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DSC STUDY OF THE DECOMPOSITION OF AZODICARBONAMIDE IN DIFFERENT MEDIA

I. Decomposition of pure azodicarbonamide; the search for the kinetic model

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The decomposition of azodicarbonamide (Genitron AC-2) in the solid state was investigated by DSC. It was found that the decomposition under non-isothermal conditions can be described by the autocatalytic reaction scheme

$$X \xrightarrow{k_1} Y, \qquad X + Y \xrightarrow{k_2'} 2Y$$

where the following dependences hold for the rate constants:

$$k_1 = 4.8 \times 10^{19} e^{-243\,600/RT} \text{s}^{-1}$$

and

$$k_2' = 1.0 \times 10^{13} e^{-133\,500/RT} \text{s}^{-1}$$

The first pre-exponential factor includes the thermal history of the sample, especially the quick heating to a certain temperature, from which normal slow heating starts.

Due to this fast heating, the decomposition reaction of AZDA may be understood as the collapse of its crystal lattice into nucleation centres with critical dimensions.

Though azodicarbonamide (AZDA) is utilized as a blowing agent for rubber and plastics, the kinetics of its decomposition is far from understood [1–4]. Since the decomposition of pure AZDA in the solid state proceeds without observable melting, a suitable kinetic model for the description of the process is required.

Waki and Yamashita [1], for example, used the Prout–Tompkins equation [5]:

$$\log \frac{P}{P_\infty - P} = kt + \text{const.} \tag{1}$$

where P is the pressure in the reactor at time t, P_∞ is the pressure at the end of the reaction, and k is the rate constant. The kinetics of AZDA decomposition was studied volumetrically at various temperatures and it was found that the observed course can be divided into 3 stages of different kinetic behaviour. From the first stage an activation energy $E = 132$ kJ/mol and pre-exponential factor $A = 1 \times 10^{12}$ s^{-1} were determined for the rate constant k. An unusually high value of the activation energy (736 kJ/mol) was found when AZDA decomposition was studied by the dynamic DSC method [6], and a first-order reaction scheme was used to evaluate the rate constant. The high activation energy was compensated by the high pre-exponential factor (10^{70} s^{-1}).

In the present paper the decomposition of AZDA of Genitron AC-2 type was studied by DSC under isothermal conditions and also with programmed heating. Some of the most common schemes utilized for the description of the course of reactions in the solid state [7] were applied in an attempt to fit the experimentally-determined kinetics of AZDA decomposition. From the non-isothermal measurements the activation energies and pre-exponential factors of the rate constants of the autocatalytic reaction scheme were determined by an optimalization procedure and the importance of the proper choice of the kinetic model was shown.

Experimental

Genitron AC-2 (azodicarbonamide, $NH_2{-}CO{-}N{=}N{-}CO{-}NH_2$), a product of Fisons Chemicals Ltd., was used in the powdered form without further purification.

The decomposition of AZDA was measured on a Perkin–Elmer DSC-2 apparatus, which records the rate of the released reaction heat $d(\Delta H)/dt$ in mcal/s. Samples of pure AZDA weighing 0.15–0.20 mg were placed in the gas-tight, closed aluminium pans, and nitrogen at a flow rate of 20 cm^3/min was passed continuously into the measuring cell of the apparatus.

In the isothermal measurements, the sample was heated to the required temperature at the maximum possible rate of 160°/min, and the changes of $d(\Delta H)/dt$ with time were then registered.

In the dynamic experiments, the sample was heated from room temperature at a rate of 160°/min to 460 K, and the rate of heating was then decreased to 5°/min. The exotherms of the dependence of $d(\Delta H)/dt$ on temperature T could thus easily be recorded. If the heating from room temperature was not sufficiently quick, no exotherm was registered.

The reproducibility of the DSC measurements of Genitron AC-2 decomposition was satisfactory. However, it is necessary to maintain carefully the uniform method of closing the aluminium pans containing the sample, and the loading of the sample powder, and to reproduce as faithfully as possible the conditions of heat transfer from the apparatus to the sample.

Results and discussion

The reaction of AZDA decomposition is exothermic. The dependence of the rate of heat release on time for the isothermal DSC measurements in the temperature interval

470–479 K is illustrated in Fig. 1. The values of $x = 1 - \alpha$, where α is the degree of conversion in the reaction, were calculated by numerical integration of the curves in Fig. 1. The maximum values of the rate of heat release, together with the times at which these maximum rates were reached, are given in Table 1. In this table the values of the overall reaction heat ΔH for individual temperatures may also be seen. Their average value is

$$\Delta H = 270 \text{ cal/g} \sim 131 \text{ kJ/mol}$$

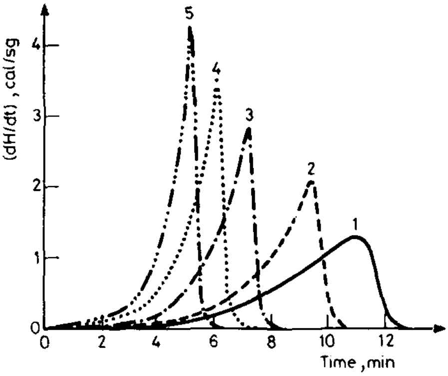

Fig. 1 Isotherms of the decomposition of AZDA (Genitron AC-2). Curve 1 – 470 K, 2 – 472 K, 3 – 475 K, 4 – 477 K and 5 – 479 K

Table 1 Parameters characterizing the isothermal decomposition of Genitron AC-2

T, K	$\left(\frac{d\Delta H}{dt}\right)_{max}$, cal/g s	t_{max}, min	ΔH, cal/g
470	1.2642	11.7	278.1
472	2.0397	9.65	278.9
475	2.8011	7.4	277.9
477	3.3624	6.3	254.2
479	4.2851	5.35	261.7

Table 2 gives a survey of the evaluation of the isothermal curves by means of the most common schemes for heterogeneous reactions, as reported in [7]. We denote them as schemes N_1–NC_2, G1–G7, D1–D6 and R2–R3; the conversion α is replaced by a residual value to 1, denoted as $x = 1 - \alpha$. The suitability of the given model was tested via the value of the correlation coefficient r for the assumed dependence

$$G(x) = f(t) \tag{2}$$

where $f(t)$ is a linear function of time such that

$$f(t) = at + b \quad \text{or} \quad f(t) = a \ln t + b \tag{3}$$

and a and b are constants.

Table 2 Survey of evaluation of the results of AZDA decomposition (Genitron AC-2) obtained by DSC by means of a set of models proposed in [7] ($x = 1 - \alpha$, where α is the conversion, and r is the absolute value of the correlation coefficient)

Symbol of model	$g(x)$	$f(t)$	Temperature, K											
			470			472			475			477		
			a	b	r	a	b	r	a	b	r	a	b	r
N1	$1-x$	$at+b$			0.9403			0.8985			0.9128			0.8973
N2	$2(1-x)^2$				0.8350			0.7694			0.8039			0.7868
N3	$3(1-x)^3$				0.7369			0.6936			0.7500			0.7388
NL	$\ln(1-x)$		0.678	−7.54	0.9652	0.727	−7.01	0.9901	0.9991	−7.31	0.9979	1.076	−6.56	0.9959
NM	$\ln(1-x)$	$a\ln t+b$	5.15	−12.53	0.9934	4.32	−10.07	0.9988	4.72	−9.71	0.9982	3.92	−7.42	0.9967
NC_1	$\ln\frac{1-x}{x}$	$at+b$	1.062	−9.81	0.9753	1.098	−8.76	0.9672	1.240	−8.19	0.9978	1.429	−7.55	0.9913
NC_2	$\ln\frac{1-x}{x}$	$a\ln t+b$			0.9552			0.9316			0.9843			0.9666
G1	$-\ln x$	$at+b$			0.7602			0.7311			0.8653			0.8287
G2	$\frac{1}{2}(-\ln x)^{1/2}$				0.9107			0.8790			0.9519			0.9287
G3	$\frac{1}{3}(-\ln x)^{1/3}$				0.9601			0.9347			0.9770			0.9627
G4	$\frac{1}{4}(-\ln x)^{1/4}$				0.9789			0.9587			0.9868			0.9769
G5	$\frac{1}{5}(-\ln x)^{1/5}$				0.9870			0.9709			0.9916			0.9840
G6	$\frac{2}{3}(-\ln x)^{2/3}$				0.8564			0.8228			0.9229			0.8924
G7	$\frac{2}{5}(-\ln x)^{2/5}$				0.9417			0.9131			0.9677			0.9498
D1	$x\ln x+1-x$				0.7812			0.7181			0.7883			0.7679
D2	$\frac{2}{3}(1-x^{1/3})^2$				0.6885			0.6544			0.7728			0.7499
D3	$\frac{2}{3}\left[1-\frac{2}{3}(1-x)-x^{2/3}\right]$	$at+b$			0.7539			0.6982			0.7873			0.7646
D4	$\frac{2}{3}\left[(2-x)^{1/3}-1\right]^2$				0.8854			0.8286			0.8403			0.8269
D5	$\frac{2}{3}(x^{1/3}-1)^2$				0.6885			0.6544			0.7728			0.7499
D6	$\frac{2}{3}\left[1-\frac{2}{3}(1-x)2/3\right]$	$a\ln t+b$			0.6631			0.5990			0.7122			0.6691
R2	$\frac{1}{2}(1-x^{1/2})$	$at+b$			0.8787			0.8287			0.8899			0.8638
R3	$\frac{1}{3}(1-x^{1/3})$				0.8450			0.7978			0.8818			0.8521

It may be seen from Table 2 that models NL, NM and NC_1, for which the chemical reaction in a surface of the newly-formed phase is the rate-determining factor of the growth of the nucleation centres, are the most suitable for the obtained results.

The nucleation centre should be understood as a microheterogeneous area of the system, in which the reaction started as a result of, for instance, the defects in the crystal lattice, and propagates from there as a reaction microfront. At the same time, nucleation proceeds according to a power (NL), exponential (NM) or autocatalytic (NC_1) scheme. For the schemes with absolute values of correlation coefficient close to 1, we also give in Table 2 the slope a and intercept b of dependence (2).

The values of constants a for scheme NC_1, which is an analog of the Prout–Tompkins scheme, are connected with the constants of Eq. (1) by the relation

$$a = k \ln 10 \tag{4}$$

and are about 3 times greater than those found by Waki [1]. Moreover, we did not observe the 3 stages reported in the kinetics of AZDA decomposition [1]. This discrepancy is probably due to the difference in the initial weight of the sample used in the volumetric measurements of paper [1] (30 mg).

Under non-isothermal conditions (heating rate 5°/min from 460 K), the decomposition of AZDA takes place in a relatively narrow temperature interval of ca 10° (Table 3). The relatively best description of the given course can be obtained by using scheme G1, which formally corresponds to a first-order reaction scheme. Schemes NL and NC_1, which under isothermal conditions gave a good correlation with the experimental results, give under non-isothermal conditions values of constant a which decrease with increasing temperature. The temperature coefficient of the reaction, E_0 (apparent activation energy), and also the pre-exponential factor A_0 obtained with scheme G1, are unusually high, in accordance with paper [6]: $E_0 = 1566$ kJ/mol, $\ln A_0 = 377.9$, with the correlation coefficient $r_0 = 0.9978$.

Table 3 Values $d\Delta H/dt$ and x for the non-isothermal decomposition of AZDA (Genitron AC-2) sample; $\Delta H = 133.5$ kJ/mol

T, K	x	$\frac{d\Delta H}{dt}$, cal/g s
485	0.996	0.108
486	0.989	0.215
487	0.974	0.466
488	0.946	0.933
489	0.889	1.722
490	0.774	3.767
491	0.547	7.17
492	0.154	9.72
493	0.002	0.251

The explanation of the validity of different schemes for the isothermal and non-isothermal conditions probably lies in the temperature-dependence of both a and b for isothermal schemes NL, NM and NC_1. If this is the case, then the original formal kinetic scheme replacing the individual model must be treated under non-isothermal conditions.

Models NL, NC_1 and NC_2, in fact, simplify the autocatalytic process

$$X \xrightarrow{k_1} Y \tag{5}$$

$$X + Y \xrightarrow{k_2} 2Y \tag{6}$$

described for non-isothermal conditions by a differential equation

$$-\frac{dx}{dT}\frac{dT}{dt} = k_1(T)x + k_2' x(1-x) \tag{7}$$

where $x = X/X_0$, $k_2' = k_2 X_0$, $dT/dt = \beta$ is the rate of heating, X_0 is the initial concentration of the reaction component X, and k_1 and k_2 are the corresponding rate constants.

While temperature is a variable instead of time, it is necessary to integrate the differential equation (7) numerically according to, for example, the Runge–Kutta procedure. The values of $k_1(T)$ and $k_2'(T)$ are assumed to depend on temperature as Arrhenius functions:

$$k_1 = A_1 e^{-E_1/RT} \tag{8}$$

$$k_2' = A_2 e^{-E_2/RT} \tag{9}$$

with corresponding doublets of parameters A_1, E_1 and A_2, E_2. By the optimalization procedure for Eqs (7–9) we have found that the experimentally-determined curve may be fitted well by parameters

$$A_1 = 4.8 \times 10^{19}\ \mathrm{s}^{-1}, \qquad A_2 = 1 \times 10^{13}\ \mathrm{s}^{-1},$$

$$E_1 = 243.6\ \mathrm{kJ/mol}, \qquad E_2 = 133.5\ \mathrm{kJ/mol}$$

(the minimum sum of the squares of deviations was $\sum \Delta_i^2 = 0.019$). The theoretical course corresponding to these parameters is shown in Fig. 2 by individual points, which correspond for experimental *line* 5 to $x \sim 0.15$.

Figure 2 also gives the theoretical courses of the non-isothermal solution of Eq. (7) for the constant parameters A_2, E_1 and E_2 corresponding to the above values and varying parameters A_1. It may be seen that with increasing A_1 the theoretical courses are shifted to lower temperatures, and at the same time the slope corresponding to the maximum rate decreases. On the back-evaluation of these theoretical courses for $0.5 < x < 1$ by means of scheme G1, adapted to the non-isothermal conditions according to Coats–Redfern [8], we obtain a set of doublets E_0 and $\ln A_0$ (Table 4).

With decreasing values of A_1, the values of E_0 increase. This increase is compensated by the increase of the pre-exponential factor A_0. The correlation coefficients close to 1 indicate that a first-order reaction scheme fits well to the given theoretical course derived from the non-isothermal autocatalytic reaction. It is of importance that, depending on the factor A_1, various values of the apparent activation energy E_0

can be obtained for the same compound from evaluation of the non-isothemal experiment.

Since reaction (6) for $E_1 > E_2$ can proceed in an accelerating manner only if a sufficient amount of Y accumulates, the values of A_1 found by optimalization will include the rate of heating at which the initial temperature (460 K) of the dynamic experiment was reached.

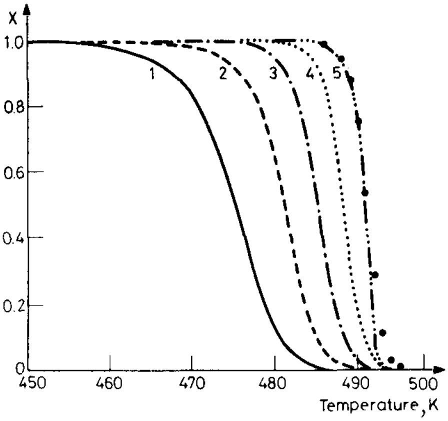

Fig. 2 Non-isothermal courses of AZDA decomposition. Curves 1, 2, 3, 4 and points in the environment of curve 5 (experimental course) are the theoretical courses for the scheme $X \xrightarrow{k_1} Y$, $X + Y \xrightarrow{k_2} 2Y$ where the activation energies E_1 and E_2 and pre-exponential factors A_1 and A_2 of the rate constants k_1 and k_2 are as follows: $E_1 = 243.6$ kJ/mol, $E_2 = 133.5$ kJ/mol, $A_2 = 1 \times 10^{13}\ s^{-1}$ and $A_1 = 4.8 \times 10^{19}$ (points on line 5), 4.8×10^{20} (line 4), 4.8×10^{21} (line 3), 4.8×10^{22} (line 2) and $4.8 \times 10^{23}\ s^{-1}$ (line 1)

The optimalization procedure of Eq. (7) was carried out assuming a uniform rate of heating of 5°/min starting from room temperature, 293 K. No exotherm can be traced experimentally, however, under such conditions. If satisfactory agreement is obtained in the experiment in which the sample was heated to 460 K at a rate of 160°/min, this means that the values of A_1 was adapted in such a way that it includes the thermal history of the sample.

By heating the sample from room temperature at only 5°/min, instead of 160°/min, we have thus decreased the sensitivity of the measurements by 160 :5 = 32 times, which explains the negative result in the former case.

In isothermal experiments, the sharp decrease in the reaction rate after the maximum corresponds to the position of inflexion points in the dependence of x on t, at about $x_{infl} = 0.2–0.3$, which is unusually low for autocatalytic nucleation. The fact that the observed kinetics depends strongly on the thermal history of the sample led us to consider the decomposition of AZDA as being governed by "collapse" of its crystal lattice to nucleation centres with certain "critical" dimensions. The rate of this "collapse" is determined by the surface of the growing nucleation centres. Taking into consideration the spherical shape of the nucleation centres, it is possible to write the equation

$$(1-x)^{1/3} = K(t-t_0) + (1-x_0)^{1/3} \tag{10}$$

where K is the rate constant of the propagation of nucleation centres, and x_0 and t_0 represent the state of the system under the initial conditions of the measurements, including the rate of heating to a given temperature in the isothermal experiment.

Table 4 Dependence of the values E_0 and $\ln A_0$ for scheme G1 on parameter A_1 of the autocatalytic reaction scheme for the kinetic courses of Fig. 2; r is the correlation coefficient of E_0 and $\ln A_0$ determination

A_1 s^{-1}	E_0, kJ/mol	$\ln A_0$	r
4.8×10^{23}	387.1	42.7	−0.9978
4.8×10^{22}	570.1	137.2	−0.9969
4.8×10^{21}	841.8	203.3	−0.9980
4.8×10^{20}	1095.4	264.2	−0.9949
4.8×10^{19}	1428.2	344.2	−0.9988

Table 5 Values of the intercepts q and the slopes K for dependence 10 of the decomposition of AZDA under isothermal conditions

T, K	q	K, min^{-1}	$K' = 1/t_{\max}$,min	r
470	−0.294	0.109	0.085	0.9997
472	−0.181	0.110	0.104	0.9939
475	−0.279	0.159	0.135	0.9923
477	−0.165	0.175	0.154	0.9902
479	−0.155	0.197	0.187	0.9873

The slopes K and intercepts $q = (1-x_0)^{1/3} - Kt_0$ of the dependence of $(1-x)^{1/3}$ *vs.* time are given in Table 5. The values of the correlation coefficients r (Table 5) indicate that the chosen approach fits the experimental data well. It is of interest that the values of $K' = 1/t_{\max}$, where $t_{\max}$ is the time of maximum reaction rate, correspond approximately to the values of K (Table 6). The abrupt end of the reaction thus corresponds much better to scheme (10) than to schemes NL, NM or

NC_1, since, neglecting the intercept in Eq. (10), and for small values of x_{infl}, when $(1 - x_{\mathrm{infl}})^{1/3} \longrightarrow 1$, we find $t_{\max} = 1/K$.

The collapse of the crystal lattice is thus a manifestation of its chemical and physical inertia with respect to the fast heating of the sample. This fact should be borne in mind when evaluating the effects of different additives on the thermal decomposition of AZDA.

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Zusammenfassung — Die Zersetzung von Azidocarbonamid (Genitron AC-2) in fester Phase wurde mittels DSC untersucht. Es wurde festgestellt, dass die Zersetzung unter nichtisothermen Bedingungen durch das autokatalytische Reaktionsschema

$$X \xrightarrow{k_1} Y, \quad X + Y \xrightarrow{k_2'} 2Y$$

beschrieben werden kann, wobei die folgenden Beziehungen für die Geschwindigkeitskonstanten gelten:

$$k_1 = 4.8 \times 10^{19} e^{-243\,600/RT}\ \mathrm{s}^{-1} \quad \text{und} \quad k_2' = 1.0 \times 10^{13} e^{-133\,500/RT}\ \mathrm{s}^{-1}.$$

Der erste präexponentielle Faktor schliesst die thermische Vorvergangenheit der Probe in sich ein, insbesondere die schnelle Erwärmung auf eine bestimmte Temperatur, von der aus die normale langsame Aufheizung einsetzt. Bedingt durch diese schnelle Erhitzung kann die Zersetzungsreaktion von AZDA als der Zusammenbruch der Kristallstruktur in Keime mit kritischen Dimensionen verstanden werden.

Резюме — Методом ДСК изучено термическое разложение твердого азодикарбоамида (АЗДА). Найдено, что разложение в неизотермических условиях может быть описано автокаталитической схемой реакции типа

$$X \xrightarrow{k_1} Y, \quad X + Y \xrightarrow{k_2'} 2Y$$

со следующим выражением для констант скорости реакций:

$$k_1 = 4.8 \times 10^{19} e^{-243\,600/RT}\ \mathrm{s}^{-1} \quad \text{и} \quad k_2' = 1.0 \times 10^{13} e^{-133\,500/RT}\ \mathrm{s}^{-1}$$

Первый предэкспоненциальный фактор включает термическую историю образца и особенно его быстрого нагрева до определенной температуры, с которой начинается нормальный медленный нагрев. Вследствии такого быстрого нагрева, реакции разложения АЗДА может быть понята как разрушение его кристаллической решетки с образованием центров кристаллизации критических размеров.