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Kinetics and Mechanism of Thermal Decomposition of Ni(II) Complex of 1-Amidino-3-phenylthiourea

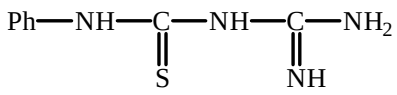
ABRAHAM GEORGE
Department of Chemistry, Mar Ivnios College, Trivandrum-695 015, India
E-mail: abraham.mankavil@gmail.com

Ni(II) complex of 1-amidino-3-phenylthiourea has been prepared, characterized and subjected to thermal analysis. The phenomenological, kinetic and mechanistic aspects of their decomposition have been studied. The Coats Redfern equation was used for the kinetic studies and various equations were invoked for the mechanistic studies and the Mampel equation gave the best fit.

Key Words: Ni(II) complex, Thermal decomposition, Amidinothiourea, Square planar, Coats-Redfern, Mampel.

INTRODUCTION

Amidinothioureas (**I**) are very useful precursors in synthesis and have many chemotherapeutic applications[1,2]. The thiol-thioketo tautomerism of amidinothioureas are also well known[3]. This leads to the possibility of forming complexes after deprotonation. It has been reported that the Ni(II) complex of 1-amidino-3-phenylthiourea (HPATU) represented as $Ni(PATU)_2$ is square planar, diamagnetic and has a tetragonal unit cell[4].



(I)

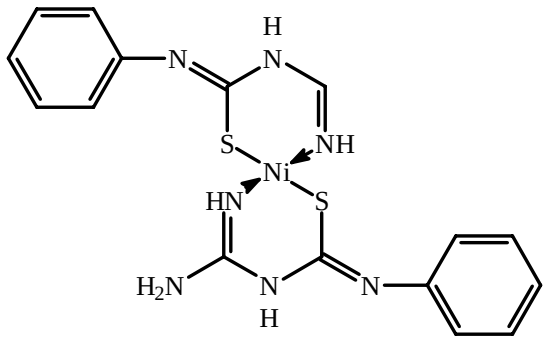
EXPERIMENTAL

The ligand and its Ni(II) complex were prepared by the reported procedure[4,5]. The TG and DTG were recorded on a Mettler Toledo Star system in nitrogen atmosphere. The heating rate was 10ºC/min. The complex was subjected to independent pyrolysis in an indentical atmosphere and the residue was compared using their IR profile.

RESULTS AND DISCUSSION

The complex $Ni(PATU)_2$ (**II**) is square with two anionic bidentate ligands having both N and S coordination. The TG profile shows four inflexions corresponding to three perceivable stages of decomposition. The

phenomenological details are provided in Table-1. The first stage shows a loss of 20.5 %, the second stage a loss of 25.9 % and the third stage 30.9 %. The TG data show that the complex is stable upto 200ºC, which rules out the presence of any coordinated or absorbed water which is also supported by other structural studies.



(**II**)

TABLE-1
PHENOMENOLOGICAL DATA OF THE DECOMPOSITION OF $Ni(PATU)_2$

Stage	T_i	T_f	T_p	Mass loss (%)	Mass loss (mg)
I	170	235	213	20.5	2.00
II	235	358	280	25.9	2.60
III	358	720	465	30.9	3.00

The computational details of the thermal decomposition in the three stages are given in Tables 2-4. All the three stages have an order parameter of n = 2. The Coats Redfern plots of the three stages were also made[6]. The kinetic parameters were calculated based on the plot (Table-5).

TABLE-2
COMPUTATIONAL DETAILS FOR THE FIRST STAGE OF THE THERMAL DECOMPOSITION OF $Ni(PATU)_2$ COMPLEX
w_α = 2.00 mg, n = 2, r = 0.998, slope = -14.7002, intercept = 25.13623

T	w	$c = \frac{(w_\alpha - w)}{w_\alpha}$	$g(\alpha) = \frac{(1-c^{1-n})}{(1-n)}$	$\log \frac{g(\alpha)}{T^2}$	$\frac{1}{T} \times 10^3$
210	0.52118	0.73941	0.35	-5.320	2.07
214	0.80636	0.59682	0.67	-5.040	2.05
218	1.09154	0.45423	1.20	-4.790	2.03
220	1.24834	0.37583	1.66	-4.651	2.02
223	1.40710	0.29645	2.37	-4.460	2.01
226	1.55606	0.22197	3.50	-4.320	2.00
230	1.70600	0.14700	5.80	-4.109	1.98

TABLE-3
COMPUTATIONAL DETAILS FOR THE SECOND STAGE OF THE THERMAL DECOMPOSITION OF $Ni(PATU)_2$ COMPLEX
w_α = 2.60 mg, n = 2, r = 0.997, slope = -4.77544, intercept = 3.55141

T	w	$c = \frac{(w_\alpha - w)}{w_\alpha}$	$g(\alpha) = \frac{(1-c^{1-n})}{(1-n)}$	$\log \frac{g(\alpha)}{T^2}$	$\frac{1}{T} \times 10^3$
261	0.56054	0.78441	0.27	-5.43	1.87
273	0.82220	0.68377	0.46	-5.20	1.83
280	1.00350	0.61404	0.62	-5.07	1.80
290	1.23870	0.52358	0.90	-4.91	1.77
297	1.43764	0.44706	1.23	-4.78	1.75
310	1.65716	0.36263	1.75	-4.62	1.71
320	1.83748	0.29328	2.40	-4.49	1.68
336	2.05406	0.20998	3.76	-4.29	1.64
350	2.18538	0.15947	5.27	-4.15	1.60

TABLE-4
COMPUTATIONAL DETAILS FOR THE THIRD STAGE OF THE THERMAL DECOMPOSITION OF $Ni(PATU)_2$ COMPLEX
w_α = 3.00 mg, n = 2, r = 0.999, slope = -3.448, intercept = -0.37666

T	w	$c = \frac{(w_\alpha - w)}{w_\alpha}$	$g(\alpha) = \frac{(1-c^{1-n})}{(1-n)}$	$\log \frac{g(\alpha)}{T^2}$	$\frac{1}{T} \times 10^3$
400	0.47062	0.81899	0.22	-5.52	1.48
425	0.67936	0.73871	0.35	-5.32	1.43
456	0.99688	0.61658	0.62	-5.07	1.37
474	1.15564	0.55552	0.80	-4.96	1.33
491	1.28598	0.50539	0.97	-4.88	1.30
531	1.59566	0.38628	1.58	-4.67	1.24
579	1.91122	0.26492	2.77	-4.42	1.17
620	2.09546	0.19405	4.15	-4.25	1.11
645	2.20228	0.15297	5.53	-4.12	1.08

TABLE-5
KINETIC PARAMETERS FOR THE THREE STAGES OF DECOMPOSITION OF $Ni(PATU)_2$

Stages	Peak temp (°C)	Activation energy (E) (kJ mol^{-1})	Pre-exponential term (A) (s^{-1})	Entropy of activation (JK^{-1} mol^{-1})
I	213	281.46	7.72×10^{24}	+227.43
II	280	91.43	6.52×10^{3}	-157.90
III	465	66.01	3.1499	-242.93

The second and third stages show comparatively low activation energy than the first stage. The entropy of activation which is positive in the first stage shows that the activated complex is less ordered than the

reactant and the reaction can be a little bit faster than normal[7]. The pre-exponential factor value is also in agreement with this observation. The second and third stages show negative values for their entropy of activation, suggesting that, the activated complex is more ordered than the reactant. This is a natural consequence of the faster first stage decomposition.

The third stages shows a very low value for its A (3.1499 s^{-1}). This is quite common in reactions involving volatalization, preventing the possibility of a collision between the molecules[8].

All the three stages of the decomposition data were subjected to mechanistic studies also. Various $g(\alpha)$ values corresponding to the various mechanistic equations were calculated and $\log \frac{g(\alpha)}{T^2}$ were plotted against 1/T. It is seen that the Mampel equation and the first two Avrami equations give linear plots[9]. But when the kinetic parameters were calculated, it is seen that the Mampel equation gives results very close to the ones calculated on the basis of the Coats Redfern equation. The kinetic parameters calculated on the basis of the Mampel equation for $Ni(PATU)_2$ is given in Table-6.

TABLE-6
KINETIC PARAMETERS FOR THE THREE STAGES OF DECOMPOSITION OF $Ni(PATU)_2$

Stages	Activation energy (E) (kJ mol^{-1})	Pre-exponential term (A) (s^{-1})	Entropy of activation (JK^{-1} mol^{-1})
I	285.21	2.45×10^{25}	+235.61
II	87.06	4.54×10^{3}	-183.01
III	71.76	1.872	-236.61

The values in Table-6 shows that the Mampel equation best suits the thermal decomposition stages. The mechanism corresponding to the Mampel equation is a random nucleation. So it can be inferred that the decomposition at all stages of these complexes takes place through random nucleation and other diffusion processes can be ruled out.

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