Thermochimica Acta, 92 (1985) 193-196
Elsevier Science Publishers B.V., Amsterdam

KINETIC PARAMETERS OF DECOMPOSITION OF AZODICARBONAMIDE DETERMINED FROM DSC RECORDS

L. Rychlá[*], J. Rychlý, P. Ambrovič, J. Svoboda[•], J. Šimonik[•]

Polymer Institute, Centre of Chemical Research, Slovak
Academy of Sciences, Bratislava, Czechoslovakia
[•]Research Institute of Rubber and Plastics Technology,
Gottwaldov, Czechoslovakia

Even though azodikarbonamide is frequently used as blowing agent for polyvinylchloride and other polymers, the mechanism of its decomposition is far from being understood. Under the conditions of linearly programmed heating the overall heat accompanying its decomposition is released within the temperature interval of 10 degrees . The scheme of the first order reaction which gives the best fit of the experimental course corresponds to unrealistic very high values (1500 kJ/mol and more) of apparent activation energy. Searching for the suitable model we have found that the changes of the rate of heat release may well be described by the mechanism of the collaps of crystal lattice of azodicarbonamide into its deffects which formally corresponds to the autocatalytic model[1].

The important problem is also explanation of the inconsistency in kinetic parameters obtained from DSC records and those determined by volumetry. From this viewpoint, we investigate the DSC course of isothermal decomposition of azodicarbonamide (AZDA) in Lucooil M50. The results are compared with those obtained from isothermal volumetric determination and probable interpretation of the difference is put forward.

EXPERIMENTAL

Azodicarbonamide (NH_2-CO-N=N-CO-NH_2) used in our experiments was the commercial product of Chemical Works Žilina. AZDA was used in powdered form of different grain size without further purification. Before each experiment AZDA (8.5 % of weight) was mixed with oil of trade mark Lucooil M50 (as a model of viscous medium) and the system of overall weight not exceeding 1 mg was placed in the gas-tight closed aluminium pan. During the DSC experiments the nitrogen flow of the rate 20 cm^3/min was passed continously into the measuring cell of the apparatus. DSC measurements were performed on

Proceedings of ICTA 85, Bratislava

Perkin-Elmer DSC-2 apparatus with on line calculator Textronix T-31.

In isothermal experiments, the sample was heated at the rate 160°/min to the required temperature at which the changes of the rate of the heat evolution with time were recorded and individual digital data stored in the memory of calculator.

RESULTS AND DISCUSSION

DSC records of the rate of the heat release on time perform the curves with maximum described by the values of time t_{max} and by the rate of heat evolution v_{max} . It is of interest that after this maximum the rate of heat release drops to the zero value so that surface under the experimental curve till the maximum corresponds to 60 % of overall value.

The example set of data t_{max} , v_{max} , $\Delta H_{reaction}$ and values of rate constants k determined according to the model of collaps of crystal lattice for decomposition of AZDA in Lucooil M50 at different temperatures are summarized in Table 1.

Table 1. The main data from isothermal DSC records for samples of AZDA decomposition in Lucooil M50

grain size mm	temperature K	ΔH J/g	t_{max} s	v_{max} J/gs	$k \times 10^3$ s^{-1}
0.125	458	960.0	689.5	2.69	-
	460	1109.4	675.6	3.38	1.63
	462	1068.4	529.1	4.53	2.16
	464	971.8	502.5	5.23	2.51
	466	1052.1	417.3	7.09	3.19
0.63-0.71	456	826.9	1104.2	1.40	1.01
	458	906.9	795.2	2.27	1.29
	460	1145.0	649.2	3.73	1.73
	462	1049.6	541.0	4.45	2.13
	464	975.0	495.0	5.23	2.44

No significant influence of Lucooil M50 on time t_{max} of maximum rate of the heat release when compared to pure AZDA in the powdered form is observed (Table 2).

Table 2. Times t_{max} of DSC records of the decomposition of AZDA and AZDA in Lucooil M50 at 468 K

grain size mm	t_{max}, s	
	pure AZDA	AZDA ([illegible] %) in Lucooil
0.125	315	[illegible]
0.63-0.71	359	[illegible]

The values of apparent activation energy E_a and preexponential factor A determined from temperature dependence of t_{max} , v_{max} and k are in Table 3.

Table 3. The apparent activation energy E_a and preexponential factor A determined from temperature dependence of main parameters of isothermal DSC records of decomposition of AZDA

grain size	dependence of	E_a, kJ/mol	ln $A^{a)}$	$r^{b)}$	$n^{c)}$
0.125	ln $1/t_{max}$ on $1/T$	117.1	23.99	-0.9802	11
	ln v_{max} on $1/T$	212.2	56.33	-0.9839	11
	ln k on $1/T$	182.5	-	-0.9895	9
0.63-0.71	ln $1/t_{max}$ on $1/T$	168.2	37.17	-0.9777	10
	ln v_{max} on $1/T$	270.4	71.39	-0.96.37	10
	ln k on $1/T$	205.3	46.91	-0.9870	10

a) A is in s^{-1}, for dependence of ln v_{max} on $1/T$, A is in J/s
b) r is correlation coefficient
c) n is the number of temperature runs.

As it was already indicated, volumetric measurements of decomposition of AZDA in Lucooil show much slower rate of gas evolution compared with DSC results (Fig. 1).

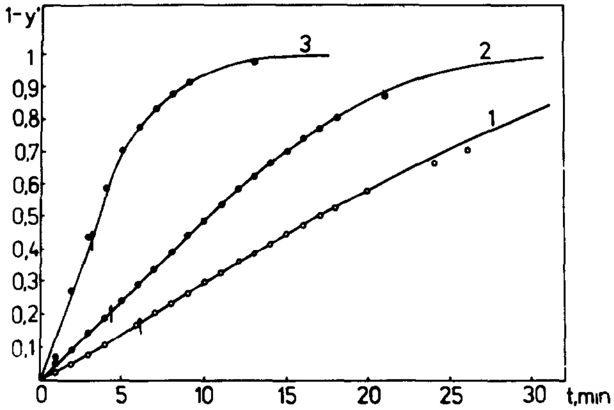


Fig. 1.

Time courses of volumetric determination of AZDA of the grain size 0.125 mm in Lucooil M50 at 468 (1), 473 (2) and 478 (3) K. Points are theoretical values ascribed to the scheme of autocatalytic reaction. 1-y' denotes the relative amount of released gas.

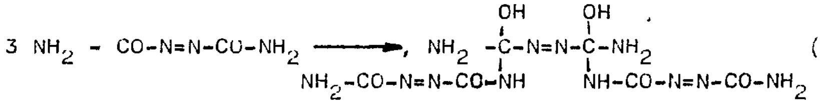
Arrows on the Fig. 1. correspond to the position of the maximum of the rate of heat release. The model of the collaps of crystal lattice into its deffects which may be in this case taken only as the first approximation gives 4 - 6 times lower values of the rate constant k.

grain size, mm	$k_{\text{from DSC at 468 K}} \cdot 10^3$ s^{-1}	$k_{\text{from volumetry}} \cdot 10^3$ s^{-1}
0.125	3.93	0.61
0.65-0.71	3.12	0.74

The course of gas evolution can well be simulated by the scheme of autocatalytic reaction (Fig. 1). The explanation of the discrepancy in kinetic paramaters obtained from DSC and volumetric measurements may at first sight consist in larger weight of sample used in the case of latter method.

Provided that we perform the same experiments on thermobalance with sample weight less than 1 mg, there are also in this case several times lower values of k received.

It was, therefore, assumed that DSC and volumetry reflect kinetically different phases of decomposition reaction. We have suggested that the gas evolution is the process subsequent to the exothermic event investigated by DSC. There exists the possibility that this exothermic process is polycondensation reaction of AZDA molecules in its crystal lattice according to the following scheme



$$3\ NH_2-CO-N{=}N-CO-NH_2 \longrightarrow NH_2-\underset{NH_2-CO-N=N-CO-NH}{\overset{OH}{C}}-N{=}N-\underset{NH-CO-N=N-CO-NH_2}{\overset{OH}{C}}-NH_2 \qquad (B)$$

Oligomer B decomposes much easily than original molecules of AZDA.

$$B \xrightarrow{II} N_2 + NH_2-CO-N{=}N-CO-NH_2 + 2\ NH{=}C{=}O + NH_2-CO-NH-NH-CO-NH_2$$

Since the process I is faster the rate of gas evolution should be governed by the proces II. The mechanisms consisting of steps I and II offer interesting possibilities in interpretation of the products formed in AZDA decomposition especially that of so far unexplained CO_2 formation. Water releasing from B may e.g. in situ initiate the decomposition of isocyanic acid to NH_3 and CO_2. Also the effect of accelerators of AZDA decomposition may be interpreted more easily in terms of their influence on the step I.

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2. J. Svoboda, L. Valová, L. Rychlá, J. Rychlý, J. Šimoník, Preprints of the 6th IUPAC sponsored Bratislava Conference on Modified Polymers, Volume II, page 333, Bratislava (1984).