



Isoconversional kinetic analysis of decomposition of nitropyrroles

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ABSTRACT

The thermal decomposition kinetics of pyrazole, N-nitropyrrole, 3-nitropyrrole and 4-nitropyrrole using TG–DTA technique under nitrogen atmosphere has been investigated. Friedman differential and Flynn–Wall–Ozawa integral methods were used to determine the kinetic parameters. The calculated activation energies are believed to be fairly well and qualitatively good in providing mechanistic clues. Pyrazole, 3-nitropyrrole and 4-nitropyrrole were decomposed by the multi step decomposition kinetics evident from the non-linear relationship of activation energy and the conversion rate. However, N-nitropyrrole was decomposed by single step decomposition or the unification of multistep decomposition kinetics evident from the linear relationship of activation energy and the extent of conversion. The present study may help to understand how the position and the number of nitro groups affect the decomposition kinetics of azoles and their possible use for the generation of vinylcarbenes.

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1. Introduction

Nitropyrroles have been used as biologically active compounds including antibiotics or their analogues, agrochemicals, dyestuffs, phosphores, non-linear optical materials, nitrogen containing solid fuels (coal and biomass), antifog additives in film and photoindustry, organic synthesis intermediates in nanochemistry and recently as energetic materials [1–4]. The measurement of kinetics and the associated Arrhenius parameters of thermal decomposition are the important aspects of the characterization of materials. Azoles are known to undergo peculiar decomposition mechanism. A retro-[3 + 2]-cycloaddition mechanism has been proposed for the decomposition of substituted azoles [1]. The reaction would follow: (i) a simple retro-[3 + 2]-cycloaddition mechanism, (ii) retro-cycloaddition with a concerted intermolecular hydrogen shift and (iii) a step-wise mechanism involving initial ring opening followed by bond dissociation with a concerted hydrogen shift. Homolysis of one or more bonds between the ring atoms and their substituents leaving the ring intact or exchange of two adjacent ring substituents followed by breakdown of the ring and nitro-nitrite rearrangement have also been proposed. Nevertheless, one of these initiation events may predominate under a given set of experimental conditions, competition among these pathways is likely depending upon the physical environment and the excess energy available. The thermal decomposition kinetics of pyrrole

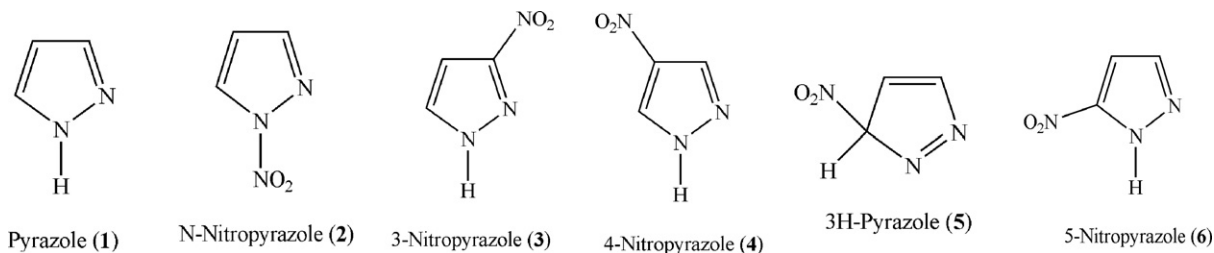
[5,6], pyrazole [7,8], triazole [9] and tetrazole [10] are known from both an experimental and theoretical perspective.

Infra red (IR) spectroscopy, thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), NO luminescence and T-jump/FT-IR spectroscopy have been used for the measurement of kinetics and the Arrhenius parameters of thermolysis of materials. TG and DTA techniques involve the continuous measurement of physical property such as weight, volume, heat capacity, etc as sample temperature is increased usually at a predetermined rate. It is possible to calculate the kinetic constants from these techniques by making a number of patterns at different heating rates. Several methods are known to calculate the kinetic parameters of solid state reactions based on the Arrhenius equation [12–15]. The recommendations of International Confederation for Thermal Analysis and Calorimetry (ICTAC) offer guidance for reliable evaluation of kinetic parameters from the data obtained by means of thermal analysis methods such as thermogravimetry, differential scanning calorimetry and differential thermal analysis [16–23]. The model dependent method needs thermal analysis measurement however it suffers from an inability to determine the reaction model uniquely. On the other hand, the model independent isoconversional methods avoid the problems originated from the ambiguous evaluation of the reaction model. The isoconversional methods yield effective activation energy as a function of the extent of conversion and permit to draw reliable mechanistic conclusions. Studies on the thermal decompositions of substituted pyrazoles are scarce and most of these thermal studies were carried out using flash vacuum pyrolysis [8,11]. To the best of our knowledge the thermal decomposition kinetics of

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N-nitropyrazole, 3-nitropyrazole and 4-nitropyrazole using the iso-conversional methods has not yet been reported elsewhere in the literature. We have investigated herein the kinetics of such compounds using TG–DTA technique under nitrogen atmosphere.



2. Experimental

All the reagents and solvents were purchased from Sigma Aldrich, Merck, Alfa-Aesar and used without further purification. Melting points were recorded by a capillary melting point apparatus and were uncorrected. All experiments were monitored by thin-layer chromatography (silica gel 60F254 Merck). FT-IR spectra were recorded on a Perkin Elmer FT-IR-1600 spectrophotometer in KBr matrix. The peak signals are reported in wave numbers (cm^{-1}). ^1H NMR spectra were recorded on a 300-MHz Varian instrument with dimethylsulfoxide ($\text{DMSO}-d_6$) and CDCl_3 solvents. Chemical shift values are reported in δ units (parts per million) relative to tetramethylsilane (TMS) as an internal standard. Gas chromatography–mass spectrometry (GC–MS) was carried out with glass columns packed with 3% OV-17 on Chromosorb W, 100–120 mesh, treated with DMCS in Varian 1400 instrument fitted with flame ionization detector and nitrogen was used as carrier gas. Thermogravimetric analysis (TGA) measurements were carried out on the TA instruments SDT Q600 instrument under nitrogen gas.

2.1. Synthesis of N-nitropyrazole (2)

Freshly prepared acetyl nitrate (HNO_3 , 1.8 mL, $d = 1.54 \text{ g cm}^{-3}$) and acetic anhydride, 4.2 mL) was added to pyrazole (1) (1.0 g) dissolved in acetic acid (2.8 mL) at 25°C . After stirring for 30 min the reaction mixture was poured into water. The crude yield after washing with water and drying was 1.4 g (84%). m.p. $91\text{--}92^\circ\text{C}$. FT-IR (KBr, cm^{-1}): 1617, 1320 (N--NO_2). ^1H NMR ($\text{DMSO}-d_6$) δ : 8.65 (d, 1H, 5-H), 7.80 (s, 1H, 3-H), 6.73 (m, 1H, 4-H). EI-MS: m/z 113 ($\text{M}^{+\bullet}$). Anal. Calcd for $\text{C}_3\text{H}_3\text{N}_3\text{O}_2$ (113.08): C, 31.83; H, 2.67; N, 37.26. Found: C, 32.88; H, 2.62; N, 37.43.

2.2. Synthesis of 3-nitropyrazole (3)

A solution of 1.0 g of N-nitropyrazole (2) in 10 mL of benzonitrile was heated for 3 h at 180°C , after cooling the reaction mixture was poured into 30 mL of hexane. 3-Nitropyrazole was collected by filtration. The crude yield after washing with hexane and drying was 0.93 g (98%). The solid was recrystallized from water. m.p. $174\text{--}175^\circ\text{C}$. FT-IR (KBr, cm^{-1}) 3180 (N–H), 1520 and 1351 cm^{-1} (NO_2). ^1H NMR ($\text{DMSO}-d_6$) δ : 7.96 (d, 1, 5(3)–H), 6.96 (d, 1, 4–H). EI-MS: m/z 113 ($\text{M}^{+\bullet}$). Anal. Calcd for $\text{C}_3\text{H}_3\text{N}_3\text{O}_2$: C, 31.86; H, 2.67; N, 37.16. Found: C, 32.19; H, 2.84; N, 37.18.

2.3. Synthesis of 4-nitropyrazole (4)

1-Nitropyrazole (2) (1 g) was slowly added to a round-bottomed flask containing H_2SO_4 (98%, 5 mL) and stirred for 20 h at room temperature. The reaction mixture was slowly transferred to a beaker containing ice with stirring. The solution was extracted with ether. The organic layer was dried with Na_2SO_4 then evaporated

to afford 4-nitropyrazole (4) as a colourless solid (0.97 g, 96%). The solid was recrystallized from ether/hexane to get white crystalline compound. m.p. $163\text{--}165^\circ\text{C}$; FT-IR (KBr, cm^{-1}) 3186 (N–H), 1526 and 1353 cm^{-1} (NO_2). ^1H NMR ($\text{DMSO}-d_6$) δ : 8.26 (d, 1, 5-H),

6.76 (d, 1, 3-H). EI-MS: m/z 113 ($\text{M}^{+\bullet}$). Anal. Calcd for $\text{C}_3\text{H}_3\text{N}_3\text{O}_2$: C, 27.54; H, 3.88; N, 32.42. Found: C, 28.31; H, 3.21; N, 31.38.

2.4. Thermal analysis

The sample ($\sim 1 \text{ mg}$) taken in alumina crucible and the reference were heated from 25 to 250°C on the TA instruments Q600 SDT instrument under nitrogen environment (flow rate of $100 \text{ cm}^3/\text{min}$) as the purge and protective gas. The reference was an empty alumina crucible. Non-isothermal TGA runs were conducted at heating rates 2.5, 5, 10 and $20^\circ\text{C}/\text{min}$. Isoconversional model free methods [13,14] were used for the kinetic analysis of the compounds. The rate constant for the solid state decomposition was assumed to follow the Arrhenius rate law and the first stage endothermic reaction based on the DTA data was used to calculate the kinetic parameters considering as a single step. The extent of conversion (α) has been computed from the weight loss data using the reported standard methods. $\Delta\alpha$ of 0.01 and a $\Delta\alpha$ of 0.025 were used to compute the activation energy from the differential and the integral methods respectively. For comparison and plotting, constant α values were shown at an interval of 0.025.

3. Kinetic analysis

The kinetic methods commonly used in thermal analysis have been derived for single reactions. For systems involving multiple reactions, the inappropriate applications of such methods can lead to misleading results. However, it has been shown that the iso-conversional methods can give meaningful values of the activation energy in a wide range of circumstances. The isoconversional methods permit a model independent estimate of the activation energy. Friedman's method is based on the Arrhenius rate law. It is the most straightforward way to evaluate the effective activation energy as a function of the extent of reaction. The magnitude of rate constant (k) is determined by temperature (T) and is usually described by the following equation:

$$kf(\alpha) = \beta \left(\frac{d\alpha}{dT} \right) = Af(\alpha) \exp \left(-\frac{E}{RT} \right) \quad (1)$$

where k is the reaction rate constant, $f(\alpha)$ is the reaction model, α is the conversion function (it should be noted that α ranges from 0 to 1), β is the heating rate, A is the pre-exponential factor, R is the universal gas constant, T is the absolute temperature.

Friedman's method applies the logarithm of conversion rate as a function of the reciprocal temperature at different degrees of conversion [13]. Friedman's equation is obtained by simple rearrangement of Eq. (1)

$$\ln \left[\beta \frac{d(\alpha)}{dT} \right] = \ln \left[\frac{d(\alpha)}{dt} \right] = \ln[Af(\alpha)] - \frac{E}{RT} \quad (2)$$

The value of $d\alpha/dt$ is obtained numerically using $\Delta\alpha = 0.02$ and linear interpolation of the experimental data. The plot of $\ln(d\alpha/dt)$

versus $1/T$ at constant α for a set of β values gives a family of straight line with slope $-E_\alpha/R$. This model-free method can be applied to the data sets obtained at different heating rates β_i and/or different temperatures, T_i .

Friedman's method may lead to erroneous estimates of the activation energy the use of isoconversional integral methods appear to be a safer alternative. The isoconversional integral method given independently by Flynn and Wall [28] and Ozawa [14,29] uses the Doyle approximation [30]. The major advantage of this method is that it does not require any assumptions concerning the form of the kinetic equation other than the Arrhenius type temperature dependence. The Flynn–Wall–Ozawa method is a model-free method which involves measuring the temperatures corresponding to fixed values of α from experiments at different heating rates, β and plotting $\ln(\alpha)$ against $1/T$ and the slopes of such plots give $-E_\alpha/R$. If E_α varies with α , the results should be interpreted in terms of multi-step reaction mechanisms. The Arrhenius rate law Eq. (1) was integrated and Doyle approximation was applied to obtain Eq. (3). The plot of $\ln \beta$ versus $1/T$ gives straight line with slope $-1.052 E/R$.

$$\ln \beta = \ln \left(\frac{AE}{Rg(\alpha)} \right) = 5.523 - 1.052 \left(\frac{E}{RT} \right) \quad (3)$$

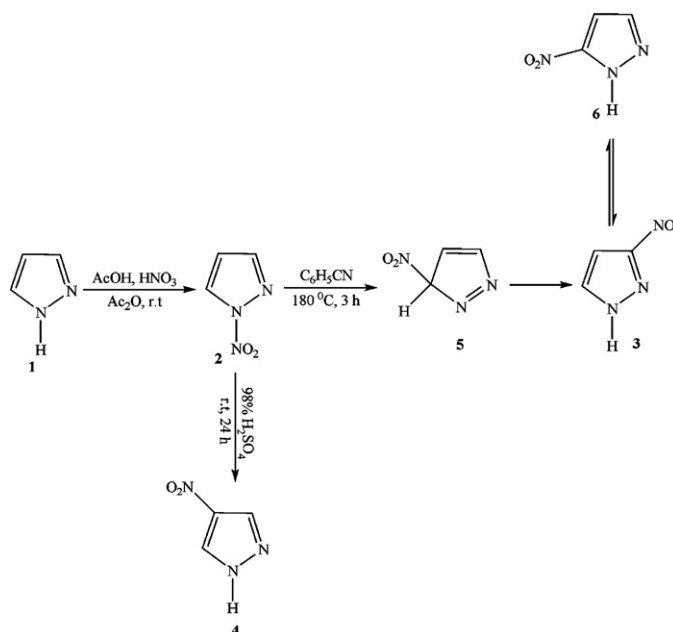
where $g(\alpha)$ is the integral form of kinetic model (i.e., $g(\alpha) = kt$). Thus, for $\alpha = \text{constant}$, a plot of $\ln \beta$ versus $1/T$ obtained from thermal curves recorded at several heating rates, should be a straight line whose slope allows evaluation of the activation energy. As far the pre-exponential factor value is concerned, its value can be obtained from the intercept if the form of the integral conversion function $g(\alpha)$ is known. For $x < 20$ (i.e., $x = E/RT$), Doyle's approximation leads to errors higher than 10%. For such cases, Flynn [31,32] suggested corrections in order to obtain correct activation energy values.

The Flynn–Wall–Ozawa method is potentially suited for use in systems where many reactions are occurring such that the activation energy varies with time. However, the method is predicted to fail if reactions of widely different type (and hence having very different activation energies) are occurring simultaneously. Competitive reactions which have different products also render the method inapplicable. Furthermore, the Flynn–Wall–Ozawa method is less precise than the Friedman's method. It was demonstrated that, if the activation energy depends on the degree of conversion, its values obtained by isoconversional differential and integral methods are different [33–37]. Dowdy [34,35] showed that for the systems of competitive or independent reactions, both the Friedman and the Flynn–Wall–Ozawa methods lead to different values of the activation energy. On the other hand, if E is independent on α , then the two methods lead to practically the same activation energy value. For this reason a comparison of the results from the two methods is useful to check on their accuracy.

4. Results and discussion

4.1. Synthesis aspects

The direct nitration of pyrazole using nitric acid or nitric acid–sulfuric acid mixture leads to substitution at 4-position. Hüttel and Büchele [24] synthesized N-nitropyrazole and its substituted derivatives. They also have described the rearrangement of N-nitropyrazoles to the 4-nitropyrazole derivatives in sulfuric acid solution in cold. We have synthesized nitropyrazoles starting from pyrazole (1) as shown in Scheme 1. N-nitropyrazole (2) was synthesized in good yield (84%) using preformed acetyl nitrate at room temperature. Usually, N-nitropyrazole could be purified by direct crystallization or by very mild acid hydrolysis of the N-acetyl derivatives prior to crystallization. We have synthesized 3-nitropyrazole (3) in higher yield (98%) heating 10% solution



Scheme 1. Synthesis of nitropyrazoles from pyrazole.

of N-nitropyrazole (2) in benzonitrile at 180 °C for 3 h. For the mechanism of the rearrangement of N-nitropyrazoles, Janssen et al [25–27] proposed a two-step process involving an unprecedented [1,5]-sigmatropic shift of the nitro group and fast rearomatization of the intermediately formed 3H-pyrazole (5). The isomerization obeys first-order kinetics perfectly and no divergent reaction paths were observed when the thermolyses were performed in the presence of phenol, quinoline or toluene [27]. The thermal rearrangement of N-nitropyrazole unsubstituted at the 3-position has been found to be a convenient method for the synthesis of 3-nitropyrazole (yield, 98%). Hüttel and Büchele method was used to synthesize 4-nitropyrazole (4) (yield, 96%) using nitric acid–sulfuric acid mixture.

4.2. Thermal decomposition kinetics of pyrazoles

Thermal analysis is concerned with thermally stimulated processes. The physical properties measured by thermal analysis methods are not species-specific and thus usually cannot be linked directly to specific reactions of molecules. Thermal reactions of pyrazoles appear as a good alternative to the generation of vinylcarbenes by nitrogen extrusion reaction. The mechanism of nitrogen extrusion reaction from pyrazoles includes several steps where nitrogen is lost from an intermediate vinyl diazomethane in the rate limiting step. The nitrogen extrusion is strongly influenced by ring substitution. The substituted pyrazoles afford different vinylcarbenes which complicates the evaluation of the substituent(s) on the activation energy although some consideration can be made. Kinetics for such reactions has been the focus of present study using TG–DTA technique. We have carried out the thermal decomposition of pyrazole, N-nitropyrazole, 3-nitropyrazole and 4-nitropyrazole under nitrogen atmosphere. The samples (~1 mg) in alumina crucible were heated from 25 to 250 °C under nitrogen environment at the flow rate 100 cm³/min. For the Arrhenius type of kinetic equation, the primary objective is to determine experimentally the frequency factor, activation energy and reaction model or conversion functions. Flynn–Wall–Ozawa method is known to give meaningful values of the activation energy in wide range of circumstances. The Friedman method is related to the Flynn–Wall–Ozawa method inasmuch as they both rely on the use

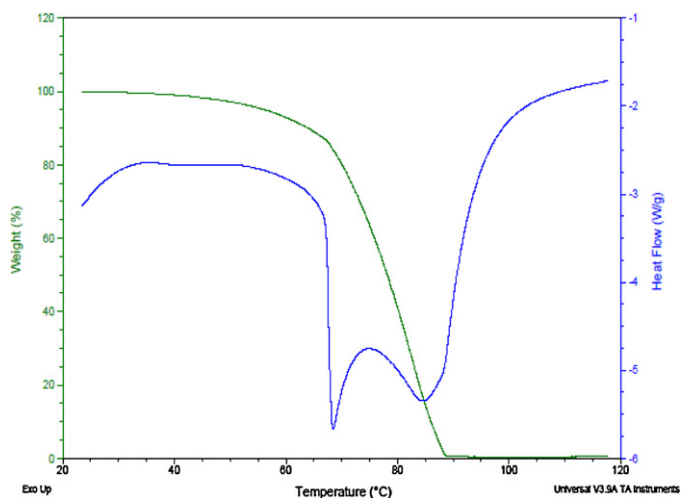


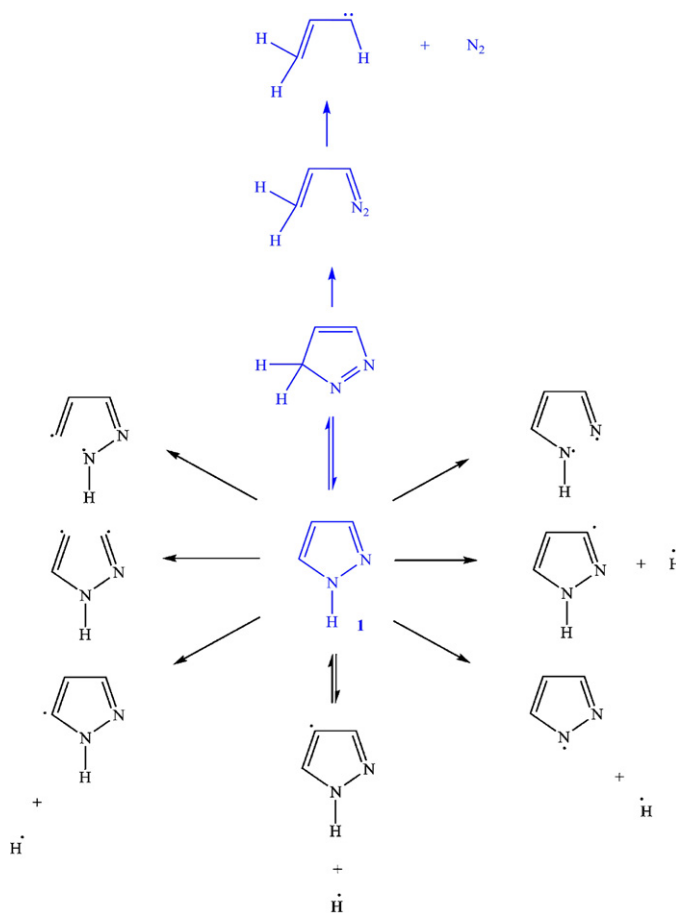
Fig. 1. TG-DTA of pyrazole recorded at heating rate 5 °C/min.

of several different heating rates both provide separate values for the activation energy at different levels of conversion and both are independent of the form of the kinetic equation. Therefore we have determined the activation energies of pyrazole, N-nitropyrazole, 3-nitropyrazole and 4-nitropyrazole using the Friedman and the Flynn–Wall–Ozawa methods.

Fig. 1 presents the melting and subsequent evaporation of pyrazole (m.p. 67–70 °C, b.p. 187 °C). Vinylcarbene has been known to be the major intermediate in the decomposition of pyrazole [11,38,39]. The mechanism was partly based on the reactions of 3H-pyrazole and vinyldiazo compound. Two competitive reactions such as cyclization to 3H-pyrazole and nitrogen extrusion, first one being lower in energy are known. The relatively unstable vinylcarbene rearranges to the propyne which is thermoneutral decomposition [40]. The plausible decomposition paths of pyrazole (1) are presented in Scheme 2. The substitution at carbon or nitrogen site in the pyrazole ring is known to affect the decomposition products and thus also the decomposition kinetics. To investigate how the position of nitro group affect the kinetics, the decomposition of N-nitropyrazole, 3-nitropyrazole and 4-nitropyrazole under similar experimental conditions have also been carried out.

TG-DTA of N-nitropyrazole (2) is shown in Fig. 2. N-nitropyrazole melts at 92–93 °C with simultaneous sublimation/evaporation. There was no change in the weight loss after 90 °C probably due to the formation of 3-nitropyrazole or 4-nitropyrazole which are known to be more stable C-nitropyrazoles. Scheme 3 presents the plausible thermal reactions of N-nitropyrazole. 3-Nitropyrazole (3) has shown good thermal stability with no weight loss observed up to 120 °C. From Fig. 3, weight loss of compound (3) begins around 120 °C with the most rapid weight loss beginning at 174 °C. Maximum weight loss in the temperature range from ~175 to 192 °C has been observed. 3-Nitropyrazole appears to be decomposed by multi stage decomposition evident from TG-DTA graph (Fig. 3). The plausible decomposition paths of 3-nitropyrazole are summarized in Scheme 4. TG-DTA of 4-nitropyrazole (4) is shown in Fig. 4. It is seen that there is some weight loss of compound (4) below 160 °C. Scheme 5 summarizes the plausible decomposition of 4-nitropyrazole. We have utilized the DTA thermograms for kinetic analysis in order to draw reliable mechanistic conclusions.

DTA analysis has been carried out at five different heating rates so as to obtain five peak values to generate the kinetic parameters using Friedman's differential and Flynn–Wall–Ozawa integral methods. The activation energy values (E_a) calculated using Friedman method are plotted as function of extent of conversion (α) pyrazoles shown in Fig. 5. Also, E_a values



Scheme 2. Plausible pathways of thermal decomposition of pyrazole.

according to Flynn–Wall–Ozawa method are plotted as function of extent of conversion (α) shown in Fig. 6. The activation energy required for the decomposition of pyrazole according to Friedman and Flynn–Wall–Ozawa methods are 74.2 and 72.8 kJ mol⁻¹ respectively comparable to the reported values [7,8]. The activation energy of N-nitropyrazole decomposition according to Friedman and Flynn–Wall–Ozawa methods are 78.1 and 83.4 kJ mol⁻¹ respectively. Substituting an acidic N–H hydrogen by the nitro group increases the stability and hence N-nitropyrazole more stable than the parent molecule. The activation energy of 3-nitropyrazole decomposition based on Friedman

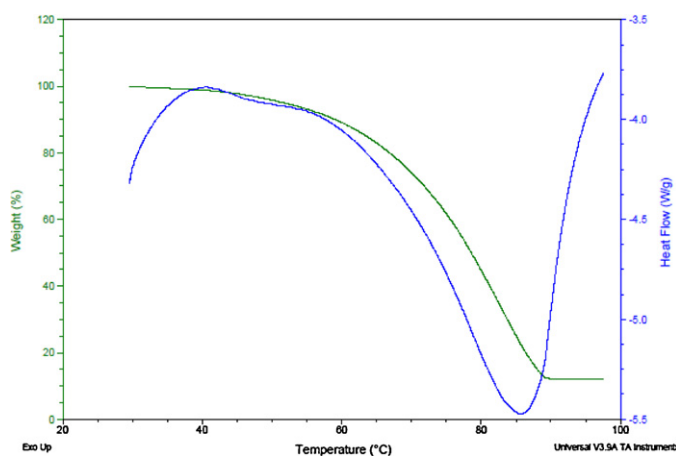
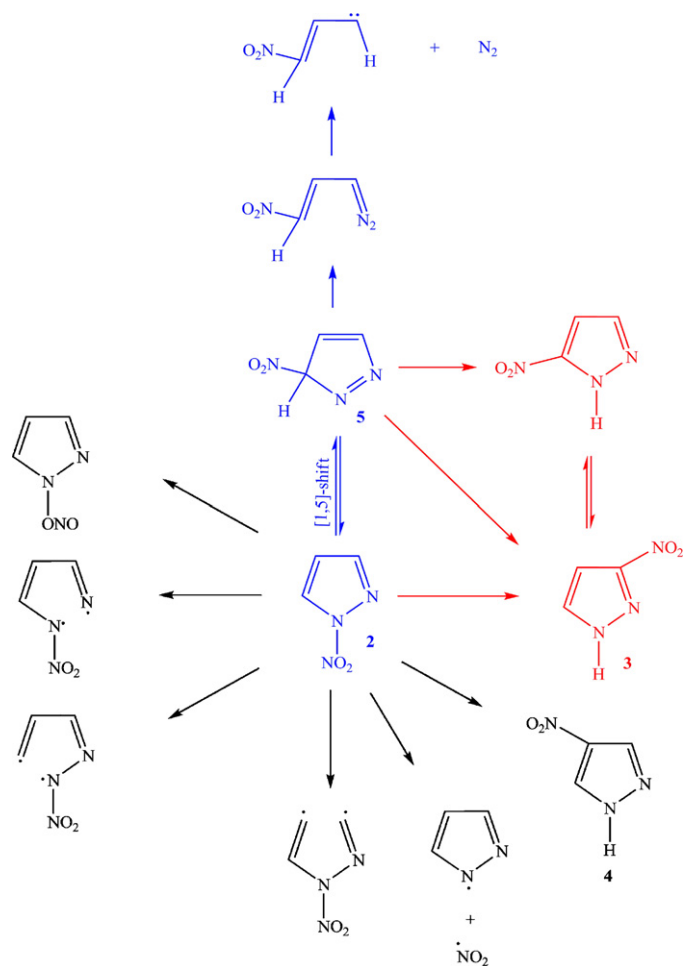


Fig. 2. TG-DTA of N-nitropyrazole recorded at heating rate 5 °C/min.



Scheme 3. Plausible pathways of thermal decomposition of N-nitropyrazole.

and Flynn–Wall–Ozawa methods are 132.7 and 115.3 kJ mol⁻¹ respectively. The activation energy of 4-nitropyrazole calculated according to Friedman and Flynn–Wall–Ozawa methods are 92.5 and 90.2 kJ mol⁻¹ respectively. The activation energy values calculated using Friedman method increased with the extent of conversion in case of N-nitropyrazole and these values gradually decreased in case 3-nitropyrazole. The activation energy values in case of pyrazole and 4-nitropyrazole decreased with the extent

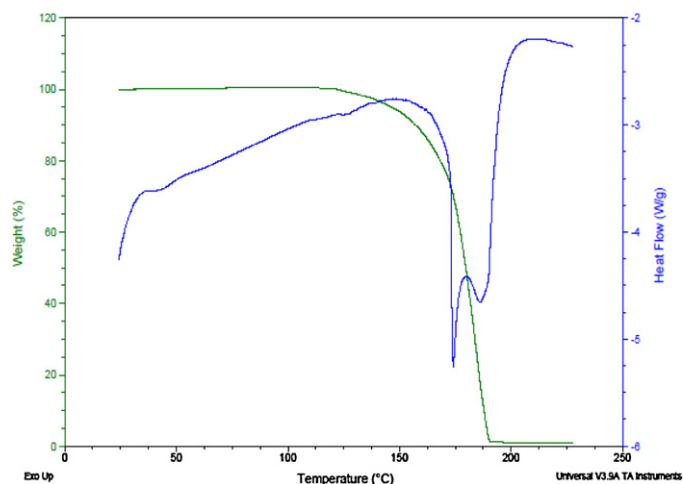
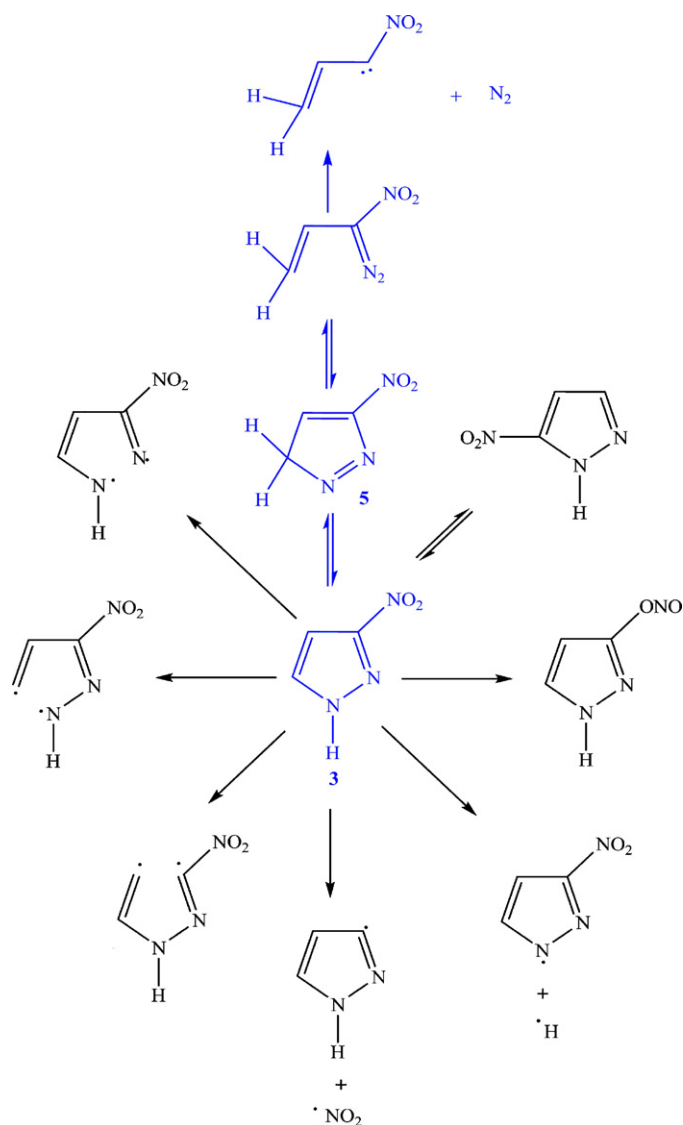


Fig. 3. TG-DTA of 3-nitropyrazole recorded at heating rate 5 °C/min.



Scheme 4. Plausible pathways of thermal decomposition of 3-nitropyrazole.

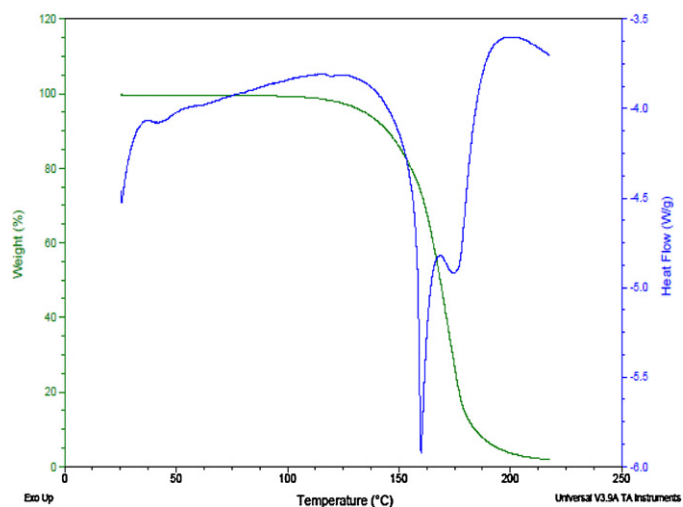
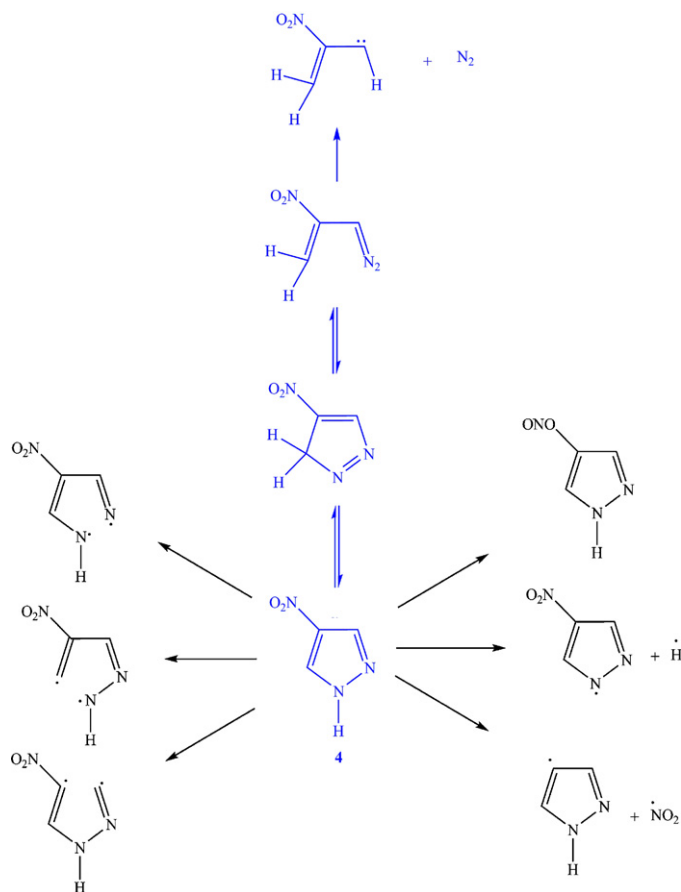


Fig. 4. TG-DTA of 4-nitropyrazole recorded at heating rate 5 °C/min.



Scheme 5. Plausible pathways of thermal decomposition of 4-nitropyrazole.

of conversion and then gradually increased. However, the activation energy values calculated according to Flynn–Wall–Ozawa method increased with the extent of conversion and then gradually decreased. It is obvious that 3-nitropyrazole is more stable than 4-nitropyrazole. A non-linear relationship of activation energy with the conversion rate indicates the possibility of multi step kinetics seen in case of pyrazole, 3-nitropyrazole and 4-nitropyrazole. Therefore, stability order may be written as: 3-nitropyrazole > 4-nitropyrazole > N-nitropyrazole > pyrazole.

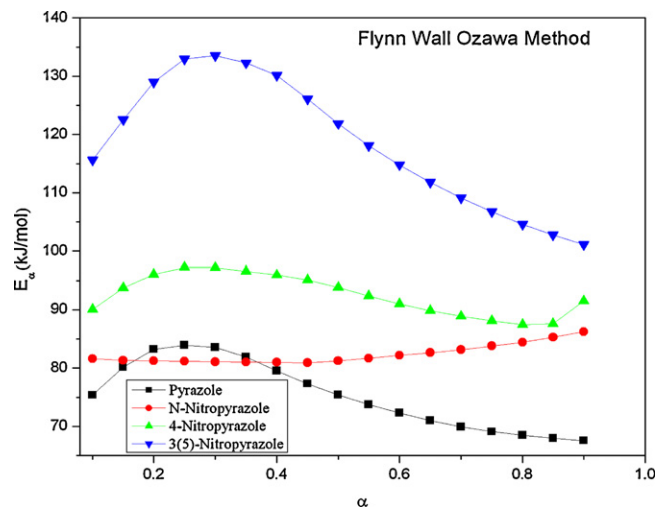


Fig. 6. Plot showing the comparison of the activation energies versus the extent of conversion of pyrazoles (Flynn–Wall–Ozawa method).

We can speculate that the decomposition of pyrazole, 3-nitropyrazole and 4-nitropyrazole occurred mainly through nitrogen extrusion. However, the decomposition of N-nitropyrazole presumably occurred through homolysis of N–NO₂ bond (nitramine) then nitrogen extrusion. Thermolysis of 3-nitropyrazole and 4-nitropyrazole yield N₂, H₂ and HCN among the most abundant gaseous products apart from small amount of HN₃. Moreover 3-nitropyrazole and 4-nitropyrazole are NH-pyrazoles, the main decomposition reaction is nitrogen extrusion affording vinylcarbene formed in a stepwise process where the elimination of nitrogen is the rate-determining step [41,42]. 3-Nitropyrazole showed maximum weight loss from 175 to 190 °C and 4-nitropyrazole showed maximum weight loss between 160 and 175 °C indicating the poor oxygen balance (Ω –77.88%) of the materials. The rate of decomposition seems to be autocatalytically increasing over temperature. As observed for many nitroazoles, the decomposition temperature increases with increase of temperature [43]. The numerical values of activation energy obtained using differential and integral isoconversional methods showed a difference. These differences presumably due to the approximation of temperature integral used in the derivations of the relations of the non-linear isoconversional methods. Nevertheless, the activation energy, preexponential factor and even the effective reaction order are known to be strongly dependent on the experimental conditions in particular on the heating rate.

5. Conclusion

The thermal decomposition kinetics of pyrazole and its mononitropyrazoles have been carried out using TG–DTA technique under nitrogen atmosphere at the flow rate 100 cm³/min. The activation energies have been determined using isoconversional methods. These isoconversional methods may be helpful in providing some mechanistic clues. However, the mechanistic clues are not yet the reaction mechanism rather a path to it that can further be followed only by using species-specific experimental techniques. The activation energy values obtained using differential and integral isoconversional methods showed a difference. These differences probably due to the approximation of the temperature integral that were used in the derivations of the relations of non-linear isoconversional methods. The kinetic parameters have been found to be influenced by the position of the nitro group on the diazole ring. Also, the activation energy, preexponential factor and the effective reaction order are strongly dependent on the experimental

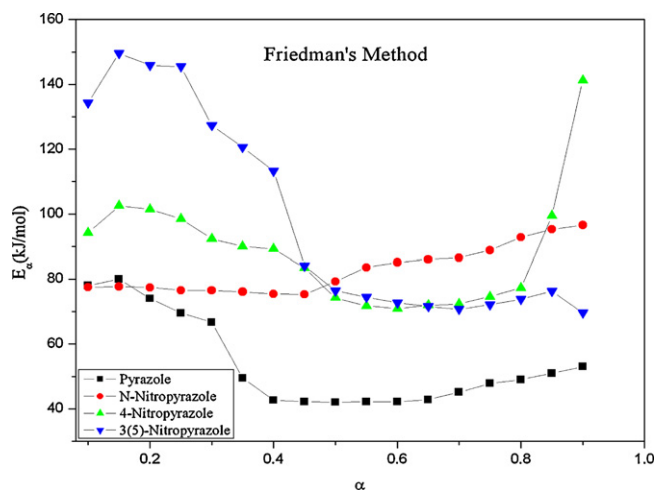


Fig. 5. Plot showing the comparison of the activation energies versus the extent of conversion of pyrazoles (Friedman method).

conditions. Pyrazole, 3-nitropyrazole and 4-nitropyrazole have been found to be decomposed by multi step decomposition kinetics evident from the non-linear relationship of activation energy with the conversion rate. N-nitropyrazole has been found to undergo single step decomposition or the unification of multistep decomposition evident from the linear relationship of activation energy and the extent of conversion.

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