Indian Journal of Engineering & Materials Sciences
Vol. 16, December 2009, pp. 423-428

Thermolysis of pyridinium perchlorate salts

Pratibha Srivastava, I P S Kapoor & G Singh*
Department of Chemistry, D D U Gorakhpur University, Gorakhpur 273009, India

Received 5 January 2009; accepted 1 September 2009

Three perchlorate salts of pyridine have been prepared and characterized by gravimetric and elemental analyses. Thermogravimetry (TG) and differential thermal analysis (DTA) have been carried out in static air, to examine the thermal decomposition process of these salts. Isothermal TG of these salts have been done to evaluate the kinetics of thermal decomposition in the temperature range 290-410°C using both model fitting and isoconversional methods. Isoconversional method has been found to be superior over conventional model fitting method and is able to describe the decomposition process of these salts. Moreover, Explosion delay (D_E) measurements have been carried out to investigate the response of the salts under the condition of rapid heating.

Keywords: Thermal decomposition; isothermal TG; model fitting; iso-conversional; explosion delay

Interest in a systematic study of the characteristics of thermal decomposition of ring substituted arylammonium nitrates[1-3] and perchlorates[4-6] thrives due to the fact that the nitrogen base salts of inorganic acids like HNO_3 and $HClO_4$ find applications in explosives and propellants[7-9]. Because of the presence of both the oxidizer and the fuel groups in the same molecule; they have also been used in propellant formulations. Perchlorate salts are generally more violent in their explosive behaviour as compared to nitrate salts[10-13].

Very recently, we have prepared, characterized and investigated the thermolysis of dinitrate and diperchlorate salts of phenylenediamine[14,15]. In the light of the above findings preparation, characterization and thermal characteristics of pyridinium perchlorate salts have been discussed in the present communication.

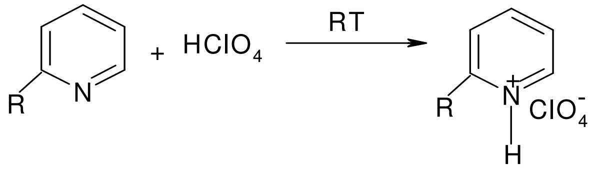
Experimental Procedure

Materials

Following AR grade commercially available chemicals were used as received; pyridine (s.d.fine); 2-chloropyridine (s.d.fine); pyridinol-2 (E-Merck); 70% $HClO_4$ (E-Merck), silica gel TLC grade (Qualigens), iodine and nitron.

Preparation and characterization of pyridinium perchlorate salts

Pyridinium perchlorate salts were prepared by reacting corresponding pyridine with 20% $HClO_4$ directly in 1:2 molar ratio at room temperature and the reaction can be represented as follows-



where R = -H, -Cl & -OH

All these salts were washed with ethyl acetate, dried and recrystallised from distilled water. Their purity was checked by TLC and R_f values along with elemental and physical parameters are reported in Table 1. Gravimetric estimation has been carried out using nitron reagent. Pyridinium perchlorate is precipitated out after keeping the reaction mixture for one hour whereas substituted salts crystallize out after about one week.

Thermal decomposition studies

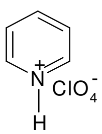
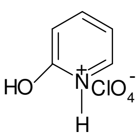
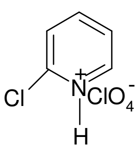
Non-isothermal TG (Fig. 1) on these salts (mass~20 mg,100-200 mesh) were undertaken using platinum crucible in static air at 10°C min^{-1} using home made thermogravimetric analyzer [16].

Isothermal TG thermograms (Fig. 2) were obtained over a short temperature range. Therefore, an optimal temperature range was selected for analysis, which varied notably from one salt to other.

---

*For correspondence (E-mail: gsingh4us@yahoo.com)

Table 1— Physical parameters, TLC, analytical and elemental data on Pyridinium Perchlorates

Comp.	Mol.Wt.	Structural formula	TLC		R_f	Element %			% of ClO_4^-
			Eluent	Spot colour		C	H	N	Exp. (Theo.)
Pyridinium perchlorate	179.5		a:b:c 8:4:3	Yellow	0.87	33.43 (34.53)	3.34 (3.87)	7.80 (7.53)	53.87 (55.43)
2-Hydroxy pyridinium perchlorate	195.5		a:b:c 8:4:3	Brown	0.79	30.69 (32.98)	3.07 (2.93)	7.16 (6.79)	49.50 (50.89)
2-Chloro pyridinium perchlorate	214.0		a:b:c 7:5:3	Reddish	0.89	28.04 (27.53)	2.34 (2.51)	6.54 (6.13)	45.52 (46.49)

a:b:c = water: DMSO: methanol
Locating reagent- Iodine

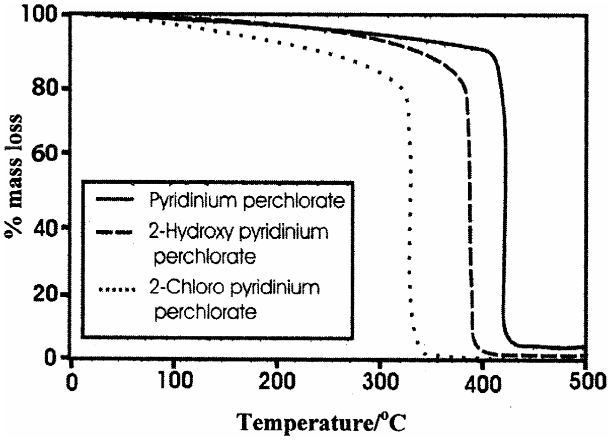


Fig. 1— Non-isothermal TG of Pyridinium perchlorate salts in static air

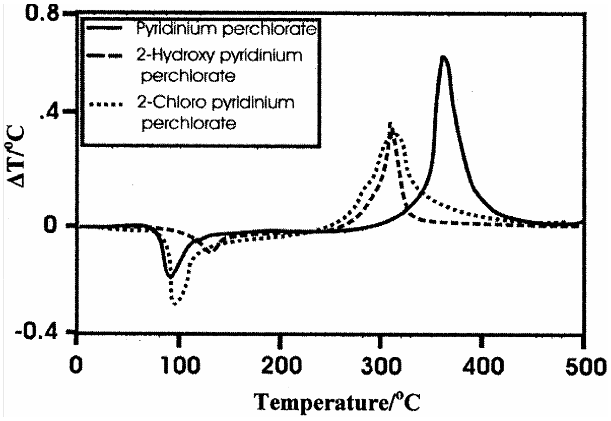


Fig.2— DTA of Pyridinium perchlorate salts

The DTA thermograms (Fig.3) were taken in static air atmosphere (mass~ 20 mg, heating rate 10°C/min) using an instrument supplied by Universal Thermal Instrument, Mumbai. The TG and DTA phenomenological data are summarized in Table 2.

Ignition delay measurements

The ignition delay (D_i) measurements were undertaken using tube furnace technique[17] in the temperature range 300-405°C. The D_i data were found to fit in the following equation [18-20]

$$D_i = A \exp(E_a^*/RT)$$

where E_a^* is the activation energy for thermal explosion, A- the pre-exponential factor and T- the absolute temperature. E_a^* was determined (Table 3) from the slope of a plot of ln (D_i) versus $1/T$ (Fig. 4).

Mathematical treatment of isothermal TG data

Two methods were used to evaluate kinetic parameters.

A general equation (1) for analyzing the kinetics of a thermally induced solid state reaction is[21]

$$d\alpha/dt = k(T) f(\alpha) \qquad \ldots (1)$$

where t is the time, T is the temperature, α is the extent of conversion ($0 < \alpha < 1$), $k(T)$ is the rate constant and $f(\alpha)$ is a function called the reaction model[21], which describes the dependence of the reaction rate on the extent of reactions. The value of α is experimentally derived from the global mass loss in TG experiments. The reaction model may take various forms. The temperature dependence of k (T) can be satisfactorily described by the Arrhenius equation, whose substitution into Eq. (1) yields

$$d\,\alpha/dt = A \exp(-E_a^*/RT).f(\alpha)\,. \qquad \ldots (2)$$

where, A is pre exponential factor, E_a^* is activation energy and R is the gas constant.

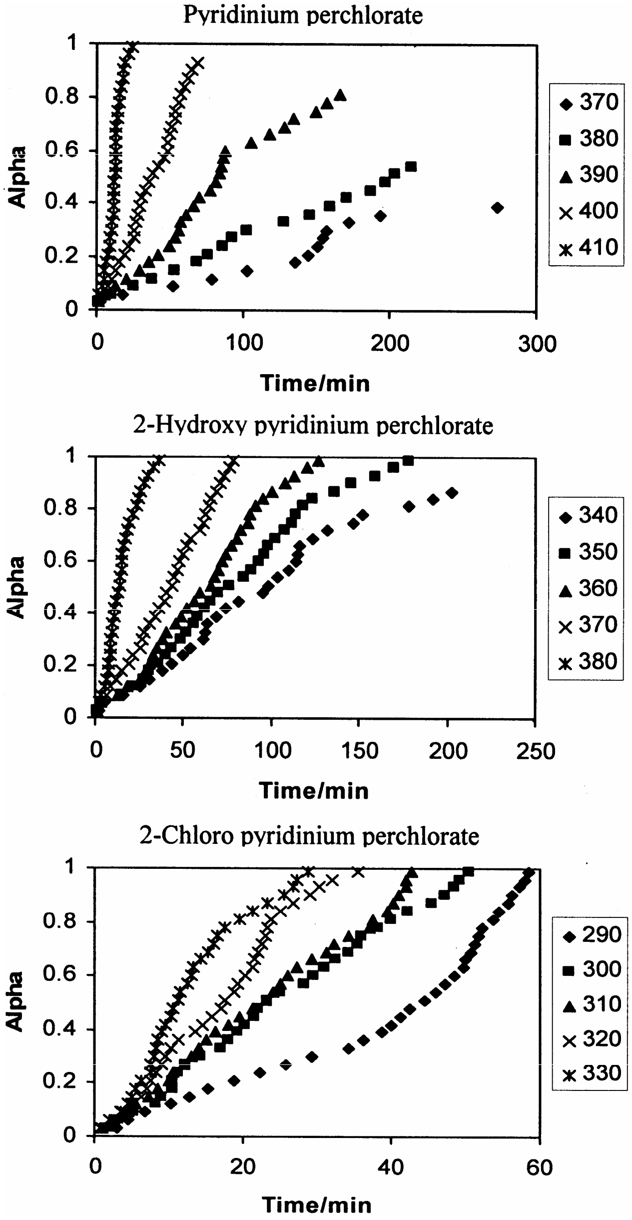


Fig. 3— Isothermal TG of Pyridinium perchlorate salts

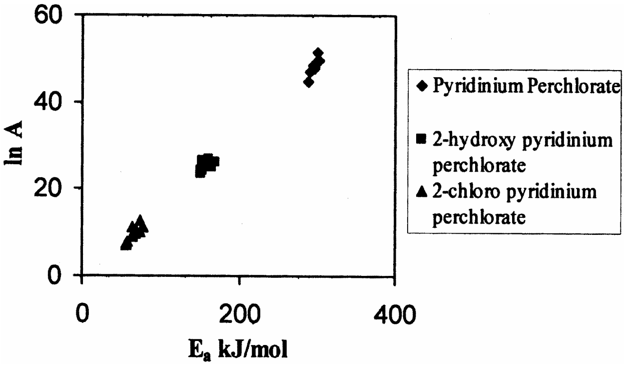


Fig. 4— Graph of ln A vs activation energy

Table 2— TG and DTA data of Pyridinium perchlorates

Compound	TG Static air			DTA Peak Temp. (°C)	
	T_i(°C)	T_f(°C)	α	Endo.	Exo.
Pyridinium perchlorate	260	392	97	101	302
2-Hydroxy pyridinium perchlorate	320	448	92	93	352
2-Chloro pyridinium perchlorate	137	340	90	122	299

T_i: initial temperature; T_f : final temperature; α : percent decomposition

Table 3— Explosion delay (D_E) and activation energy for thermal explosion (E_a^*) for Pyridinium Perchlorates

Compound	Mass, mg	D_E/s at Temp. (°C)								E_a^* kJ/mol	r
		300 ±1	315 ±1	330 ±1	345 ±1	360 ±1	375 ±1	390 ±1	405 ±1		
Pyridinium perchlorate	20	161	128	105	96	75	68	54	49	36.47	0.9965
2-Hydroxy pyridinium perchlorate	20	DNE	DNE	DNE	183	139	103	86	74	53.43	0.9931
2-Chloro pyridinium perchlorate	20	82	41	32	24	15	12	-	-	76.24	0.9893

DNE- did not explode

Model fitting method

Rearrangement and integration of Eq. (1) for isothermal conditions gives

$$g_j(\alpha) = k_j(T)\,t \qquad \text{... (3)}$$

where $g(\alpha) = {}_0\int^{\alpha} [f(\alpha)]^{-1}\, d\alpha$ is the integrated form of the reaction model. The subscript *j* has been introduced to emphasize that, substituting a particular reaction model in Eq. (3) results in evaluating the corresponding rate constant, which is determined from the slope of a plot of $g_j(\alpha)$ verses *t*. For each reaction model selected, the rate constants are evaluated at several temperatures T_i, and Arrhenius parameters are determined using the Arrhenius Eq. (4) in its logarithmic form

$$\ln k_j(T_i) = \ln A_j - E_j / RT_i \qquad \text{... (4)}$$

Arrhenius parameters were evaluated for isothermal data by the model fitting method.

Isoconversional method

This method allows the activation energy to be evaluated without making any assumptions regarding reaction model. Additionally, this method evaluates the effective activation energy as a function of the extent of conversion, which allows one to explore multistep kinetics.

The basic assumption of the isoconversional method[22] is that the reaction model as defined in Eq. (1) is not dependent on temperature or heating rate. Under isothermal conditions, on combining Eq. (3) and (4) we get-

$$-\ln t_{\alpha,i} = \ln [A_\alpha / g(\alpha)] - E_a^* / RT_i \qquad \text{… (5)}$$

where E_a^* is evaluated from the slope of the plot of $-\ln t_{\alpha,i}$ against T_i^{-1}. Thus E_a^* at various α have been evaluated Fig. 5.

Results and Discussion

Interaction of $HClO_4$ with pyridine form salts easily as compared to substituted pyridines which may be due to the *-I* effect of substituents which decreases the electron density at nitrogen making substituted pyridine comparatively a weak base. However, TG data taken in air (Fig. 1) show that each salt decompose in single step only. Each sample undergoes slight weight loss prior to an audible explosion. A very thin layer of sublimate collects on the sides of the TG crucible for each salt. DTA curves (Fig. 2) show an endotherm which may be due to melting/phase transformation while an exotherm is due to the oxidation reduction leading to explosion.

There is always an uncertainty in analyzing the kinetics from isothermal TG of the solid-state decomposition of energetic compounds using a model fitting method. One of the most important reasons is the composite nature of decomposition of the salts, which generally involves complex physicochemical changes. Analyses of the kinetics using fourteen mechanism based kinetic models involve the selection of a “best fit” model based on the value of statistical parameter, *r,* close to 1. Among various values of *r* calculated for different models, the highest value of *r* for pyridinium perchlorate, 2-hydroxypyridinium perchlorate and 2-chloropyridinium perchlorate correspond respectively to model 4 (Power law), model 11 (Three dimensional diffusion) and model 5 (One dimensional diffusion). The corresponding values of E_a as reported in Table 4 for pyridinium perchlorate, 2-hydroxypyridinium perchlorate and 2-chloro pyridinium perchlorate are respectively 293.9, 168.8 and 68.0 kJmol^{-1}. A plot (Fig. 4) of all of the values of the activation energy against the respective ln *A* values obtained from different models for each salt (Table 4) indicates that all of these values fall in an almost straight line, showing the existence of a kinetic compensation effect. The kinetic compensation effect refers to the fact that under a variety of conditions, an approximately linear relationship exists between the pre-exponential factor, ln *A*, and the apparent activation energy, E_a, which are determined for a process from the Arrhenius equation

$$\ln k = \ln A - E_a/RT \qquad \text{… (6)}$$

When ln *A* and E_a are linearly related, the compensation parameters *a* and *b* are defined by Eq. (7) for all measurements

$$\ln A = a\,E_a + b \qquad \text{… (7)}$$

An increase in E_a does not cause the expected decrease in the reaction rate because *A* increases to compensate for E_a. Equations (6) and (7) are closely related as E_a increases, an offsetting increase in ΔS^* occurs

$$\Delta G^* = E_a - T\Delta S^* \qquad \text{… (8)}$$

Although the physical and chemical meanings of Arrhenius parameters for heterogeneous processes are uncertain, the origin of the discrepancies and validity of individual data sets can be assessed by the compensation effect as a single, general, chemical phenomenon.

Moreover, it is evident from our thermal analysis that there are multiple competing reaction pathways during the course of thermolysis. As the various models may represent the experimental data mathematically, support for mechanistic conclusions of thermoanalytical data is not provided by the kinetic parameters obtained from model fitting. Isoconversional method is known to allow for model independent estimation of the apparent activation energy. Several isoconversional methods have been reported; we have adopted the method reported by Vyazovkin[22]. This approach indicates that the decomposition of these salts is not as simple as indicated by the model fitting approach. As is clear from the Fig. 5 that for a particular sample activation energy has different value at different α. It is true that energetic materials appear to have reaction characteristics that are generally consistent with the isoconversional principle as long as the confinement conditions are constant and appropriate to the intended application.

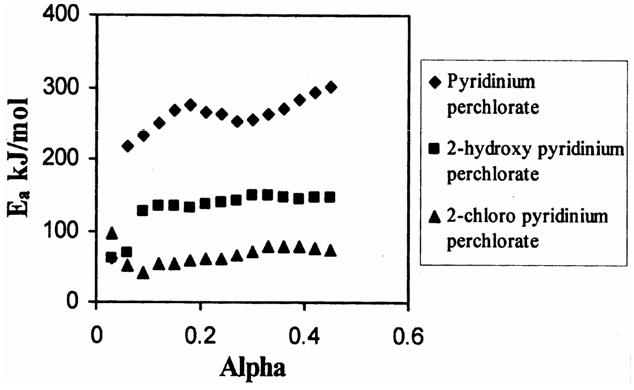
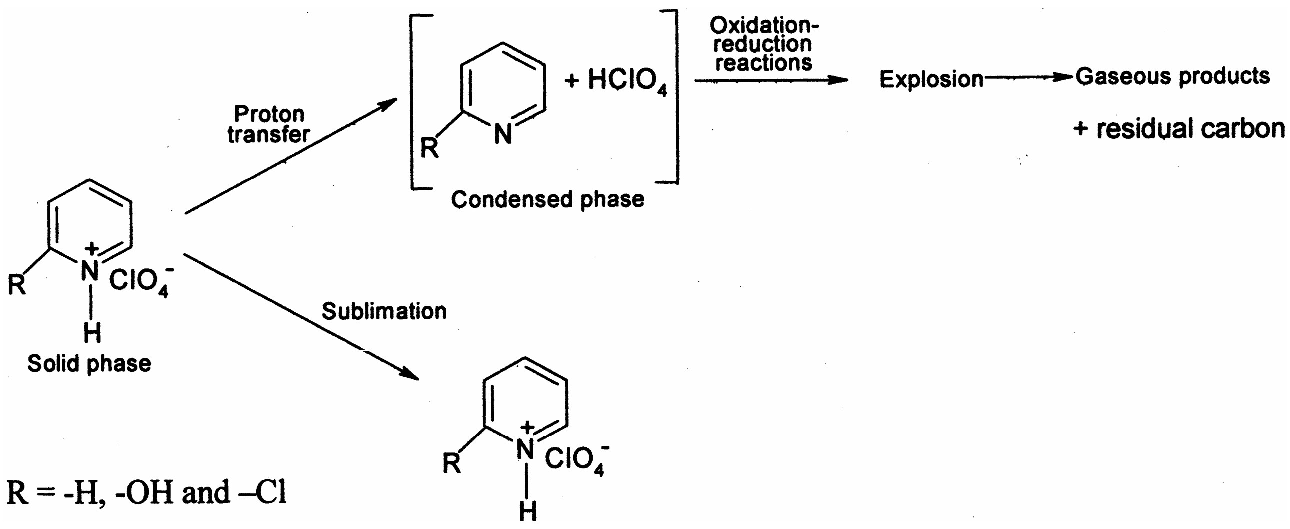


Fig. 5— Variation of activation energy with extent of conversion (α)

Table 4— Arrhenius parameters for isothermal decomposition of Pyridinium perchlorates

	Pyridinium perchlorate			2-Hydroxy pyridinium perchlorate			2-Chloro pyridinium perchlorate		
Model	E_a(kJ/mol)	-ln *A*	*r*	E_a(KJ/mol)	-ln *A*	*r*	E_a(kJ/mol)	-ln *A*	*r*
1	301.5	49.4	0.9870	150.4	23.5	0.9227	55.5	7.0	0.9766
2	301.1	49.5	0.9871	150.9	23.7	0.9231	56.2	7.3	0.9783
3	300.0	49.4	0.9873	151.7	24.1	0.9239	57.5	7.9	0.9812
4	293.9	47.8	0.9876	157.4	25.3	0.9279	64.9	9.6	0.9884
5	290.9	46.9	0.9874	160.4	25.8	0.9299	68.0	10.3	0.9886
6	294.9	48.6	0.9874	161.9	26.9	0.9318	74.3	12.7	0.9847
7	300.5	49.4	0.9871	153.8	24.4	0.9255	62.7	9.0	0.9841
8	299.9	49.4	0.9872	154.6	24.8	0.9262	64.0	9.5	0.9849
9	298.6	49.3	0.9873	156.3	25.4	0.9276	66.7	10.4	0.9858
10	295.6	47.6	0.9875	159.0	25.0	0.9295	69.0	10.0	0.9868
11	288.8	44.6	0.9872	168.8	26.0	0.9364	77.0	11.2	0.9732
12	295.9	48.0	0.9875	157.7	25.0	0.9285	66.7	9.8	0.9873
13	301.4	51.5	0.9869	154.0	26.4	0.9257	64.4	11.3	0.9836
14	289.5	44.6	0.9872	165.4	25.0	0.9338	74.3	10.1	0.9859



Scheme 1

The thermal stability of pyridinium perchlorates may depend upon the tendency of pyridinium ion to release a proton to perchlorate ion in condensed phase. Moreover, the tendency of a perchlorate ion to accept proton depends on its basicity at higher temperatures. The transfer of proton through an activated complex, from pyridinium ion to perchlorate ion, form pyridine and $HClO_4$ molecule. Further at higher temperatures, interaction between $HClO_4$ and pyridine induce ring rupture causing explosion with the formation of gaseous products. It is inferred that interaction between pyridine(s) and $HClO_4$ at room temperature is corresponding salt formation whereas, at higher temperature it cause explosion. The reaction pathways are summarized in Scheme 1.

Conclusions

The thermolysis of pyridinium perchlorates involves proton transfer from the pyridinium ion to the ClO_4^- ion as the primary rate controlling step. At higher temperature, interaction between pyridine and $HClO_4$ leads to an explosion.

Acknowledgements

Thanks are due to Head, Chemistry Department for providing laboratory facilities and to CSIR for Emeritus Scientistship to Dr. Gurdip Singh and SRF-extended to Dr Pratibha Srivastava.

References

1 Singh G, Kapoor I P S, Mannan S M & Agrwal J P, *Combust Flame*, 97 (1994)355.

2 Singh G & Kapoor I P S, *Combust Flame*, 92 (1993) 283.

3 Singh G, Kapoor I P S & Mannan S M, *Thermochim. Acta*, 262, (1995) 117.

4 Singh G, Kapoor I P S & Mannan S M, *J Energ Mater*, 13 (1992) 141.

5 Singh G, Kapoor I P S & Mannan, S M, *J Energ Mater*, 13 (1995) 141.

6 Singh G, Kapoor I P S & Mannan S M, *J Thermal Anal*, 46 (1996) 1751.

7 Lyerly W M, *US Pat*. 3, 629, 021 (1972).

8 Lundsgaard C, *Br. Pat*. 168, 338 (1921).

9 Dunglinson C & Lyerly W M, *US Pat*. 3,431,155, 1969, CA, 7011678n.

10 Russel T P & Brill T B, *Propellants Explos Pyrotech*, 15 (1990) 281.

11 Russel T P & Brill T B, *Propellants Explos Pyrotech*, 15(1990) 27.

12 Russel T P & Brill T B, *Combust & Flame*, 76 (1989) 393.

13 Chem R, Russel T P, Rheingold A L & Brill T B, J Cryst Spectr Res, 21(1991) 167.

14 Kapoor I P.S, Srivastava P & Singh G, *J Hazard Mater*, 150 (2008) 687.

15 Kapoor I P S, Srivastava P & Singh G, *J Phys Chem A*, 112(4), 2008, 652.

16 Singh G & Singh R R, *Res Ind*, 23 (1978) 92.

17 Singh G, Vasudeva S K & Kapoor I P S, *Indian J Technol*, 29 (1991) 589.

18 Semenov N, *Chemical Kinetics and Chain reactions*, (Clarendon Press: Oxford), 1935, Ch. 18.

19 Freeman E S & S.Gordon, *J Phys Chem*, 60 (1956) 867.

20 Zinn J & Rogers R N, *J Phys Chem*, 66 (1962) 2646.

21 Brown M E, Dollimore D & Galway A K, *Comprehensive Chemical Kinetics*, vol. 22, (Elsevier, Amsterdam), 1960.

22 Vyazovkin S, *Ind J Chem Kinetics*, 28 (1996) 95.