International Letters of Chemistry, Physics and Astronomy *Online: 2015-01-14*
ISSN: 2299-3843, Vol. 44, pp 124-129
doi:10.18052/www.scipress.com/ILCPA.44.124

Thermal Analysis of some Imidazolinone Derivatives

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ABSTRACT

Thermal analysis of some imidazolinone derivatives derived from 1, N-phenyl-3-p-nitrophenyl-4-formyl pyrazole, have been carried out by TGA technique. From these thermograms, various kinetic parameters such as order of degradation (n), energy of activation (E), frequency factor (A) and entropy change (ΔS) have been evaluated. Further, thermal stability of imidazolinone derivatives have been determined, which is found to depend on the type of substituent present in the compounds.

Keywords: imidazolinone derivatives; physical and chemical properties; pharmaceutical industry

1. INTRODUCTION

Thermal analysis has become an established method to study the thermal behavior of materials and finds wide applications in diverse industrial and research fields. It has been used to determine the physical and chemical properties of various compounds, polymers, geological materials and coals[1-7]. Further, various reversible and non-reversible reactions[8,9], the decomposition of molecules absorbed on a surface, phase transitions etc. can also be studied. Several investigations have been carried out on the application of thermal methods in pharmaceutical industry[10-15].

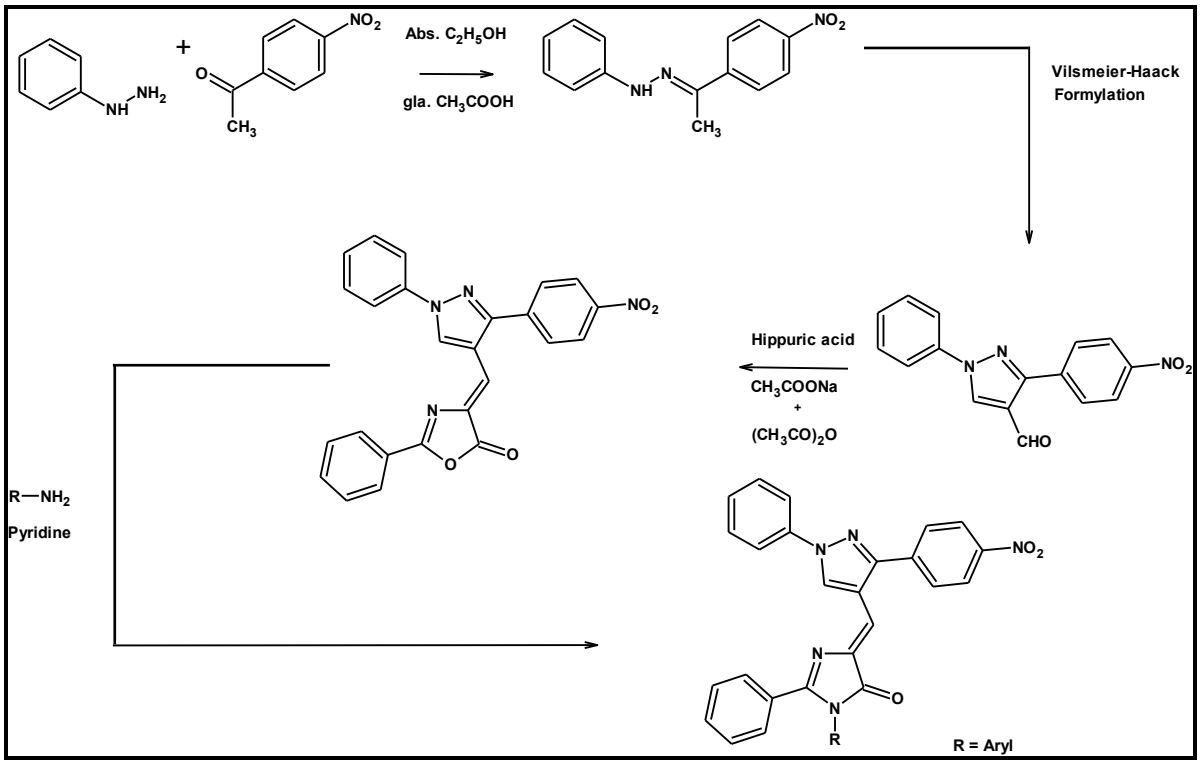
In present paper, thermal properties of some imidazolinone derivatives have been studied by using TGA technique.

2. EXPERIMENTAL

2.1. Materials

Most of the chemicals used were of analytical grade, while the solvents were purified and double distilled before use.

2.2. Preparation of Imidazolinone derivatives



Reaction Scheme

2.3. Instrumentation

The Thermo gravimetric analysis (TGA) measurements were made on the instrument "Universal V2.6D TA Instrument" at the heating rate of 10°C per minute in nitrogen atmosphere for imidazolinone derivatives.

3. RESULTS AND DISCUSSION

Various physical constants of imidazolinone derivatives are given in Table 1.

Thermogram of only one compound PAIM-1 is shown in Figure 1. It is observed from thermograms that except PAIM-4 and PAIM-9, all the derivatives degrade in more than one step and each step is of different order. The variation in the trend of thermal decomposition might be interpreted by taking into account some intermolecular interactions (structural as well as electronic) and also because of several experimental factors.

Further, various thermal properties such as initial decomposition temperature (IDT), the decomposition temperature range and the maximum degradation along with the percentage weight loss and Exo / Endo transitions of all the imidazolinone derivatives are evaluated from the thermograms and are reported in Table 2. It is observed from Table 2 that PAIM-4 is most stable whereas PAIM-8 is less stable. This suggests that the presence of 1-napthylamine (as in PAIM-4) causes greater stability than 3-Cl-4-F-aniline (as in PAIM-8), which is less stable.

Further, various kinetic parameters, such as order of the degradation (n), energy of activation (E), frequency factor (A) and entropy change (ΔS) for each step are calculated by

Anderson-Freeman method[16] and Horowitz and Metzger[17] method and are given in Tables 3 and 4.

It is evident from Tables 3 and 4 that order of reaction is quite different in different steps for different imidazolinone derivatives. For first step, order of reaction varies from 2.5 to 21. For second step also, values of n varies from 2.5 to 6.7.

In first step, energy of activation (E) is maximum for PAIM-5 and minimum for PAIM-4. The frequency factor (A) also varies in the same order i.e., maximum for PAIM-5 and minimum for PAIM-4. In second step, energy of activation is found to be maximum for PAIM-3 and minimum for PAIM-6. The frequency factor A is also maximum for PAIM-3 and minimum for PAIM-6. Comparison of E and A values in Tables 3 and 4 shows that the values of E and A are minimum for second steps of all the imidazolinone derivatives.

Further, change in entropy ($\Delta S°$) for all these reactions were also calculated by equation (7). It is observed that the change in entropy are positive for all the compounds except PAIM-4 and PAIM-9 for the first step while in second step, entropy changes are negative for all the imidazolinone derivatives. The positive $\Delta S°$ indicates that the transition state is in less ordered state. Whereas the negative $\Delta S°$ values indicate that the activation complex has a more ordered or more rigid structure than the reactants and the reaction is slower than the normal[18].

Thus, the degradation in imidazolinone derivatives is multi step process with different order of reaction. Further, thermal stability depends upon the type of substituent present. It is observed that presence of 1-napthylamine (as in PAIM-4) increases the stability whereas 3-Cl-4-F-aniline (as in PAIM-8) decreases the stability.

Acknowledgement

Authors are thankful to Head of Chemistry Department for providing necessary facilities.

Table 1. Physical constants of Imidazolinones.

Sr. No.	Code	R	M.F.	M. Wt. (g/mol)	R_f* Value	M.P. ^oC	Yield %
1.	**PAIM-1**	4-CH_3-C_6H_4-	$C_{32}H_{23}O_3N_5$	525	0.48	215	69
2.	**PAIM-2**	4-OCH_3-C_6H_4-	$C_{32}H_{23}O_4N_5$	541	0.51	205	72
3.	**PAIM-3**	2-OCH_3-C_6H_4-	$C_{32}H_{23}O_3N_5$	525	0.42	226	65
4.	**PAIM-4**	$C_{10}H_7$-	$C_{35}H_{25}O_3N_5$	564	0.47	232	67
5.	**PAIM-5**	4-F-C_6H_4-	$C_{31}H_{20}O_3N_5F$	529	0.42	198	62
6.	**PAIM-6**	4-Cl-C_6H_4-	$C_{31}H_{20}O_3N_5Cl$	546	0.43	203	65
7.	**PAIM-7**	C_6H_5-	$C_{31}H_{21}O_3N_5$	511	0.33	189	66
8.	**PAIM-8**	3-Cl-4-F-C_6H_3-	$C_{31}H_{19}O_3N_5FCl$	564	0.32	211	68
9.	**PAIM-9**	2,5-di-Cl-C_6H_3-	$C_{31}H_{19}O_3N_5Cl_2$	580	0.53	212	69

*Acetone:Benzene: 1:9

Table 2. TGA data for synthesized imidazolinone derivatives.

Comp. Code	Amt. (mg.)	Initial Decomp. Temp. (^oC)	Decomp. range (^oC)	% Wt. loss	Residual Wt. Loss (mg.)	Max Degradt. Temp. (^oC)
PAIM-1	4.0279	240	240 – 596	37.7891	1.5221	596
PAIM-2	5.3698	239	239 – 581	37.3425	2.0052	581
PAIM-6	5.1339	240	240 – 588	38.4844	1.9758	588
PAIM-4	5.6007	332	332 – 586	36.2675	2.0313	586
PAIM-5	5.3908	252	252 – 596	36.3415	1.9591	596
PAIM-6	4.6280	252	252 – 579	33.3523	1.6920	579
PAIM-7	4.1518	240	240 – 592	37.3890	1.5523	592
PAIM-8	4.5548	212	212 – 594	38.9758	1.7753	594
PAIM-9	4.2117	330	330 – 590	40.6477	1.7119	590

Table 3. The kinetic parameters for all the imidazolinone derivatives for 1st step.

Comp. code	n	E (kJ)	A (Sec^{-1})	Δs^o (kJ^{-1})
PAIM-1	6.00	239.83	1.54×10^{19}	269.25
PAIM-2	7.00	221.71	5.34×10^{17}	241.33
PAIM-6	5.00	232.22	4.10×10^{18}	258.27
PAIM-4	8.20	34.44	4.65	-87.37
PAIM-5	2.50	270.21	5.37×10^{21}	317.92
PAIM-6	15.00	100.96	3.61×10^{7}	46.72
PAIM-7	8.00	203.23	1.48×10^{16}	211.52
PAIM-8	21.00	87.76	1.71×10^{6}	21.21
PAIM-9	7.15	46.80	36.61	-70.27

Table 4. The kinetic parameters for all the imidazolinone derivatives for 2nd step.

Comp. code	n	E (kJ)	A (Sec^{-1})	Δs^o (kJ^{-1})
PAIM-1	6.60	44.56	26.18	-73.01
PAIM-2	6.30	61.40	415.84	-50.04
PAIM-6	2.50	119.72	6.77×10^{6}	-7.50
PAIM-4	-	-	-	-
PAIM-5	6.40	42.91	19.39	-75.53
PAIM-6	6.0	33.81	4.31	-87.95
PAIM-7	6.70	50.64	77.85	-63.89
PAIM-8	5.30	92.01	6.94×10^{4}	-7.37
PAIM-9	-	-	-	-

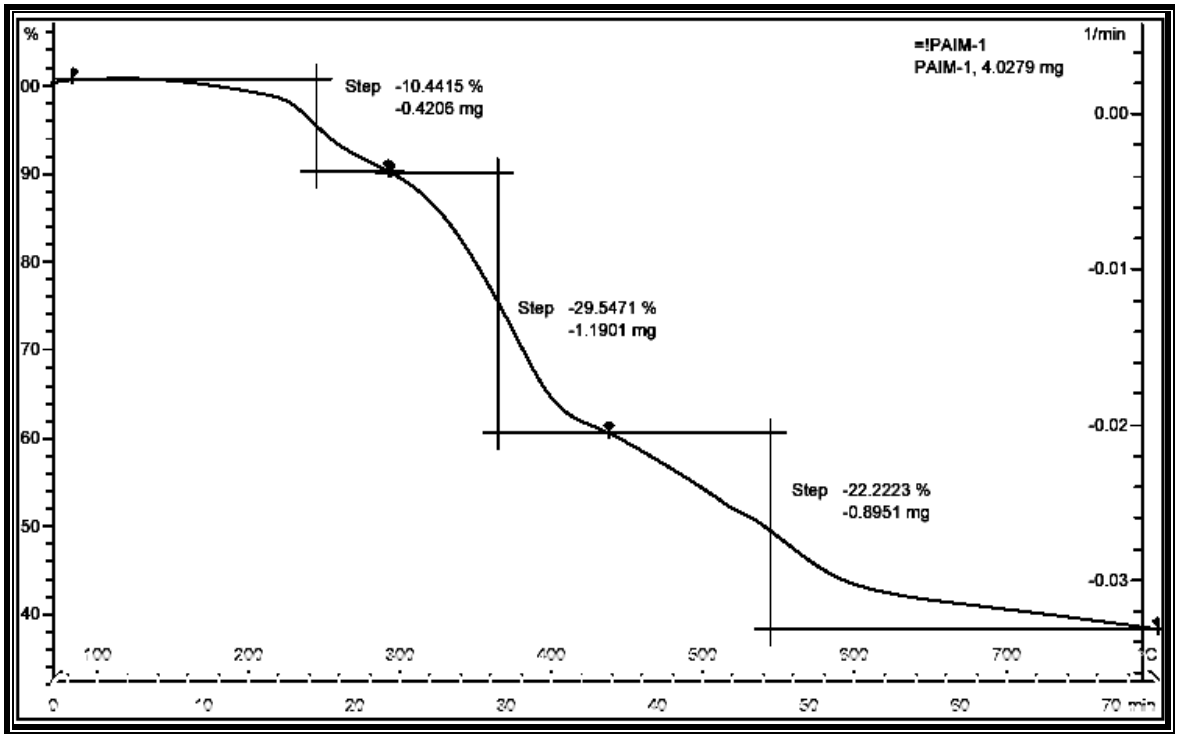


Fig. 1. The TGA graphs of PAIM-1.

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(Received 11 December 2014; accepted 22 December 2014)