

Exploring Thermal Gravimetric Analysis Data Towards the Determination of Non-Isothermal Kinetics of Oxalic Acid

Marathe Y. V¹., Patil C. M²., Wagh A. G²., Gupta G. R.^{1,2*}

*¹G.T. P. College, Nandurbar-425412, India, Grgupta83@Gmail.Com

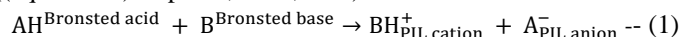
²School of Chemical Sciences, KBC-North Maharashtra University, Jalgaon-425001, Grgupta83@Gmail.Com

Abstract: Picrate compounds are well-known addition compounds, which are thoroughly analyzed by using modern analytical tools. The present study deals with an elegant exploration of the thermal profiles of the synthesized picrate compounds to disclose the pattern of thermal degradation of naphthalene, indole, pyridine and 1, 2, 3,4-tetrahydrocarbazole. Furthermore, non-isothermal kinetic investigations providing sound information about kinetic parameters, such as activation energy and frequency factor by using the Coats–Redfern equation was performed.

Index Terms: Thermal Gravimetric Analysis, Coats–Redfern, Non – Isothermal Kinetics.

I. INTRODUCTION

During the last few decades, molten salts are classified on the basis of their melting temperature (Wikes J.,2002; Patil P. et al.,2018; Vasim R., et al.,2013; Gupta A., et al.,2013) into ionic liquids (liquid below 373K) and molten salts (liquid above 373K) (Pietro B, et al.,2012; Welton T.,1999; Gaurav R., et al.2012). Subsets of ionic liquids are protic ionic liquids, which have an exceptional hydrogen-bonded network (Fumino K., et al.,2002) and are very easily been synthesized in the laboratory, simply by performing reaction between Bronsted acid and Bronsted base ((equation 1) Lopes J., et al.,2010).



In all these protic ionic liquids availability of a proton for hydrogen bonding interactions, is responsible for their exceptional set of properties which are tuned by changing either cation or anion. Pirates have also been classified as molten salts and were synthesized by performing simple acid-base reaction between Bronsted acid and Bronsted base. Moreover, the

hydrogen bonding interactions in picrates have substantially been examined by the chemists. Indeed, by taking advantages of the features accounted of the picrates, the pirates have found very important applications in recent years (Miguel A., et al.,2016; Sidney D., et al.,1954; Vladimir S., et al.,2011; Athmane M., et al.,2017).

In the next, thermogravimetric analysis (TG) has primarily aimed to study the weight change of a sample or material as a function of temperature (Tomar P., et al.,2014; Shirsath N., et al.,2018; Gaurav R., et al.,2018). The technique marks its importance where the transformations have been indulging in the absorption or emission of gases from a sample or material in condensed phase. The exploration of the thermal data towards kinetic analysis of thermal decomposition processes have seizes an attention of quite a large number of investigators (Patil K, et al.,2019; Gupta G., et al.,2018; Tomar P., et al.,2020). The interest has been fully reasonable. On one side, designing of any kind of device, in which the thermal decomposition takes place requires highly precise kinetic data. While, on the other side, kinetics is to be fundamentally interrelated with the decomposition mechanisms. In this regard, Bamford and Tipper (Bamford C., et al.,1980) in their book entitled "comprehensive chemical kinetics" accounts a historical development in the field of solid-state kinetics. The thermal decomposition of solidshave usually been considered as the process which encompasses all the processes such as the destruction of the stabilizing forces of the crystal lattice of a reactant solid, including both chemical reactions and physical reorganizations (e.g., melting, sublimation and recrystallization) (Robert F.,1994; Nobuyoshi J., et al.,2013)

Reaction kinetics in the solid-state have been studied by thermo-gravimetry, however other analytical methods such as differential scanning calorimetry (DSC), powder X-ray diffraction (PXRD), and nuclear magnetic resonance (NMR) have also been exploited to study the solid-state kinetics. Notably, kinetic analysis (isothermal or non-isothermal) can be performed by either model-fitting or model-free (iso-conversional) methods. Different solid-state kinetic analysis methods have been recently reviewed (Urbanovici E., et al.,1999; Gopalakrishnan S, et al.,2019; EbrahimiKahrizangi R, et al.,2007).

Although, it is to be cleared that the selection of an appropriate model is a very crucial point in kinetic analysis. There is availability of variety of different methods to study the kinetics of non-isothermal processes in the literature (Gupta G., et al.,2019). The method reported by Coats-Redfern (CR), very aptly utilizes the asymptotic series expansion for approximating the exponential integral in Equation (8), giving

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[\frac{AR}{\beta Ea} \left(1 - \frac{2RT}{Ea} \right) \right] - \frac{Ea}{RT} \quad \text{----- (1)}$$

A critical scrutiny was made on the reliability of kinetic parameters of non-isothermal thermo-analytical rate measurement by the widely applied Coats-Redfern (CR) method, and TGA analysis for the samples of naphthalenium picrate, indolium picrate, pyridinium picrate and 1,2,3,4-tetrahydrocarbazolium picrate using Coats-Redfern (CR) equation have been reported for the first time in this article.

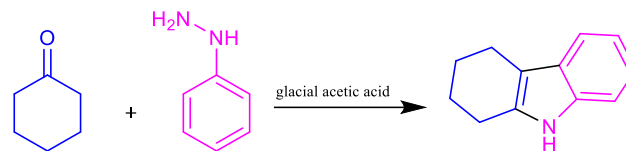
II. MATERIALS AND METHODS

Cyclohexanone, glacial acetic acid, phenyl hydrazine, indole, pyridine and picric acid were purchased from S. D. Fine Chemicals, Pvt. Ltd. Mumbai (India) and used with prior purification. Ethanol was procured from Merck and quartz double distilled water was used for preparation of solutions. All the melting points were recorded using open capillary method.

A. General procedure for the synthesis of 1,2,3,4 tetrahydro carbazole

Around bottom flask fitted with reflux condenser, and loaded with a mixture of 1ml of cyclohexanone and 6ml of glacial acetic acid was heated under reflux conditions with occasional stirring. Thereafter, 1.6ml of phenyl hydrazine was added to the reaction mixture gradually. Once, the addition was completed the reaction mixture was to be poured into a beaker containing crushed ice, resulting crystals of 1,2,3,4 tetrahydrocarbazolium. The resulting crystals had been separated over Buckner funnel, washed with plenty of cold water, and finally these crystals were recrystallized from ethanol to obtained pure 1,2,3,4-tetrahydrocarbazolium having

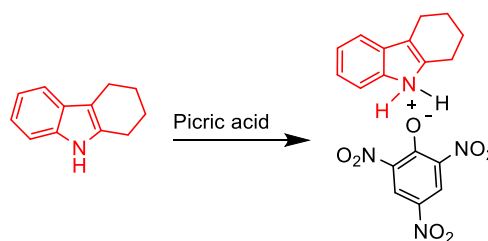
melting point between 118 and 120 °C. (Sethi A.,2003).



Scheme 1: Synthesis of 1,2,3,4 tetrahydrocarbazole

B. General procedure for the preparation of 1,2,3,4 tetrahydrocarbazolium picrate

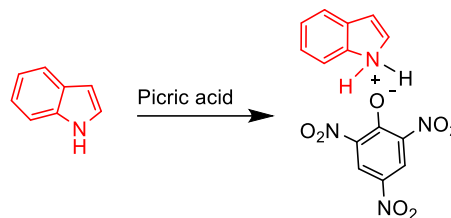
Cold saturated solution of recrystallized 1, 2, 3, 4-tetrahydrocarbazole and of picric acid in ethanol was mixed and stirred to obtain the chocolate-brown crystals of the 1, 2, 3, 4-tetrahydrocarbazolium picrate. The resulting crystals were collected over Buckner funnel and recrystallized from ethanol to obtained pure picrate having melting point between 144 and 146 °C.



Scheme 2: Preparation of 1,2,3,4 tetrahydrocarbazolium picrate

C. General procedure for the preparation of indolium picrate

Saturated ethanolic solution of the recrystallized indole and of picric acid were mixed thoroughly and the solution was allowed to develop dark orange-colored crystals of indolium picrate. The resulting crystals were collected over Buckner funnel and recrystallized from ethanol to obtained pure picrate having melting point between 198 and 200 °C (Vogels ,1989).



Scheme 3: Preparation of indolium picrate

III. METHODS

A. FT-IR analysis

Fourier Transform Infra-Red (FT-IR) analysis of the synthesized molten picrate compounds was performed on the FT-

IR affinity model, Shimadzu; dry KBr was used to set the

background; thereafter, a KBr pellet was developed and analyzed.

Table 1: FT-IR frequencies of synthesized picrate compounds

Entry	Picrate compound	FT-IR frequencies (cm ⁻¹)
A	Indolium Picrate	632.65, 732.95, 1311.59, 1342.46, 1435.04, 1454.33, 1487.12, 1541.12, 1604.77, 1631.78, 2854.65, 2920.23, 2987.74, 3103.46, 3142.04, 3412.08
B	1,2,3,4-Tetrahydrocarbazolium Picrate	642.3, 732.95, 1141.86, 1234.44, 1274.95, 1321.24, 1344.38, 1367.53, 1433.11, 1467.83, 1541.12, 1604.77, 1631.78, 2843.07, 2883.58, 2943.37, 3068.75, 3105.39, 3398.57
C	Pyridinium picrate	678.94, 754.17, 999.13, 1346.31, 1427.32, 1473.62, 1593.2, 1637.56, 1994.4, 2621.26, 2787.14, 3076.46, 3130.47
D	Naphthalenium Picrate	655.8, 732.95, 916.19, 1151.5, 1257.59, 1342.46, 1436.97, 1541.12, 1604.77, 1633.71, 3024.38, 3101.54

B. TGA-DTG analysis

To examine the thermal response of picrate samples, the samples were subjected to TGA analysis. A Perkin-Elmer TGA-4000 thermogravimetric analyser was used to study the thermal stability of the resulting picrates under a N₂ atmosphere, which was kept in an air-conditioned lab with a humidity of 5–10%. Samples having weights in the range of 4 to 6 mg were used for the measurements. The details regarding overall experimentation have already been reported in our previous communications.

C. Coats-Redfern model

The details regarding Coats-Redfern model have already been reported in our previous communication.

IV. RESULTS AND DISCUSSION

As we know, the picrate compounds of carbocycle like naphthalene are categorized as the addition compounds of the carbocycle with picric acid, and on the other hand picrates of heterocycles like indole, 1, 2, 3, 4-tetrahydrocarbazole and pyridine are categorized as molten salts.

A. FT-Infrared Spectral analysis of the synthesized picrates

Infrared spectra of the synthesized picrate compounds reveals that the characteristic group frequencies of molecular vibrations have been manifested the masses of the vibrating atoms, the molecular geometry, and the restraining forces holding the atoms in their equilibrium positions in the molecule (Vladimir S., et al., 2011; Pimmental G., et al., 1960). Since the restraining forces (force constants) are simply related to chemical bond orders, vibrational spectra advance sound information about chemical bonding and molecular structure. It has also been noted that the magnitude of vibrational spectra is very significantly disturbed by -H bond formation. The infrared frequencies of the synthesized picrate compounds are tabulated in the following Table 1.

The closer scrutiny of Table 1 reveals that, in case of indolium and carbazolium picrate the extent of hydrogen bonding has significantly been retarded due to the steric crowding in the structure. On the other hand, promising hydrogen bonding interactions have been observed in pyridinium and naphthalenium picrate compounds.

B. Thermal gravimetry analysis of the synthesized picrate compounds

Thermo-gravimetric analysis or thermal gravimetric analysis (TGA) in general has been considered as a method of thermal analysis in which changes in physical and chemical properties of samples or materials are investigated as a function of elevating temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). As we know, in case of differential thermal analysis the temperature changes in the sample are associated with the results of number of structure induced transformations such as phase

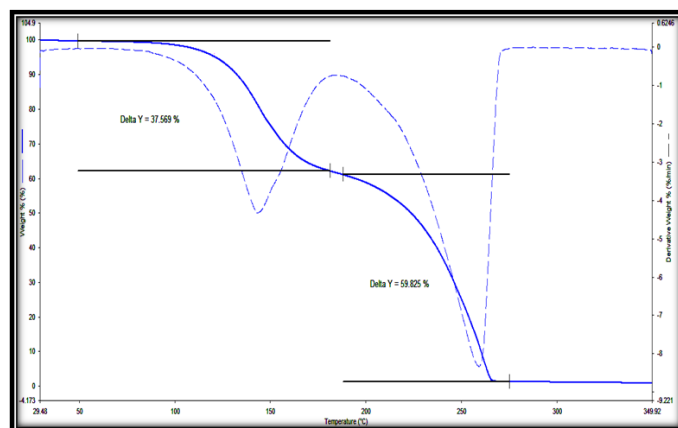


Figure 1: TGA-DTG of indoliumpicrate

As we know, in case of differential thermal analysis the temperature changes in the sample are associated with the results of number of structure induced transformations such as phase changes, decomposition, oxidation, reduction or other chemical reactions. The thermograms of the synthesized picrate compounds have been reported in the following Figures 1-4. The closer scrutiny of the Figure 1 reveals that the indolium picrate having good thermal stability, this molten salt starts decomposition over 100 °C. It is to be noted that there is no significant weight loss before 100°C that indicates the salt is free from moisture.

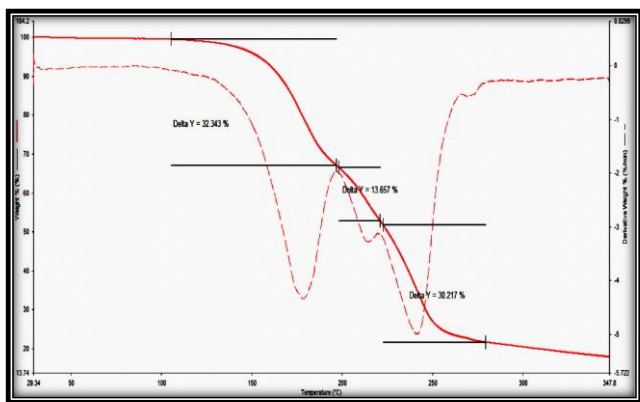


Figure 2: TGA-DTG of naphthalenium picrate

The thermal response of the naphthalenium picrate has been reported in Figure 2, and it has been cleared from Figure 2 that the picrate of the carbocycle have a good thermal stability and it involves two stage decomposition mechanism

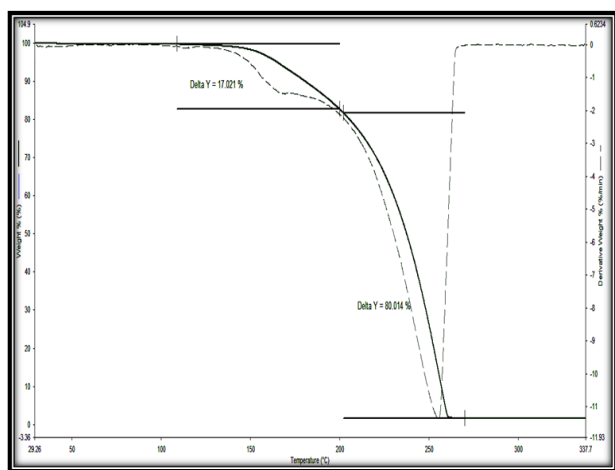


Figure 3: TGA-DTG of pyridinium picrate

Figure 3 represents the thermogram of pyridinium picrate, it is also to be noted that this molten salt has an exceptional set of thermal stability, very similar to indolium picrate the picrate of pyridine is also free from moisture and is said to be a moisture stable salt.

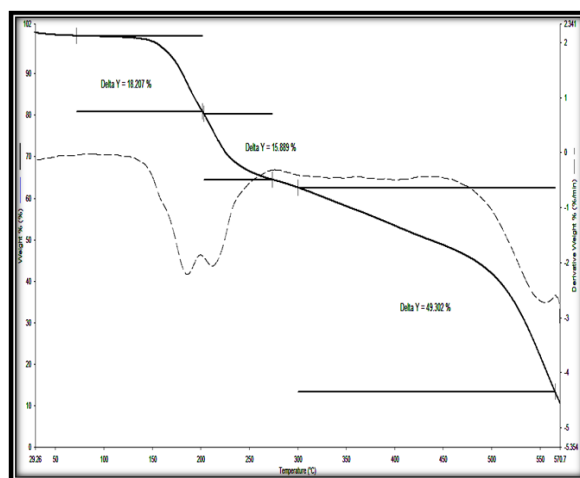


Figure 4: TGA-DTG of 1,2,3,4-tetrahydrocarbazolium picrate
The closer scrutiny of the Figure 4 reveals the thermal response of highly strained 1,2,3,4-tetrahydrocarbazolium picrate. Due to high structural crowding this salt is stable up to 150°C, quite much more stable as compare to the picrate of indole and pyridine.

C. Coats-Redfern model fitting

The left-hand side of equation 1 versus 1/T was plotted and the slope of these lines gave the E values. In testing the present data of dehydration of the samples, equation 8 expressing the order 1 was plotted. The first order equation was found to fit better. The straight-line plots for Picrates are given in the following Figures 5-12, and the calculated activation energies are cited in Table 2.

The values of Energy of activation for synthesized picrates are obtained by using following relation. $Slope = -\frac{Ea}{R}$

$\therefore Ea = -[Slope \times R]$ The intercept of the straight line is frequency factor of the reaction.

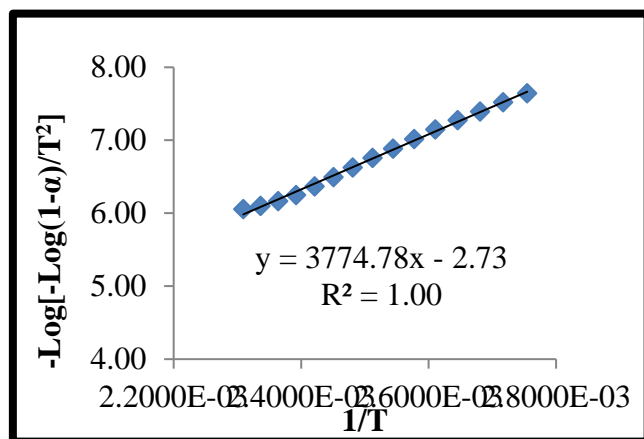


Figure 5: First decomposition point in naphthalenium picrate

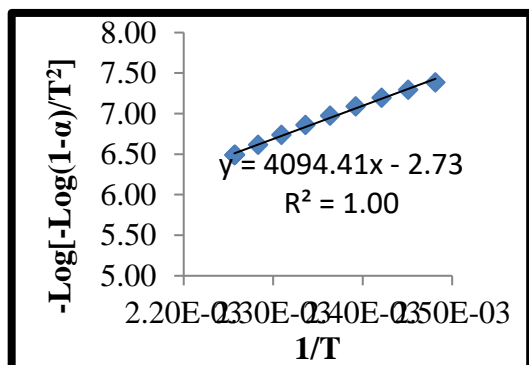


Figure 6: First decomposition point in indolium picrate

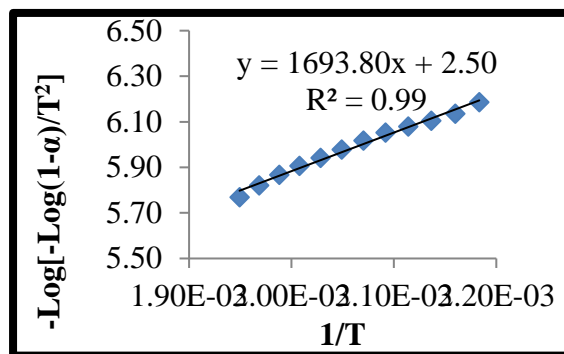


Figure 7: Second decomposition point in indolium picrate

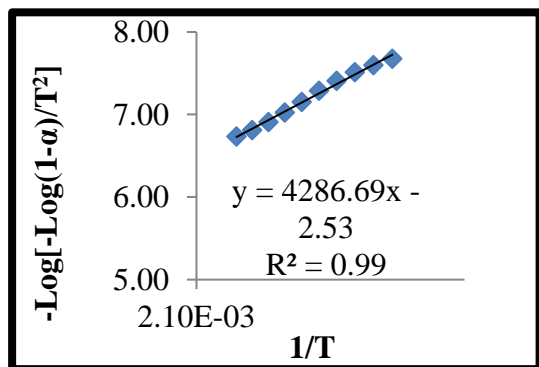


Figure 8: First decomposition point in pyridinium picrate

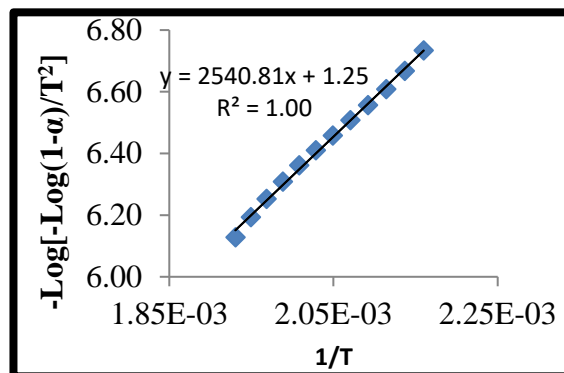


Figure 9: Second decomposition point in pyridinium picrate

Table 2: Energy of activation and the frequency factor of the synthesized picrates

Sr. No.	Name of the Compound	Ea (KJ.mol ⁻¹)			Frequency factor			r ²		
		A	B	C	A	B	C	A	B	C
2	Naphthalenium Picrate	72.276	--	--	5.37E+02	--	--	1.00	--	--
3	Indolium Picrate	78.396	32.431	--	5.37E+02	3.16E-03	--	1.00	0.99	--
4	Pyridinium Picrate	82.078	48.649	--	3.39E+02	5.62E-02	--	0.99	1.00	--
5	1,2,3,4-tetra-hydro-carbazolium Picrate	66.817	30.234	79.711	1.07E+01	9.12E-04	0.1259	1.00	0.99	0.98

A – First decomposition, B – Second Decomposition, and C- Third Decomposition

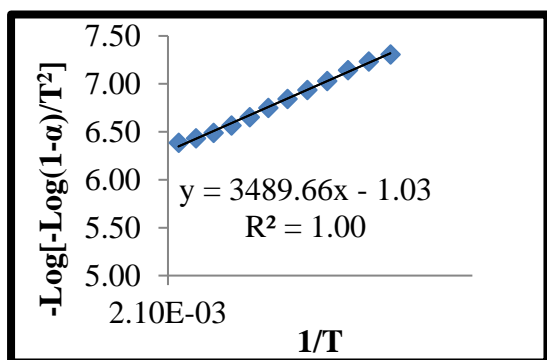


Figure 10: First decomposition point in 1, 2, 3, 4-tetrahydrocarbazolium picrate

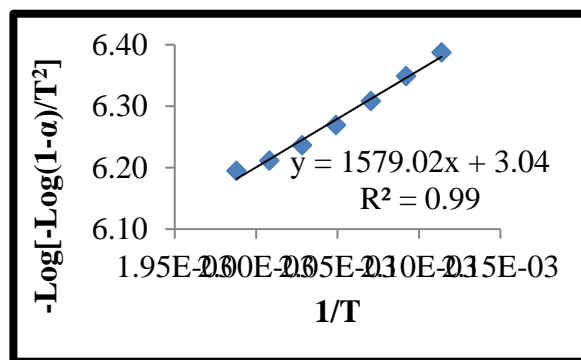


Figure 11: Second decomposition point in 1, 2, 3, 4-tetrahydro-carbazolium picrate

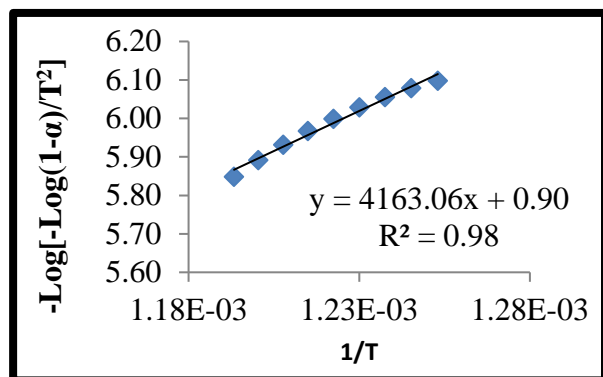


Figure 12: Third decomposition point in 1, 2, 3, 4-Tetrahydrocarbazolium Picrate

The closer scrutiny of Figures 5-12 and Table 2 reveal that the details regarding energy of activation and the frequency factor for the synthesized picrates using Coats-Redfern model.

It is to be noted that the value of energy of activation follows the order, which is given below

Pyridinium picrate > Indolinium picrate > 1, 2, 3, 4-tetrahydrocarbazolium picrate.

The order of energy of activation amongst the picrate compounds of indole, pyridine and 1,2, 3,4-tetrahydrocarbazole manifests that steric crowding have significant impact on the energy of activation values of the synthesized picrates and this is the highlight of the work.

CONCLUSION

If the molten salts or fused organic salts or ionic liquids are to be applied in industrial processes, their thermal response along with other thermodynamic properties is essential for the design of sustainable chemical facility. We obtained such thermal data from thermal techniques, for the picrates of naphthalene, indole, pyridine and 1,2,3,4-tetrahydrocarbazole over the temperature range of 25 to 570 °C. The calculations of energy of activation and frequency factor using thermal data by applying Coats-Redfern model as a function of temperature were made for the first time in the literature. The magnitude of energy of activation values are indicative of effects exerted by the structure i.e. steric crowding present in the structure. More detailed studies of spectroscopic properties at different temperatures are required to understand the structure and the structure induced thermal transitions for the studied salts.

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