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THERMAL STUDIES ON TETRAZOLE DERIVATIVES USING A DIFFERENTIAL SCANNING CALORIMETER. I

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ABSTRACT

The thermal decomposition of arylidene tetrazolyl hydrazones has been studied under dynamic and isothermal conditions using a differential scanning calorimeter. Attempts have been made to evaluate the thermochemical and kinetic parameters of these compounds. It has been observed that the thermal stability of the tetrazole derivatives decreases with increasing substitution of nitro groups in the aromatic ring.

INTRODUCTION

A number of tetrazole derivatives have found applications in the explosives industry as components of initiating compositions. For example, various tetrazole salts such as lead azotetrazole, cadmium tetrazolyl azide, copper diazoamino tetrazole and copper nitrotetrazole have been claimed for use as primers [1—3]. Tetrazolyl hydrazones have also shown promise as potential explosive compounds. Thiele [4] mentioned that 5,5′-azotetrazole is unstable as a free compound and should be stored as an alkali metal salt. On neutralization with a mineral acid, it gives rise to 5-hydrazino tetrazole, which is also unstable and should be stored either as the hydrochloride or trapped as benzaldehyde hydrazone. Individual tetrazoles have been found to exhibit a considerable variation in stability towards heat. For example, diazotetrazole is very sensitive and explodes even in solution, while 5-guanyl amino tetrazole does not decompose up to 300°C [5].

A literature survey reveals that the thermal decomposition characteristics of tetrazole derivatives, especially tetrazolyl hydrazones, have not been studied in detail. Investigations carried out thus far reveal that the thermal breakdown of tetrazoles follows different routes depending upon the nature and location of substituents [6—8].

In the present study, we have selected six aldehydes for the synthesis of arylidene tetrazolyl hydrazones: (a) benzaldehyde, (b) 2-nitrobenzaldehyde, (c) 3-nitrobenzaldehyde, (d) 4-nitrobenzaldehyde, (e) 2,4-dinitrobenzalde-

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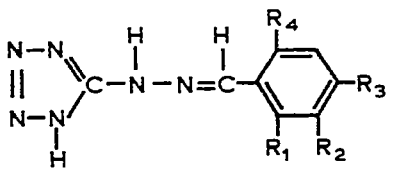
hyde, and (f) 2,4,6-trinitrobenzaldehyde. These aldehydes have been chosen so as to synthesize tetrazolyl hydrazones which will have oxygen balance values varying over a wide range and thus obtain compounds with varying sensitivities. These compounds can be represented by the general structure as shown below



(Ia) Benzaldehyde-1H(2H)-tetrazol-5-yl-hydrazone

(R_1, R_2, R_3 and R_4 = H)

(Ib) 2-Nitrobenzaldehyde-1H(2H)-tetrazol-5-yl-hydrazone

(R_1 = NO_2, R_2, R_3 and R_4 = H)

(Ic) 3-Nitrobenzaldehyde-1H(2H)-tetrazol-5-yl-hydrazone

(R_2 = NO_2, R_1, R_3 and R_4 = H)

(Id) 4-Nitrobenzaldehyde-1H(2H)-tetrazol-5-yl-hydrazone

(R_3 = NO_2, R_1, R_2 and R_4 = H)

(Ie)2,4-Dinitrobenzaldehyde-1H(2H)-tetrazol-5-yl-hydrazone

(R_1 and R_3 = NO_2, R_2 and R_4 = H)

(If) 2,4,6-Trinitrobenzaldehyde-1H(2H)-tetrazol-5-yl-hydrazone

(R_1, R_3 and R_4 = NO_2, R_2 = H)

The present paper discusses the results of the thermal studies carried out on six (a—f) arylidene 5-hydrazino tetrazoles using a differential scanning calorimeter. The objectives of this study are to

(1) evaluate the heat of decomposition of these compounds;

(2) establish the kinetic parameters for decomposition; and

(3) throw some light on the mechanism of thermal decomposition, if possible.

EXPERIMENTAL

Synthesis of arylidene tetrazolyl hydrazones

Arylidene tetrazolyl hydrazones have been prepared by reacting aldehydes with 5-hydrazino tetrazole. There are a number of methods available for the synthesis of 5-hydrazino tetrazole. The method adopted in the present study involved the following steps:

(1) reaction between dicyandiamide and hydrazoic acid to yield 5-amino tetrazole [4];

(2) oxidation of 5-amino tetrazole with potassium permanganate in alkaline medium to yield sodium 5,5′-azotetrazole [4];

(3) hydrolysis of sodium 5,5′-azotetrazole to yield 5-hydrazino tetrazole.

5-Hydrazino tetrazole is not isolated as the process is tedious and the compound is unstable even at room temperature. Arylidene tetrazolyl hydrazones are prepared by reacting 5-hydrazino tetrazole hydrochloride in aqueous solution with aldehydes in alcohol. The reaction product is filtered, washed with enough water to make it acid free, followed by washing with alcohol and drying. The product is finally recrystallized from an alcohol—dioxane mixture for thermal analysis. Detailed analytical studies were made to establish the purity and structure of the hydrazones synthesized using UV, IR, NMR and mass-spectrophotometric techniques and the results will be reported elsewhere.

Thermal studies

A Perkin-Elmer differential scanning calorimeter (Model DSC-1B) was used for the thermal studies. The decomposition studies were carried out under both dynamic and isothermal conditions. The powdered samples were weighed on a Perkin-Elmer auto balance AM2 in DSC cups (Perkin-Elmer Kit No. 210-0041) and then crimped with a lid having a pin-hole for the escape of the gases produced during the decomposition. The amount of sample taken varied from 0.3 to 1.5 mg. Tin was used as a standard for the calibration of the instrument and proper adjustments were made for range setting, scan speed, and zero control position so that a visible signal could be obtained for accurate measurements. The areas under the DSC curves were measured using a planimeter. The base lines under the thermograms were drawn by the method outlined by Breenan et al. [9].

Dynamic measurements were made at scan speeds of 4, 8, 16, 32 and 64 K min^{-1}. In these runs, the temperature was raised to 30° C below the temperature of interest by manually rotating the knob and from there it was programmed with various scan speeds. Isothermal runs were performed between 470 and 530 K. In these runs, the temperature was quickly raised to the desired temperature by manual operation. All experiments were carried out under nitrogen atmosphere.

RESULTS AND DISCUSSION

Thermochemical data

Typical DSC curves representing the thermal decomposition of tetrazolyl hydrazones under dynamic conditions are shown in Fig. 1. It can be seen that the decomposition temperatures (T_{decomp}) of these compounds follow the expected trend, i.e. $T_{decomp.}$ (trinitro derivative) $< T_{decomp.}$ (dinitro derivative) $< T_{decomp.}$ (mononitro derivative). Table 1 gives the values for decomposition temperature and oxygen balance (calculated assuming CO_2 and H_2O as the decomposition products) for the different tetrazolyl hydrazones.

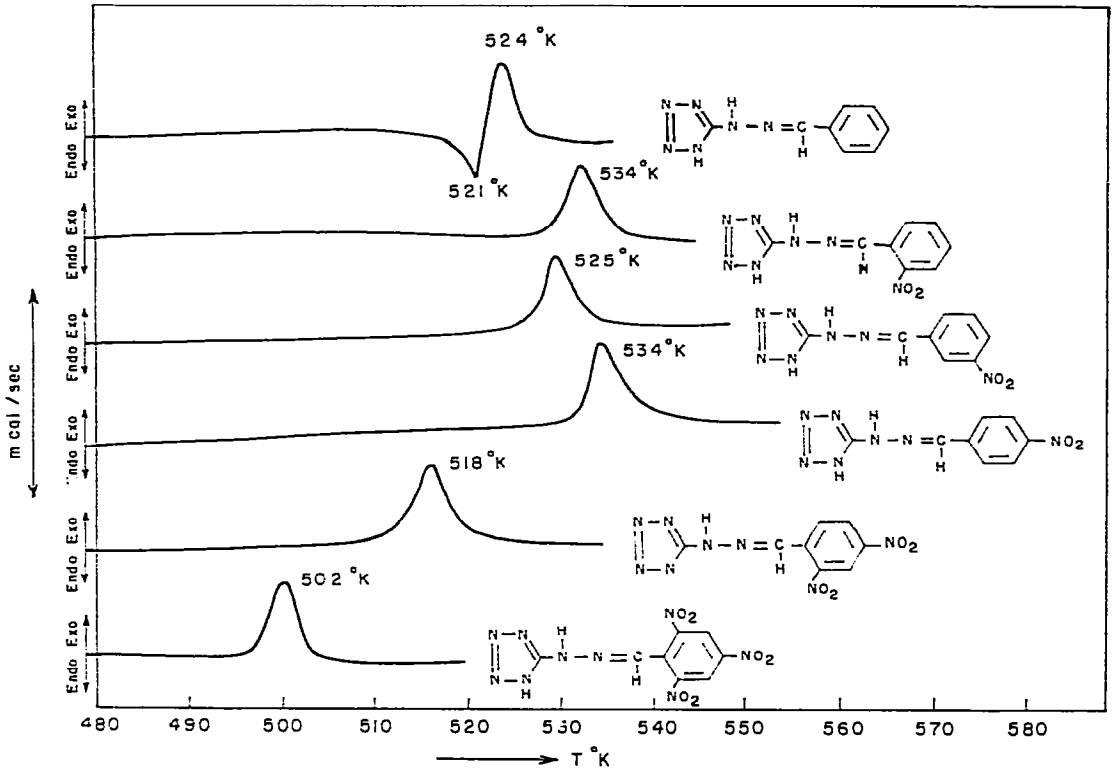


Fig. 1. DSC traces of benzylidene 1H (2H) tetrazol-5-yl-hydrazones. All the runs were made at a heating rate of 16 K min^{-1}.

Table 2 lists the heat of decomposition values computed from the dynamic DSC runs carried out at a heating rate of 16 K min^{-1}, and also gives the estimated heats of formation (ΔH_f) and combustion ($-\Delta H_c$) using the method of Handrick [10]. In view of the high oxygen deficiency of the tetrazole derivatives and the differences in the product composition for the combustion and the decomposition reactions, the measured heats of decomposition ($-\Delta H_d$) are far lower than the corresponding heats of combustion for the different tetrazolyl hydrazones. However, a rough estimate of the heats of decomposition for these compounds (assuming that

TABLE 1

Decomposition temperature and oxygen balance values for tetrazolyl hydrazones

Compound	Oxygen balance (g oxygen/100 g compound)	Decomposition temp.
Ia	—170.21	524
Ib	—120.17	534
Ic	—120.17	525
Id	—120.17	534
Ie	—86.33	518
If	—61.92	502

TABLE 2

Thermochemical parameters for tetrazolyl hydrazones

Compound	Heat of formation [a] ($kJ\ g^{-1}$)	Heat of combustion [a] ($kJ\ g^{-1}$)	Heat of decomposition [a] ($kJ\ g^{-1}$)	Heat of decomposition [b] ($kJ\ g^{-1}$)
Ia	2.48	25.28		0.63 ± 0.02
Ib	1.83	19.61	0.44	0.76 ± 0.03
Ic	1.83	19.61	0.44	0.67 ± 0.01
Id	1.83	19.61	0.44	0.73 ± 0.03
Ie	1.47	15.87	2.29	1.09 ± 0.04
If	1.25	13.19	3.09	1.30 ± 0.05

[a] Estimated values.
[b] Measured values.

the oxygen available in the molecule goes into the formation of H_2O and CO_2, in that order) gives values which are close to the measured heats of decomposition. The estimated $-\Delta H_d$ values are also included in Table 2. Further, the observation that the thermal decomposition of benzylidene tetrazolyl hydrazone (Ia) is also exthermic, indicates that the exothermic bond breakage (N—N bond) of the tetrazole moiety could also contribute to the overall exothermicity of the decomposition reaction. The heat release due to this is approximately 1.0 $kJ\ g^{-1}$ for compound (a) assuming the N—N bond energy to be about 200 $kJ\ mole^{-1}$. It has to be pointed out here that the above estimations serve the purpose of obtaining an approximate idea regarding the significance of measured heats of decomposition and do not have any strict validity.

Kinetic data

Typical fraction decomposed (α) vs. time (t) curves for dynamic and isothermal runs are shown in Figs. 2 and 3, respectively. The α—t curves are sigmoid in shape and, as can be seen from these curves, the rate increases with increasing scan speeds in the case of dynamic runs and with increasing temperature for the isothermal runs. Typical fraction decomposed (α) vs. reduced time ($t/t_{\alpha=0.5}$) plots are given in Figs. 4 and 5 for dynamic and isothermal runs. It may be concluded from these plots that the kinetic behavior of the decomposition reaction is similar at various temperatures (in the case of isothermal runs) and at different heating rates (in the case of dynamic runs).

The reaction orders for the decomposition reaction of arylidene tetrazolyl hydrazones have been calculated using Kissinger's method of "Shape Index" [13]. The calculated reaction orders for the thermal decomposition of different compounds were found to be between 0.96 and 1.16. The reaction order was also calculated using the Rogers' method [12] for the isothermal runs and found to vary from 0.91 to 1.20 at different temperatures. Therefore, it may be concluded that the decomposition of tetrazolyl hydrazones

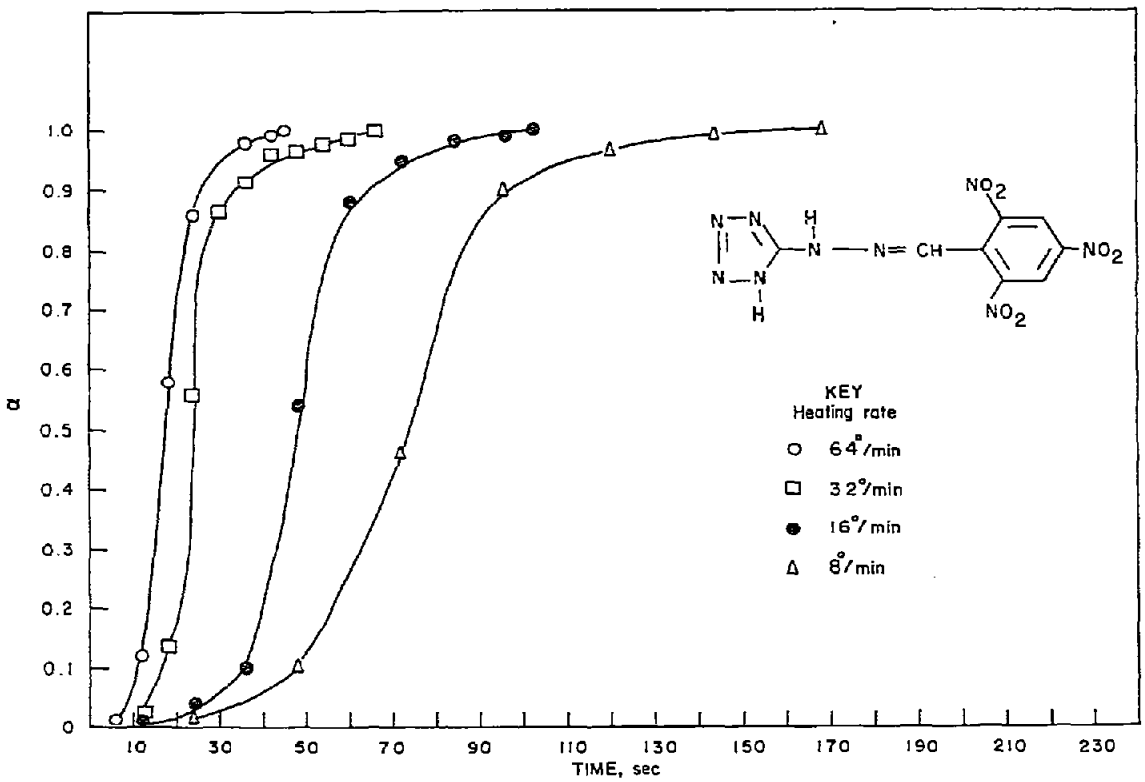


Fig. 2. Fraction decomposed (α) vs. time (t) plots for dynamic DSC runs.

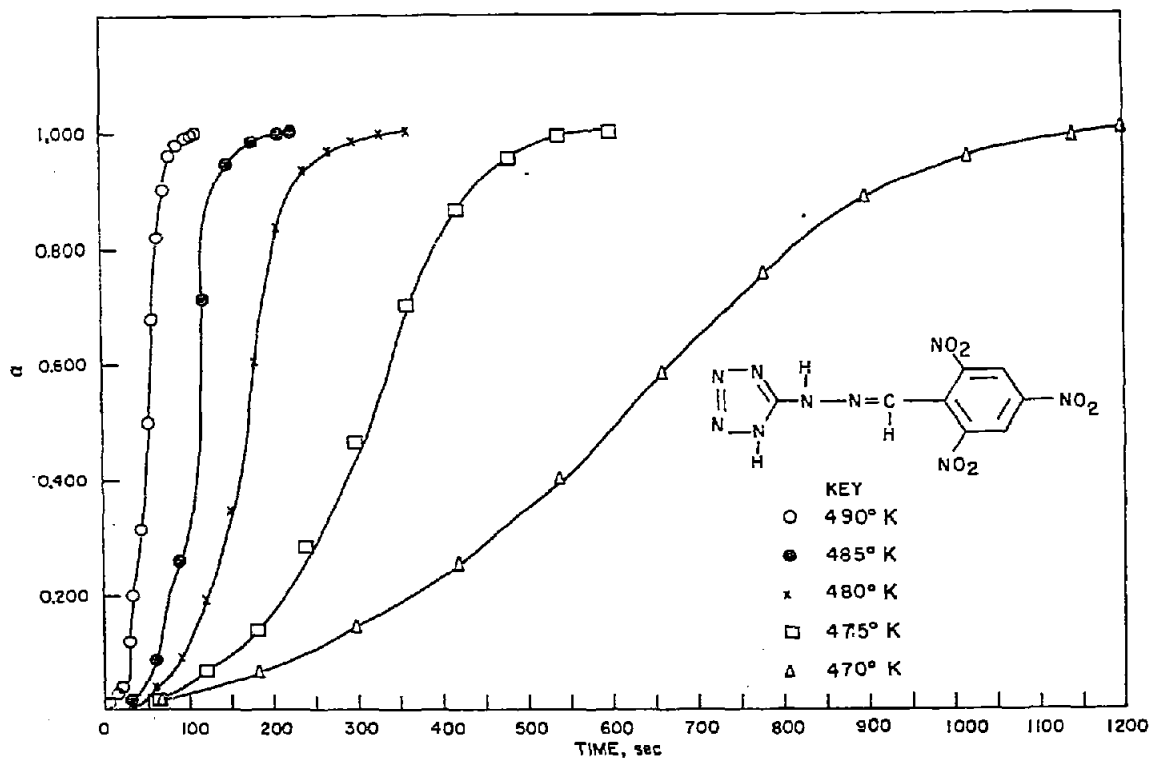


Fig. 3. Fraction decomposed (α) vs. time (t) plots for isothermal DSC runs.

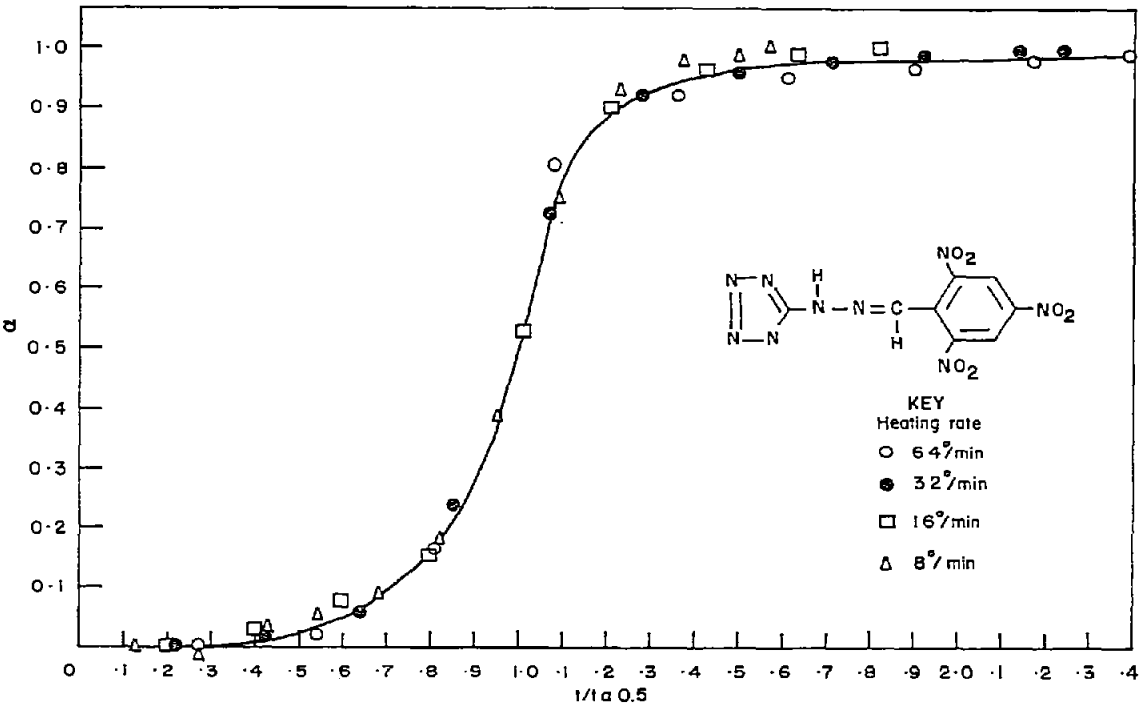


Fig. 4. Fraction decomposed (α) vs. reduced time ($t/t_{\alpha=0.5}$) plots for dynamic DSC runs.

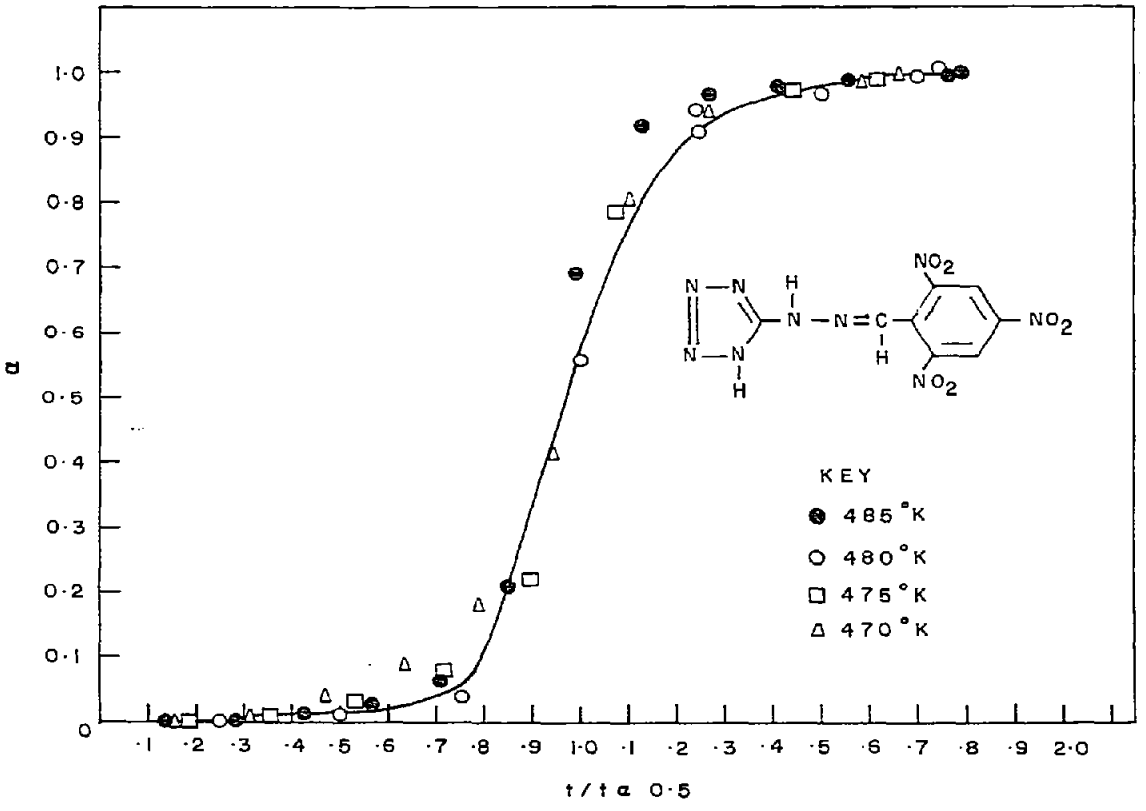


Fig. 5. Fraction decomposed (α) vs. reduced time ($t/t_{\alpha=0.5}$) plots for isothermal DSC runs.

could be assumed to be a first order reaction under both dynamic and isothermal conditions.

The kinetic parameters, namely, activation energy and the frequency factor, were also calculated for the thermal decomposition of arylidene tetrazolyl hydrazones using different methods. A brief outline of the basic principle underlying each of these methods is given first, followed by a comparison of the activation energy values obtained.

Kissinger's method [11]

The method utilizes the shift in peak temperature with heating rate. The working form of the expression is

$$\frac{d(\ln \phi/T_m^2)}{d(1/T_m)} = -\frac{E}{R} \tag{1}$$

where ϕ is the heating rate (dT/dt), T_m is the peak temperature, E is the activation energy and R is the universal gas constant. This method is based on the premise that the maximum reaction rate takes place at the apex of the peak.

The shift in peak temperature with heating rate is shown for a typical compound 2,4-dinitro benzadehyde 1H (2H) tetrazol-5-yl-hydrazone in Fig. 6. The plot of $\ln \phi/T_m^2$ vs. $1/T_m$ is shown in Fig. 7 and the values for

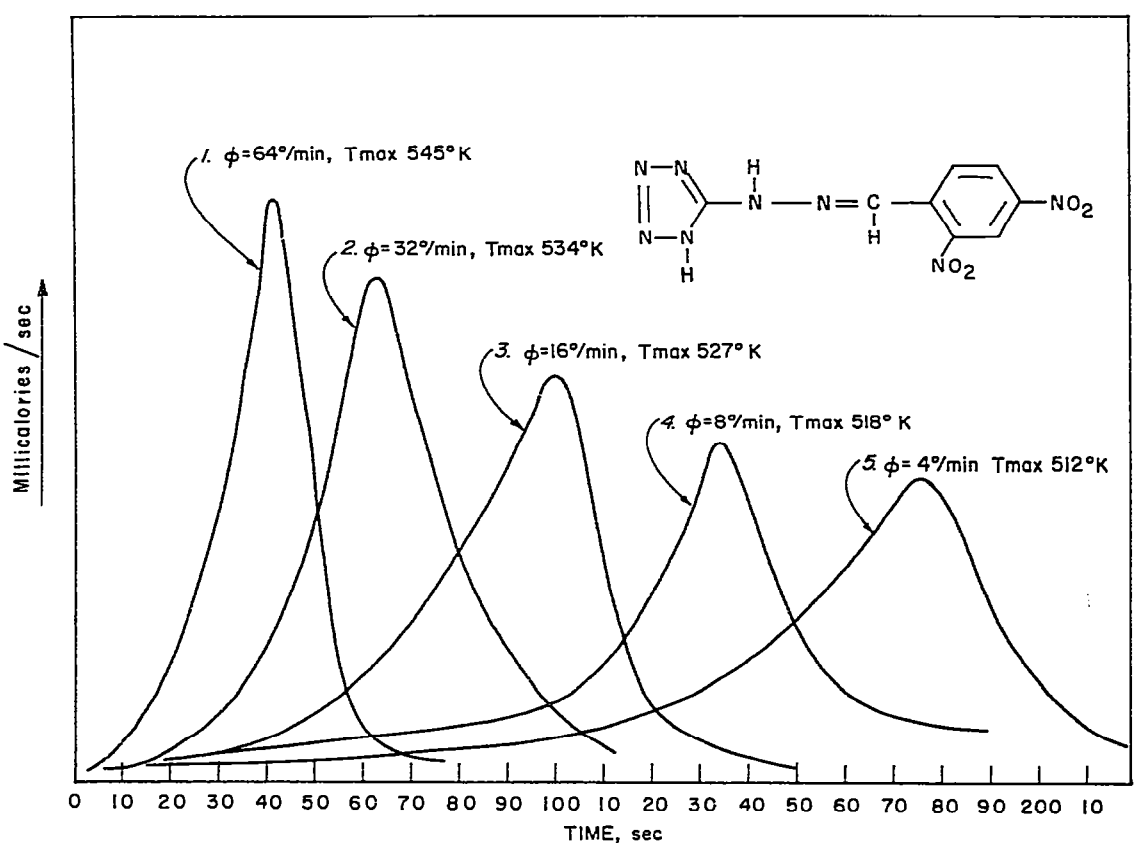


Fig. 6. Effect of rate of heating on the DSC curve of 2, 4-dinitrobenzaldehyde 1H(2H)-tetrazol-5-yl-hydrazone.

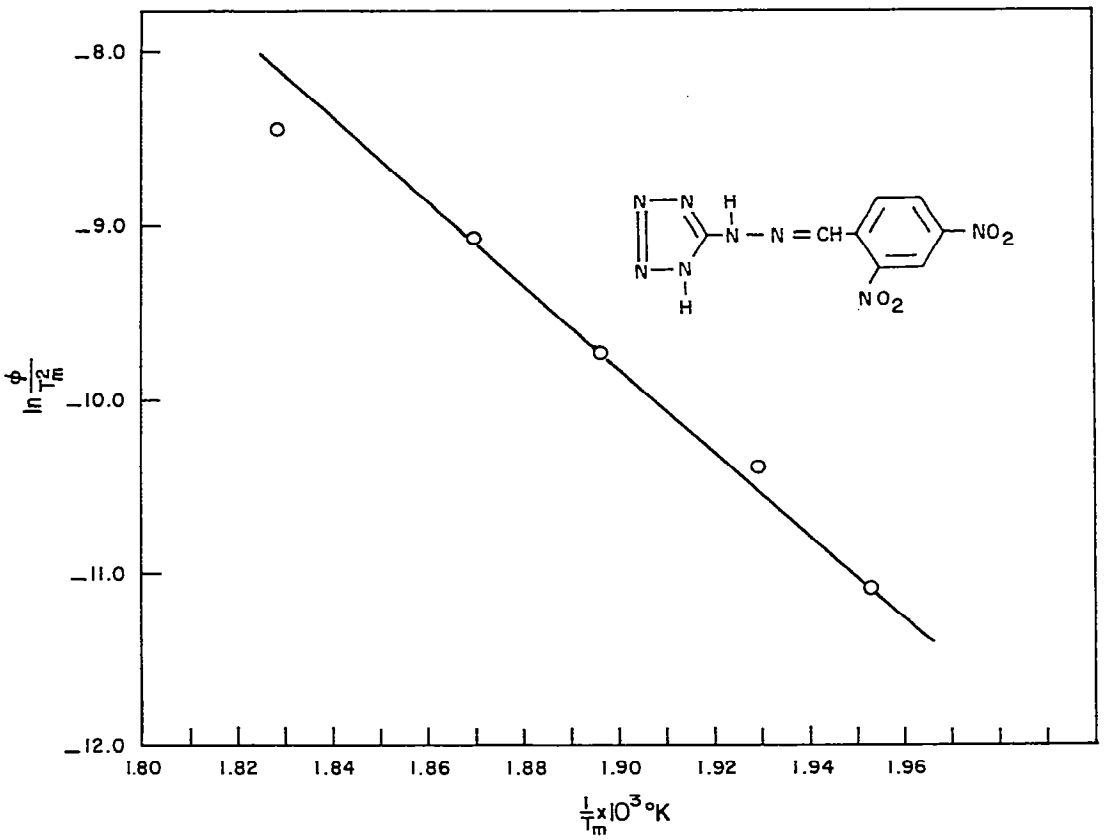


Fig. 7. Activation energy plot by the Kissinger method.

activation energy and frequency factor are given in Table 3. The frequency factor (A) is obtained from the following equation

$$A \frac{e^{-E}}{RT_m} = \frac{E}{RT_m^2} \frac{dT}{dt} \quad (2)$$

TABLE 3

Kinetic parameters for the thermal decomposition of tetrazolyl hydrazones (dynamic runs)

Compound	Method			
	Kissinger E (kJ mole^{-1})	Log A (sec^{-1})	Ozawa E (kJ mole^{-1})	Rogers and Morris E (kJ mole^{-1})
Ia	199.6 ± 10.2	19.9 ± 0.9	200.1 ± 10.5	1078.2 ± 13.1
Ib	195.5 ± 9.1	18.8 ± 0.7	192.7 ± 8.5	1118.1 ± 15.7
Ic	184.1 ± 6.8	17.9 ± 0.7	185.1 ± 10.2	1048.3 ± 12.5
Id	190.3 ± 5.1	18.5 ± 0.8	190.6 ± 6.3	1134.5 ± 11.5
Ie	176.5 ± 6.2	18.2 ± 0.5	178.7 ± 8.7	1006.5 ± 13.0
If	166.8 ± 7.4	17.4 ± 0.4	168.0 ± 7.3	785.8 ± 16.5

Ozawa's method [14]

This method yields the following relation for a given conversion.

$$\log_{10}\phi + 0.4567\,\frac{E}{RT} = \text{constant} \qquad (3)$$

The activation energy is obtained from a plot of $\log_{10}\phi$ vs. $1/T$. Table 3 lists the activation energy values obtained by this method.

Rogers and Morris' method [15]

This method employs a single dynamic run to calculate the kinetic parameters. The distance (b) measured from the base line to the curve is proportional to the rate of heat evolution or absorption and, therefore, is proportional to the reaction rate constant. The activation energy for the decomposition reaction is estimated from the plots of ln b vs. $1/T$ using the relation

$$\ln b = \frac{-E}{RT} + \text{constant} \qquad (4)$$

An important assumption in this method is that the mass of the sample remains constant throughout the reaction. The validity of this method is doubtful when the weight loss is more than 30% [16]. The activation energies calculated by this method are presented in Table 3.

A comparison of the activation energy values calculated by different methods reveals that while the methods of Kissinger and Ozawa give comparable values, the technique of Rogers and Morris predicts very high activation energies for the thermal decomposition of tetrazolyl hydrazones. Similar observations have been made by Patel and Chaudri [17] from their DSC studies on lead azide and tetracene. They found that the activation energies obtained using the method of Rogers and Morris are three times greater than those given by the other two methods. This could be explained on the basis of the following observations made in the present study:

(1) the reaction order is close to 1;

(2) preliminary weight loss measurements indicate that the percentage weight loss is more than 30 for all the compounds investigated.

The kinetic parameters for the thermal decomposition of arylidene tetrazolyl hydrazones were also calculated for the isothermal DSC runs. As mentioned earlier, the order of decomposition was found to be close to 1 for the isothermal runs. Two methods have been used for the determination of kinetic parameters.

(1) Slow thermal decomposition (first order equation): the rate constants for the thermal decomposition at various temperatures are obtained from a plot of ln b vs. t where b is the distance measured from the base line to the curve and t is the time. A typical plot is shown in Fig. 8. A plot of ln$K$ vs. $1/T$ gives the activation energy for thermal decomposition in the isothermal mode. Table 4 lists these values along with those for the frequency factor.

(2) Delay time method [18]: when a reactive material is suddenly raised to a high temperature, it decomposes with a certain induction period or delay time ($t_{\text{decomp.}}$). It is found that the delay time is related to the activa-

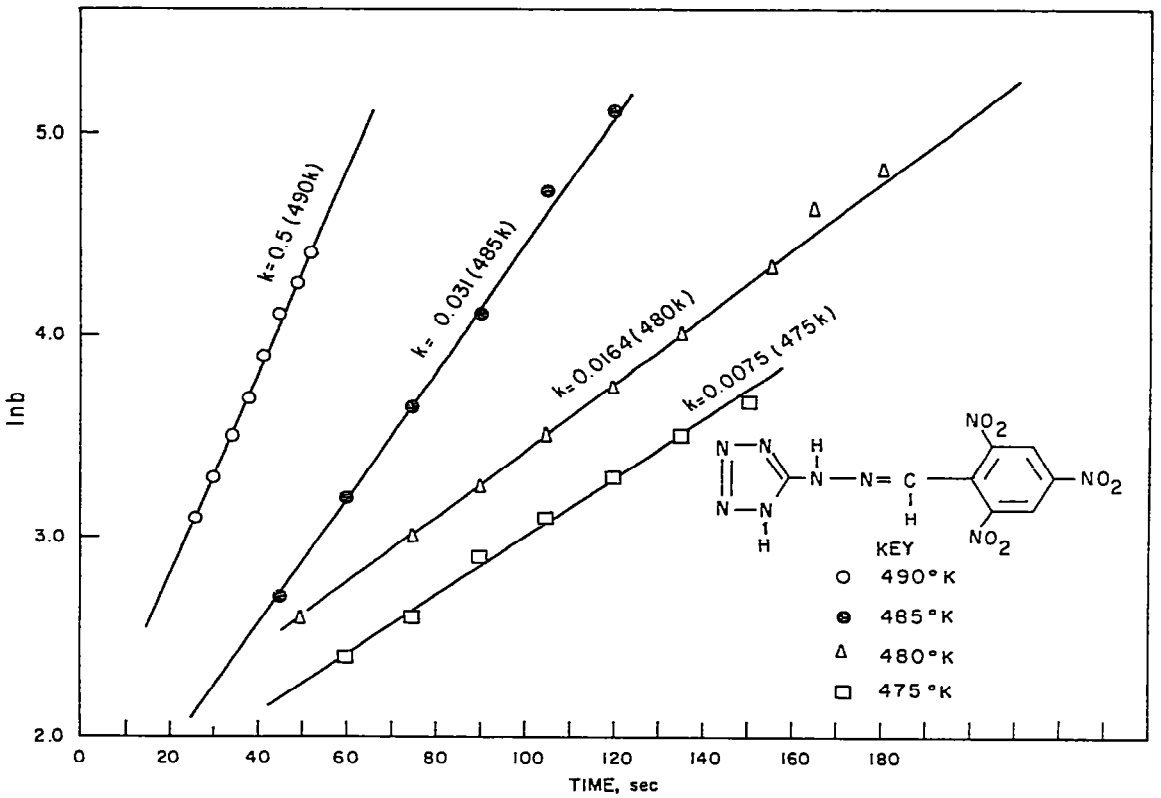


Fig. 8. Plot of ln b vs. time for isothermal DSC runs.

tion energy by an equation of the form

$$\ln t_{\text{decomp.}} = B + \frac{E}{RT} \tag{5}$$

where B is a constant while E, R, and T have their usual significance. The activation energy for decomposition reaction is calculated from a plot of

TABLE 4

Kinetic parameters for the thermal decomposition of tetrazolyl hydrazones (isothermal runs)

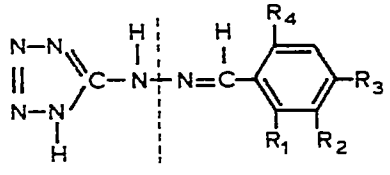
Compound	Method		
	First order equation		Delay time method E (kJ mole^{-1})
	E (kJ mole^{-1})	Log A (sec^{-1})	
Ia	252.2 ± 5.9	23.8 ± 1.1	249.8 ± 6.3
Ib	260.1 ± 6.5	24.9 ± 0.9	229.1 ± 7.5
Ic	250.2 ± 5.6	24.1 ± 0.9	253.4 ± 10.0
Id	265.3 ± 8.0	25.3 ± 1.2	222.4 ± 8.6
Ie	253.5 ± 7.5	26.6 ± 1.1	216.6 ± 9.4
If	243.9 ± 6.2	24.8 ± 0.8	192.8 ± 10.2

ln $t_{dec.}$ vs. $1/T$. The activation energy values calculated by this method are also given in Table 4.

The isothermal activation energies for the decomposition of tetrazole derivatives are higher than those obtained from the dynamic DSC runs. While it is well known that the isothermal method gives a slightly higher value for the activation energy compared to the dynamic method, the large differences observed between the two methods in this study could be due to the differences in the temperature range used for carrying out the isothermal and dynamic runs. It was not possible to run the samples in the isothermal mode in the same temperature range used for performing the dynamic runs as the delay times were very short at these temperatures. However, there was a considerable overlap in the temperature ranges employed for carrying out the dynamic and isothermal DSC studies. Another remark which could be made, based on the activation energy values presented in Tables 3 and 4, is that the activation energy for the thermal decomposition of arylidene tetrazolyl hydrazones decreases with increasing substitution of nitro groups in the aromatic ring.

Thermal decomposition mechanism

In the present study the emphasis has been mainly on the evaluation of the thermochemical and kinetic parameters for the thermal decomposition of arylidene tetrazolyl hydrazones. Studies are under progress to elucidate the mechanism of thermal decomposition of these compounds based on weight loss measurements and analysis of decomposition products. In fact, we have observed six spots on TLC (thin-layer chromatography) plate during our attempt to identify the decomposition products indicating the possible complex nature of the decomposition reaction. Based on preliminary weight loss measurements, it appears that the tetrazole moiety is lost during decomposition as shown.



TAPLE 5

Weight loss values for the thermal decomposition of tetrazolyl hydrazones

Compound	Calculated	Observed weight loss (%)	
		Isothermal runs	Dynamic runs *
Ia	44.6	49.9	51.4—56.7
Ib	36.0	41.9	49.2—55.1
Ic	36.0	30.5	32.2—45.3
Id	36.0	30.7	35.5—43.1
Ie	30.2	38.9	48.2—53.5
If	26.0	33.8	44.2—55.2

* The weight loss is dependent upon the heating rate employed.

There is a rough agreement between the calculated and the experimental weight loss values, presented in Table 5.

CONCLUSION

In this investigation, we have studied the thermal decomposition of tetrazolyl hydrazones under dynamic and isothermal heating conditions. The decomposition temperature and heat of reaction of the tetrazole derivatives indicate that the reactivity of these compounds increases with increasing number of nitro groups in the aromatic ring. It also appears that the activation energy for the thermal decomposition reveals a similar trend — E_a (trinitro derivative) $< E_a$ (dinitro derivative) $< E_a$ (mononitro derivative). At this stage, no definitive mechanism can be proposed for the thermal decomposition of these compounds. However, it may be probable that the N—N bond rupture of the tetrazole moiety is one of the "primary" steps in the decomposition process.

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