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THERMAL DECOMPOSITION OF TETRAZOLE. PART I. PROGRAMMED HEATING

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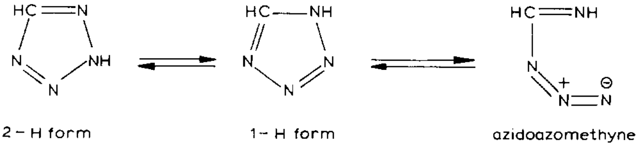
ABSTRACT

The thermolysis of tetrazole was studied using differential scanning calorimetry, differential automatic gas volumetry and complex thermal analysis. The thermoanalytical and kinetic parameters from heat-evolution, gas-release and thermogravimetry data were calculated. The results reveal the complex nature of the tetrazole thermolysis. The mechanisms of thermal decomposition seem to be different in the gas phase and in the liquid state.

INTRODUCTION

The information concerning the thermal changes of tetrazole is restricted to the evaporation data [1] and to the estimation of the composition of the gaseous thermolysis products of tetrazole when heated to 498 K in a gas IR cell [2]. The difficulties in studying the thermal decomposition of tetrazole in a condensed phase are due to its high volatility and explosiveness above the melting point.

According to theory, tetrazole is known to exist in three forms determined by the prototropic and ring-chain tautomerism [3]



Therefore, a comprehensive study of the thermal decomposition of tetrazole may possibly elucidate the role of structural specificities on thermal changes. Such a study is also of practical interest in connection with the every-growing application of tetrazole derivatives [4,5].

In Part I of our work, the thermal decomposition of tetrazole is studied using differential scanning calorimetry (DSC), differential automatic gas

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volumetry (DAGV) and complex thermal analysis. Some subtle specificities in tetrazole decomposition are more reliably revealed by the application of allied methods and instruments.

EXPERIMENTAL

Tetrazole was synthesized by the interaction of sodium azide with ammonium chloride and ethyl orthoformate in acetic acid [6]. The product was recrystallized from ethyl acetate and then sublimed in a vacuum of 1×10^{-2} mm Hg at 373 K. The tetrazole purity was estimated from the phase transition data (428.6 K) using the "Purity" program included in the software of the TC-10 processor in the Mettler-TA-3000 scanning calorimeter. The basic matter content was 99.99 wt.%.

DSC was chosen as one of the investigation methods because, in this technique, all conditions in the calorimeter can be attained without any sample superheating, a necessary condition when studying such energetic compounds as tetrazole. The experiments were carried out on a DuPont-1090 thermoanalyser, using open holders in a stream of helium, and on a Mettler-TA-3000 thermoanalyser with DSC-20 cells in sealed capsules which can withstand the pressure of vapours and gaseous decomposition products at a heating rate of 10 K min^{-1}.

The differential automatic gas volumeter DAGV-70-2M was used together with the programmable temperature controller PTC-1000M. A tetrazole sample weight of about 50 mg (with large portions, the sample exploded during the experiment) was placed in a quartz ampoule 200 mm long and 4 mm in diameter. The lower end of the ampoule, containing the sample, was placed in a furnace, the upper one in a water-cooled metal unit; the sample heating rate was 10 K min^{-1}. In the absence of easily condensed reaction products, such an approach allows one to separate the evaporation and thermodestruction processes because only gaseous decomposition products get into the probe whereas the tetrazole condensate remains at the top of the ampoule walls. The changes in gas volume in the heated ampoule due to the thermal expansion during the experiment were determined experimentally and taken into account when processing the volumetric measurements.

In the course of the complex thermal analysis of tetrazole, its strong self-heating was suppressed by the use of crystalline silicon with less than 50 μm particles, which has a higher thermal conductivity than tetrazole. Special experiments on the Mettler-TA-3000 thermoanalyser showed that silicon powder did not change the tetrazole thermolysis character. Complex thermal analysis was performed on the Paulik–Paulik–Erdey derivatograph (Hungary) at different heating rates from 0.6 to 20 K min^{-1} in platinum crucible holders with caps in a stream of argon at 5 l h^{-1}. Carefully mixed samples containing 300 mg of silicon and 30 mg tetrazole with particles of $\leqslant 50$ μm were used.

RESULTS AND DISCUSSION

The DSC curve showing the thermal changes of tetrazole in an open crucible in a stream of helium has three partially overlapping endo-effects (see Fig. 1). The first corresponds to tetrazole melting, the two others to its two-stage evaporation which is probably a result of the two equilibrium tautomeric forms in the melted tetrazole [3]. The 2-H form possesses a higher volatility and is more stable in the gas phase [7,8]. The total heat of vaporization is about 75 kJ mol^{-1}.

A typical DSC curve for the thermal decomposition of a sealed tetrazole sample is plotted in Fig. 2. Thermal decomposition includes an exo-effect which falls within 445–580 K. On the ascending exo-peak branch, there is a narrow endo-effect resembling the tetrazole melting effect, but is about 5 times smaller in area. The endo-effect was also reproduced for tetrazole samples synthesized by another procedure [9] and purified by vacuum sublimation.

Thermal decomposition of tetrazole under DAGV conditions proceeds within a temperature range of 443–543 K i.e. it starts decomposing at a lower temperature than its vapours [2,3]. The maximum gas release was about 360 ml g^{-1}, about 40 wt.% being lost (60 wt.% was left as a solid condensate in the cooled reactor section). The gas release curve of the thermal destruction of tetrazole is shown in Fig. 3, while the basic decomposition characteristics are cited in Table 1.

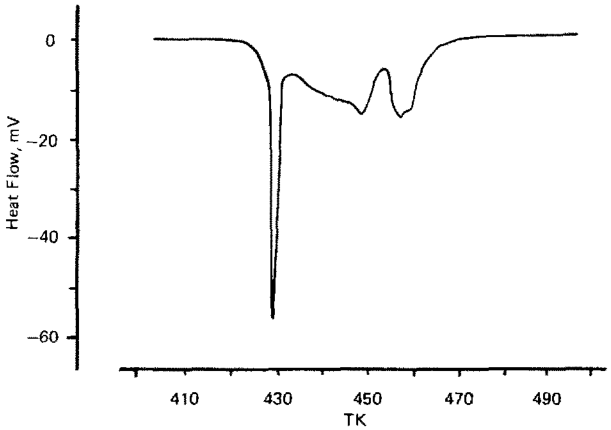

Fig. 1. DSC curve for tetrazole thermolysis in open holders in a stream of helium. Heating rate, 10 K min^{-1}.

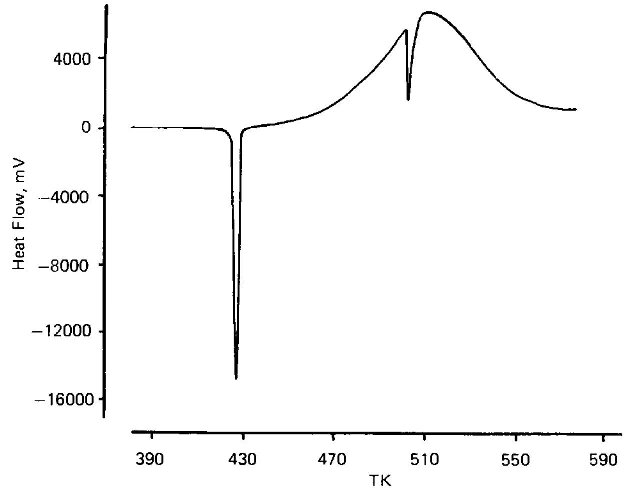

Fig. 2. DSC curve for tetrazole thermolysis in sealed capsules. Heating rate, 10 K min^{-1}.

The DSC kinetic thermolysis parameters were computed using the TC-10 processor software using the equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\,\mathrm{e}^{-E/RT}(1-\alpha)^n \qquad (1)$$

where α is the decomposition degree determined from the areas under the DSC curve.

The kinetic parameters from the gas release data were calculated by the Coats–Redfern method [10] using the n values numerically calculated by the

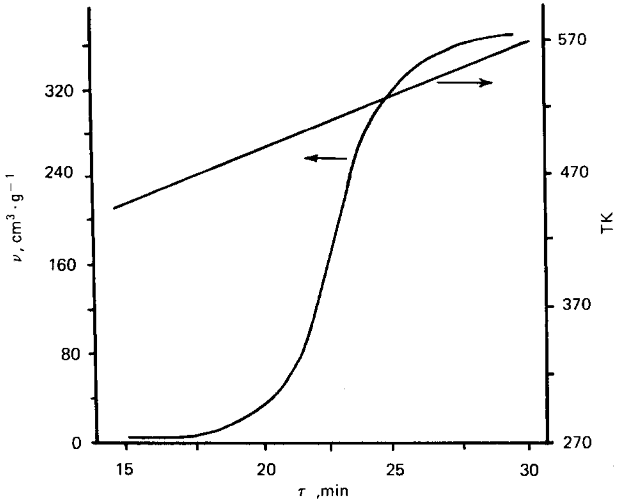

Fig. 3. Gas release curve for tetrazole thermal decomposition. Heating rate, 10 K min^{-1}.

TABLE 1

Thermoanalytical parameters of tetrazole decomposition, heating rate 10 K min^{-1}

Instrument	Sample weight (mg)	$T_{\text{melt.}}$ (K)	$\Delta H_{\text{melt.}}$ (kJ mol^{-1})	Initial temp. of decompos. (K)	$T_{\text{max.exo}}$ (K)	ΔH_{exo} (kJ mol^{-1})	T_{endo} (K)	ΔH_{endo} (kJ mol^{-1})
DSC	0.65– 0.75	428.6	20.1 ± 0.15	447.0	516.0	158.8 ± 1.6	503.0	3.8 ± 0.2
DAGV	45–50			443.0	513.0			
Derivatograph	30	435.0		445	521			

method suggested in ref. 11. Obtained values of E, lg A and n are listed in Table 2.

In contrast with the DAGV and DSC experiments, the tetrazole decomposition in the derivatographic experiments was studied in an unsealed volume. Thus, the effect of gaseous products entrained by the argon flow was eliminated. The TG and DTA curves obtained using a heating rate of 10 K min^{-1} are presented in Fig. 4. Addition of silicon powder to the tetrazole does not completely suppress the sublimation and a slow weight loss starts at the melting point. However, unlike the samples which do not contain silicon, the DTA curve shows a wide exothermic effect with a maximum corresponding to the highest rate of weight loss. The shape of this curve is like that of the DSC curve, but no narrow endothermic effect is observed on the ascending branch.

The DSC and the derivatograph were used to study the thermal decomposition of the tetrazole at different heating rates. This enabled us to estimate the activation energy of the process by displacement of the maximum heat release using the Kissinger approach [12] as well as to find the invariant kinetic parameters, as suggested earlier in ref. 13, using the TG curves obtained from the derivatograph. The kinetic parameters of the

TABLE 2

Kinetic parameters of tetrazole thermal decomposition

Instrument	Calculation method	E (kJ mol^{-1})	lg A (s^{-1})	n
DSC	Equation (1)	152.4 ± 9.5	14.4 ± 2.5	0.24 ± 0.04
	Kissinger approach	178 ± 10		
DAGV	Coats–Redfern approach	173.0 ± 15.5	17.3 ± 2.1	1.65 ± 0.12 [a]
Derivatograph	Kissinger approach (DTA)	97 ± 10		
	Invariant kinetic parameters (thermogravimetry)	172.5 [b]	15.47 [b]	

[a] Reaction order by the method of ref. 11.

[b] Mean values.

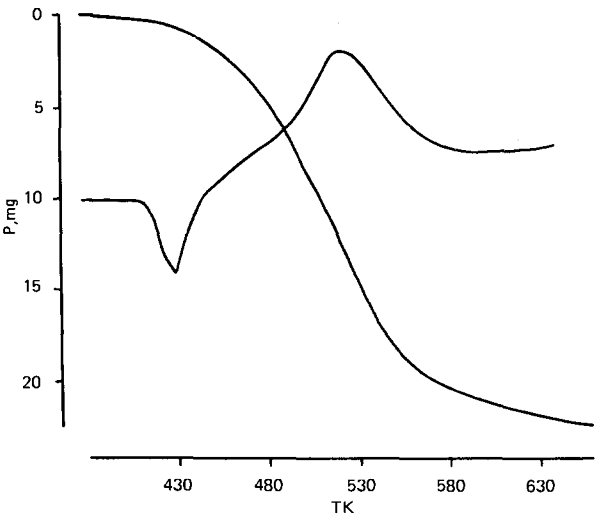

Fig. 4. DTA and TG curves for tetrazole thermal decomposition. Heating rate, 10 K min^{-1}.

tetrazole thermal decomposition obtained by the different methods are listed in Table 2.

As can be seen from Table 2, the activation energy estimated by the Kissinger approach is essentially less than the values found by other methods. This can be explained as follows. In the derivatograph case where there is a flow of gas, the heat release process responsible for the peak on the DTA curve mainly reflects the kinetics of reactions occurring in the condensed phase. Evaporation accompanying decomposition decreases heat release in the condensed phase. However, the low boiling heat (77.3 kJ mol^{-1}) determined from the difference between the sublimation heat of 97.4 kJ mol^{-1} [14] and the melting heat (Table 1), in contrast with the thermal effect of decomposition, does not significantly affect the location of the heat release maximum. In all other cases, the influence of the gas phase reactions or of the evaporation of tetrazole (in thermogravimetry) on the kinetic parameters were more important. This conclusion concerning the role of evaporation and decomposition processes in the gas phase is supported by the analysis of the temperature dependence of the saturated tetrazole vapour pressure studied by the Knudsen method in the temperature range from 333 to 404 K [15]. The estimate using the dependence of ref. 15 extrapolated to the decomposition temperature range at atmospheric pressure, shows that the tetrazole vapour pressure within the decomposition temperature range is significant and achieves atmospheric pressure at the upper limit (537 K). Thus, under the conditions studied, tetrazole thermolysis can proceed both in the liquid and in the gas phase and the kinetic parameters obtained seem to characterize the gross process. The high activation energy values obtained for closed-volume thermolysis are consistent with the high thermal stability of tetrazole in the gas phase [7,8].

Substantial differences in the effective reaction order n are due to the fact that for the DAGV method the parameter n characterizes the kinetic process in the entire temperature range whereas in the DSC method it only reflects the temperature range from the onset of the process to the endo-effect.

It should be noted that the narrow endo-effect on the ascending branch of the exo-effect was also observed when studying the thermal decomposition of a number of other tetrazole derivatives, in particular 1-ethyltetrazole, 1-aminotetrazole and 1,5-diaminotetrazole. In all the cases, its falls into the range 470–510 K. At the same time for the thermolysis of 2-substituted tetrazole derivatives (for instance, 2-ethyltetrazole and 2,5-dimethyltetrazole), the DSC curves have the other shape. Thus it seems likely that the endo-effect is due to opening of the tetrazole ring including formation of the corresponding azidoazomethyne. The latter is hardly possible for 2-isomers because their structure makes the tautomeric tetrazole–azide transitions impossible. Such a mechanism seems to characterize the first stage of the tetrazole thermolysis as well as that of its 1- and 1,5-substituted derivatives, which is supported by the thermal decomposition data for 1-aryl-5-methyltetrazoles [16,17] and some fused [1,5*d*]-tetrazoles [18,19].

The activation energy calculated for the endothermic process from the DSC data using the Kissinger approach is 137 kJ mol^{-1} [20] and it testifies to the chemical nature of the process. The thermal effect of the process is 3.80 kJ mol^{-1}, which on the whole, conforms to the heat values for the endothermic tautomeric tetrazole–azide transitions which are from 4.0 to 29.5 kJ mol^{-1}, according to refs. 21 and 22. It should be remembered here that the endothermic effect for tetrazole is observed together with an exothermic one i.e. the thermal effect in the former case seems to characterize a total process in the given temperature range and can by no means be attributed to the tautomeric transition alone.

The obtained data show that tetrazole thermolysis is a complex process, its mechanisms seem to be different during decomposition in the gas phase and in the liquid phase. This problem will be considered in the next study.

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