538	-0.22521	-0.04345	0.16774
12	290	1.74	0.72832	-0.13768	0.11499	0.42827
13	300	1.45	0.89595	-0.04771	0.35467	0.93506

Initial weight at 170°C =3.00mg

Final weight at 310°C =1.27mg

In each case of the $\overline{B}_0$,$\overline{B}_1$ and$\overline{B}_2$ arithmetical mean and ∂(standard deviation) was obtained using

$$\partial = \sqrt{(\overline{B}_i - B)^2/r}$$

Table III

Calculation of B_0 for different activation energies and ∂_0 values at different temperature for the complex [Mn(5-ATTZ)($CH_3COO)_2$]

Serial no	Temperature(^{0}C)	12 kcal	14 kcal	16 kcal
1	180	6.33508	7.42508	8.50008
2	190	6.61804	7.69004	8.74304
3	200	6.69390	7.73990	8.77590
4	210	6.76717	7.80117	8.81417
5	220	6.81132	7.82232	8.81932
6	230	6.85317	7.84717	8.82617
7	240	6.87829	7.85529	8.82029
8	250	6.83128	7.79028	8.73828
9	260	6.75458	7.70158	8.63158
10	270	6.69544	7.62444	8.24044

11	280	6.66179	7.57779	8.47679
12	290	6.65232	7.55032	8.43632
13	300	6.64529	7.53529	8.40429
14	$\overline{B}_0$	6.70751	7.68928	8.63282
15	∂_0	0.13539	0.13158	0.19029

Table IV

Calculation of B_1 for different activation energies and ∂_1 values at different temperature for the complex [Mn(5-ATTZ)(CH $_3$COO)$_2$]

Serial no	Temperature(^{0}C)	16 kcal	18 kcal	20 kcal
1	180	8.50387	9.57087	10.62287
2	190	8.75328	9.79328	10.82828
3	200	8.79275	9.81575	10.82775
4	210	8.84197	9.84297	10.83897
5	220	8.86149	9.84449	10.81849
6	230	8.88994	9.85594	10.81194
7	240	8.91492	9.86392	10.80292
8	250	8.85188	9.78288	10.70388
9	260	8.75733	9.67033	10.57933
10	270	8.38565	9.58665	10.48265
11	280	8.65855	9.54655	10.42455
12	290	8.68899	9.56499	10.42899
13	300	8.80667	9.66767	10.51467
14	$\overline{B}_1$	8.74671	9.72356	10.66810
15	∂_1	0.14895	0.12009	0.15871

Table V

Calculation of B_2 for different activation energies and ∂_2 values at different temperature for the complex [Mn(5-ATTZ)(CH $_3$COO)$_2$]

Serial no	Temperature(^{0}C)	18 kcal	20 kcal	22 kcal
1	180	9.57467	10.62667	11.66967
2	190	9.80361	10.83861	11.86061
3	200	9.83282	10.84482	11.84982
4	210	9.87138	10.86738	11.84938
5	220	9.88807	10.86207	11.83207
6	230	9.92300	10.87900	11.82700
7	240	9.96595	10.90495	11.83495
8	250	9.90732	10.82832	11.74632
9	260	9.80950	10.71850	11.61750
10	270	9.75006	10.64606	11.52806
11	280	9.75774	10.63574	11.50474
12	290	9.87827	10.74227	11.59427
13	300	10.24806	10.09506	11.93906
14	$\overline{B}_2$	9.86234	10.80688	11.74257
15	∂_2	0.14666	0.12621	0.13719

The table given below show the least value of ∂min 0.12009 in b=1 suggestive of order of reaction=1 and activation energy=18Kcal/mol.

Table VI

b_0		b_1		b_2	
E^*	∂_0	E^*	∂_1	E^*	∂_2
12	0.13539	16	0.14895	18	0.14666
14	0.13158	18	0.12009	20	0.12621
16	0.19029	20	0.15871	22	0.13719

Table VII

Methods	Order of reaction [n]	Activation energy E*
Freeman & Caroll	**1.10**	**19.87397Kcal/mol**
J.Zsako	**1.00**	**18.00000Kcal/mol**

The frequency factor Z was calculated using the equation
$\log Z = B + \log Rq - \log E^*$
q =Heating rate 10^0 /minutes
E* = 18Kcal/mol
R = gas constant
Thus the frequency factor for the thermolysis step under consideration was found to be 9.79873×10^4 sec^{-1}
The apparent entropy of activation was calculated to be -154.31138 e.u after solving the equation $\Delta S^{\#} = R \ln Zh/KT$
Where T stands for the absolute temperature 543K at which the steps under consideration was half complete.
The values i.e. order of reaction and activation energy evaluated by two different methods is in good agreement within limit.

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