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THERMAL DECOMPOSITION OF TETRAZOLE PART II. KINETIC ANALYSIS

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ABSTRACT

This article elucidates the kinetic scheme of the process of tetrazole thermolysis and ascertains the results of the kinetic investigations described in Part I (Thermochim. Acta, 145 (1989) 195). Based on the processing of a series of DSC curves, an overall scheme for tetrazole thermolysis is proposed which represents two parallel processes, one of which proceeds through a reversible endothermal stage. A physical interpretation of this scheme and evaluation of the parameters of some of the stages are given. The scheme in question explains the unusual character of the heat release (a narrow endo effect against the background of a wide exo effect) as a result of the superposition of the endo- and exothermal processes forming it.

INTRODUCTION

It was shown in the first part of our work [1] on tetrazole thermolysis using several methods of thermal analysis that the process under investigation proceeded simultaneously in the gas phase and in the melt. Therefore, the effective values of the kinetic parameters obtained depend on the peculiarities of the experiment which determine the ratio of the thermolysis rates in the gas phase and in the melt. In particular, it was previously noted on the DSC curve [1] that during thermolysis of an encapsulated tetrazole sample, a narrow endo effect manifested itself against the background of a wide exo effect. The presence of such an unusual endo effect was attributed to the azidoazomethine rearrangement accompanying the transformation of the tetrazole 1-H form. At the same time it was supposed that this endo effect reflected the total process and its magnitude could not be explained by the tautomeric transformation alone.

The aim of the present paper is to elucidate the kinetic scheme of tetrazole thermolysis with the evaluation of the parameters of some of the stages, as well as to interpret kinetically the heat-release curve. The attaining of this aim presupposes the use of kinetic data obtained under closely controlled conditions and of reliable methods of calculating the kinetic parameters. It is also obvious that the reliability of the kinetic data obtained can be verified by their agreement with the results of independent experi-

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ments. Therefore, the independent study made in this work makes it possible not only to gain a deeper insight into the results of preliminary kinetic experiments [1], but also to verify the mutual reliability of the results of both works.

EXPERIMENTAL

The investigation of the thermal decomposition of tetrazole obtained according to ref. 1 was made on an encapsulated sample using a Mettler TA 3000 DSC thermoanalyser with heating rates of 1, 2, 4, 8 and 16 °C min^{-1}. The sample weight was around 1 mg. As in ref. 1, the characteristic curve of heat release shows a pronounced exo effect with a narrow endothermal effect on the upgoing branch. The transformation degree of the original substance was calculated as the ratio of the area under the curve up to a certain given temperature to the total area. The areas were calculated by numerical integration for which purpose the DSC curve was spline-approximated (Fig. 1), which made it possible to determine the transformation values at all given temperatures including those in the region of the endo effect. The kinetic parameters of tetrazole thermolysis were determined by the isoconversion method [2], by the method of invariant kinetic parameters (IKP) [3] and by the method forming part of the thermoanalyser software [4].

RESULTS AND DISCUSSION

Calculations by the isoconversion method have revealed a dependence of the effective value of the activation energy on the transformation degree (Fig. 2), indicating the complex character of the process [5]. The decreasing portion of the curve, see Fig. 2, to transformation degree 0.6 (taking into account the temperature dependence of the rate constant

$$\mathrm{d} \ln k/\mathrm{d}(1/T) = -E/R \qquad (1)$$

and the increase in the change of transformation degree with increasing temperature), corresponds to the convex Arrhenius dependence. The values

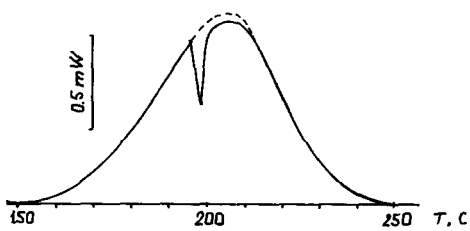


Fig. 1. DSC curve for the encapsulated tetrazole sample (heating rate 1 °C min^{-1}, weight 1.05 mg) and its spline-approximation (dashed line).

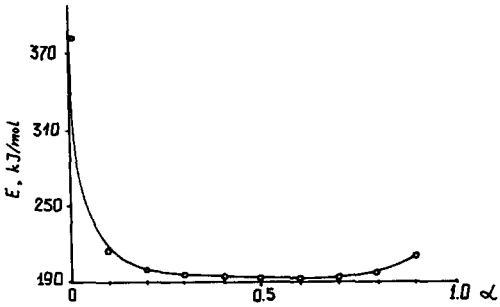
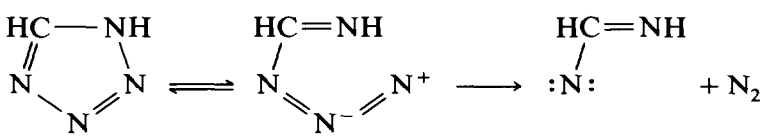


Fig. 2. Dependence of the effective activation energy value on the transformation degree for the process of tetrazole thermolysis.

of the IKP calculated for a transformation degree as low as 0.01 (the number of points required for calculation was obtained by spline-approximation) were $E = 386.2 \pm 36.8$ kJ mol^{-1} and lg $A = 43.2 \pm 4.1$. Obviously, such values are difficult to interpret from the point of view of the overall single-stage mechanism of thermolysis. It is known [6] that convex Arrhenius dependences are characteristic of complex processes proceeding through the reversible stage

$$A \rightleftharpoons B \longrightarrow C \qquad (2)$$

or of the change from a kinetic to a diffusion regime. In this case, the process proceeding through the endothermic stage at low transformation degrees (temperatures) is characterised by a high value of the effective activation energy which represents the sum of the enthalpy of the reversible process and of the activation energy of the irreversible process [6]. Very low values (less than 40 kJ mol^{-1}) of effective activation energy at high transformation degrees (temperatures) are characteristic of the processes proceeding through a reversible exothermal stage or with the change from a kinetic to a diffusion regime. Therefore, in order to interpret the observable dependence of the effective activation energy on the transformation degree, see Fig. 2, it is logical to assume a kinetic scheme with a reversible endothermal stage, as in eqn. (2). This scheme is physically interpretable. Isothermal studies [1,7–9] of the thermolysis mechanism of tetrazole and some of its derivatives show that it proceeds through a reversible stage of azidoazomethine formation



(3)

In the transformation degree range from 0.5 to 0.7, the effective activation energy is practically independent of the transformation degree, which is

indicative of the overall single-stage character of the irreversible process. The IKP values for this range of transformation degrees are $E = 192.7 \pm 4.6$ kJ mol^{-1} and lg $A = 19.0 \pm 0.5$. The reversible process enthalpy determined as the difference between the effective activation energies at the initial stage and at the stage corresponding to the plateau, is 193.5 ± 41.4 kJ mol^{-1}. Unfortunately, it is difficult to estimate the reliability of the obtained value of enthalpy, since such data are not to be found in the literature. However, we can try to estimate this value on the basis of the approach proposed in ref. 10 where, from the analysis of numerous organic compounds, mean values for the ring strain energy of cycles with different sizes have been found. From the point of view of this approach, the azidoazomethine rearrangement is the transition of a compound containing two two-member cycles (double bonds) and one five-member cycle (tetrazole) to a compound containing three two-member cycles (azidoazomethine). Thus, the tetrazole-to-azidoazomethine transition enthalpy is equal to the difference between the ring strain energy of the two-member (~ 94 kJ mol^{-1}) and of the five-member (~ 25 kJ mol^{-1}) cycles plus addition energy associated with the formation in azidoazomethine of an ion-type compound (~ 25–30 kJ mol^{-1}). All the above-mentioned ring strain energy values taken from ref. 10 relate to the gas phase. Hence the enthalpy of azidoazomethine formation from tetrazole in the gas phase is about 100 kJ mol^{-1}. Taking into account the error in the value (193.5 ± 41.4 kJ mol^{-1}) found by us and the fact that it relates to the liquid phase, we can ascertain the fact that this value is not only reasonable, but that it does quantitatively correspond, in part, to the enthalpy estimated based on the structure of the compounds in question.

Comparing the obtained values of kinetic parameters with those given in the previous work [1], it should be noted that the activation energy is close to that found, according to DSC data, by the Kissinger method (178 ± 10 kJ mol^{-1}). This agreement naturally results from the methodological equivalence (no discrimination) of the IKP and Kissinger methods and the fact that the DSC-curve maximum falls within the range of transformation degrees for which the IKP was calculated. Noteworthy also is the agreement between the obtained values of the kinetic parameters and those calculated by the IKP method using thermogravimetric data [1]. The decrease in the activation energy compared to the value obtained in this work can be attributed to the inevitable superposition of evaporation on the process of thermolysis occurring under the conditions of the thermogravimetric study. Thus, based on the analysis of the dependence of the effective activation energy value calculated by the isoconversion method on the transformation degree, we can make substantiated assumptions about the kinetic scheme of the process. The application of the IKP method in this case makes it possible to estimate the parameters E and lg A of some stages and the reversible process enthalpy.

It has been previously shown by us [11] that the methods of solving the

TABLE 1

The reaction order n and activation energy E values calculated for some heating rates by means of the method forming the Mettler TA 3000 thermoanalyser software

β (°C min^{-1})	n	E (kJ mol^{-1})
1	1.56 ± 0.19	144.93 ± 14.36
2	1.82 ± 0.20	146.37 ± 21.24
4	1.38 ± 0.28	128.25 ± 21.23
8	1.02 ± 0.21	117.40 ± 16.22
16	1.29 ± 0.32	125.26 ± 23.87

inverse kinetic problem which do not use discrimination of the formal models of the process (among them are the isoconversion and the IKP methods) permit reliable information to be obtained about the overall kinetics of the process on the basis of non-isothermal data. In addition, in ref. 11 we demonstrated the inapplicability, for non-isothermal data processing, of discrimination-based methods, a particular case of which is the method for calculating kinetic parameters that forms part of the Mettler TA 3000 thermoanalyser software. For comparison Table 1 gives the results of the activation energy calculation by means of the thermoanalyser software. It can be seen from the table that the values of the reaction order and activation energy depend on the heating rate, which makes one doubt their reliability.

Our data substantiate the assumption [1] concerning the nature of the endothermal effect observed on the heat-release curve (Fig. 1). From the point of view of the kinetic scheme, eqn. (1), providing rapidly established equilibrium, the heat-release curve must first display a significant endo effect (193.5 ± 41.4 kJ mol^{-1}) corresponding to the transition to the azide form, and then the exo effect corresponding to the azidoazomethine decomposition (curve 1, Fig. 3). In reality, however, the endo effect manifests itself on the upgoing branch of the heat-release curve, closer to the middle, and its estimated value, taking into account the level of the exo effect, is about 10 kJ mol^{-1}. To match the proposed scheme with the heat-release curve actually observed, one should assume that, simultaneously with eqn. (1), an exothermal process (curve 2, Fig. 3) which has an activation energy value higher than that found for the irreversible stage is occurring. The real existence of such a process is evidenced by the portion of increasing dependence of the effective activation energy on the transformation degree (Fig. 2) in the 0.6–0.9 range. Such a process is probably the exothermal thermolysis in the gas phase of a more volatile tautomeric 2-H form of tetrazole for which the azidoazomethine rearrangement is scarcely probable. Therefore, on the heat-release curve (curve 3, Fig. 3) an exo effect with a narrow endo effect is observed which represents the result of the superposition of the exothermal process of the 2-H form gas-phase thermolysis and endothermal formation of azidoazomethine, subsequently decomposing exo-

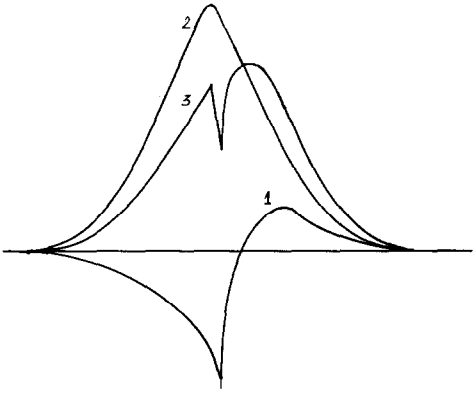


Fig. 3. Scheme of the kinetic interpretation of the tetrazole thermolysis DSC curve. The experimentally observed curve (curve 3) is the result of the superposition of the heat-release curves for the reversible endothermal formation of azidoazomethine with the next exothermal transformation (curve 1) and the process of a tetrazole 2-H-form thermolysis in the gas phase (curve 2).

thermally (curve 1, Fig. 3). The above-mentioned combination of endo- and exothermal processes also explains the fact that the experimental value of the endo effect is much lower than the theoretical one.

Thus, the analysis performed has made it possible to establish the kinetic scheme of tetrazole thermolysis and to evaluate the parameters of some stages. The reliability of the kinetic parameters obtained is demonstrated by their agreement (to an accuracy of errors of the values and differences in experimental conditions) with the parameters found by analogous (using no discrimination) methods of calculation from the results of the independent kinetic experiments of the present paper and ref. 1.

REFERENCES

1 A.I. Lesnikovich, O.A. Ivashkevich, V.A. Lyutsko, G.V. Printsev, K.K. Kovalenko, P.N. Gaponik and S.V. Levchik, Thermochim. Acta. 145 (1989) 195.
2 A. Irabien, C. Santiago and A. Araiz, J. Therm. Anal., 29 (1984) 1131.
3 A.I. Lesnikovich and S.V. Levchik, J. Therm. Anal., 27 (1983) 89.
4 Mettler TA 3000, Operating Instructions, p. 320.
5 S.V. Vyazovkin and A.I. Lesnikovich, Thermochim. Acta, 128 (1988) 69.
6 R. Shmid and V. Sapunov, Non-Formal Kinetics, Verlag Chemie, Weinheim, 1982.
7 V.V. Nedelko, V.P. Rotchupkin, G.G. Asatryan, G.V. Asratyan, N.A. Afanas'ev, G.V. Korolev, G.S. Larikova and E.V. Fronchek, Vysokomol. Soed. Ser. A., 29 (1987) 2088.
8 V.Ya. Pochinok, L.F. Avramenko, T.F. Grigorenko and V.N. Skopenko, Usp. Khim., 45 (1976) 354.
9 Yu.V. Shukhin, N.A. Klyuev, V.A. Ostrovsky, G.I. Koldobsky and G.B. Erusalimsky, Zh. Org. Khim., 20 (1984) 2485.
10 G.Ya. Kabo, G.N. Roganov and M.L. Frenkel, Thermodynamics and Equilibrium of Isomers, Universitetskoe, Minsk, 1986.
11 S.V. Vyazovkin, A.I. Lesnikovich and E.A. Gunin, Thermochim. Acta, 130 (1988) 269.