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Thermal decomposition of 2,2'-azobis(2-methyl-4-hydroxybutyl)propionate in the *N,N*-dimethylformamide/methyl methacrylate system

Summary — The thermal decomposition of the initiator 2,2'-azobis(2-methyl-4-hydroxybutyl)propionate (AIB-BD) at 333 K in *N,N*-dimethylformamide (DMF), methyl methacrylate (MMA) and various DMF/MMA mixtures was studied by volumetric method. The values of the stationary rate AIB-BD of decomposition for various initial concentrations of the initiator $[I]_0$ (within the range of 0.067–0.132 mol · dm⁻³) were determined according to differential eq. (7). These values, according to eq. (8), allowed to determinate the order (x) of initiator decomposition reaction [defined in eqs. (2) and (4)]. The order x can be regarded as equal to 1 for the whole system, *i.e.*, from a pure solvent (DMF) to pure monomer (MMA). The presented method of determination of the order x cannot be replaced by the estimation of linearity of eq. (10) what is frequently used in the publications, since the other kinetic dependences are also linear for $x = 1$ and $x = 2$. The thermal decomposition rate constant (k_d) of AIB-BD is equal $5.19 \cdot 10^{-4}$ min⁻¹ and $4.12 \cdot 10^{-4}$ min⁻¹ in pure DMF and MMA, respectively. The k_d values concerning DMF/MMA mixtures were found to be dependent on the mixture composition. This dependence is represented by a monotonically decreasing function of the monomer mole fraction (x_M). The relation $k_d = f(x_M)$ has been interpreted on the basis of a model of initiator solvation by monomer MMA and solvent DMF [eqs. (11) and (12)]. The results obtained for the DMF/MMA/AIB-BD system were compared with (previously studied) DMF/MMA/AIBN system.

Key words: methyl methacrylate radical polymerization, azo-initiators thermal decomposition, order of decomposition reaction, thermal decomposition rate constant, initiator solvation.

Dissolution of solids in solvents (also including their mixtures) depends on the interaction forces between a solid and a solvent. Generally, this interaction does not have the chemical character and cannot be observed by instrumental methods (IR, UV, NMR *etc.*). Therefore the interaction forces are evaluated by the intermediate methods, which determine a change of solution properties in relation to a solvent (vapour pressure, the Huggin's coefficient, expansion of macromolecule coil, virial coefficients *etc.*) An analogous consideration can be applied for evaluation of the influence of solvent on the properties of solid dissolved in the solvent, *e.g.* polymerization initiator. This effect may be visualized by a variation of the course of the initiator thermal decomposition. In the case when the thermal decomposition of the initiator is characterized by the rate constant (k_d) whereas a varied environment by the monomer mole fraction (x_M), the dependence $k_d = f(x_M)$ requires an in-

terpretation. A model of initiator solvation by monomer and solvent was proposed for the interpretation of this dependence [1]. According to this model the course of the dependence $k_d = f(x_M)$ in the systems 2,2'-azoisobutyronitrile (AIBN)/acrylonitrile (AN)/*N,N*-dimethylformamide (DMF) [2], AIBN/methyl methacrylate (MMA)/DMF [3, 4], and AIBN/AN/MMA/DMF [5] was explained.

Investigations of such systems, in which one of the components is varied in a defined way, *i.e.* that the systems comprise series of the reactions of the same type (thermal decomposition), permit the generalization in the description of a solvation phenomenon. Azo-initiators and macro-azo-initiators are interesting objects of the investigations with regard to this aspect.

The objective of this work was experimental determination of the reaction order and the rate constant of thermal decomposition of 2,2'-azobis(2-methyl-4-hydroxy-

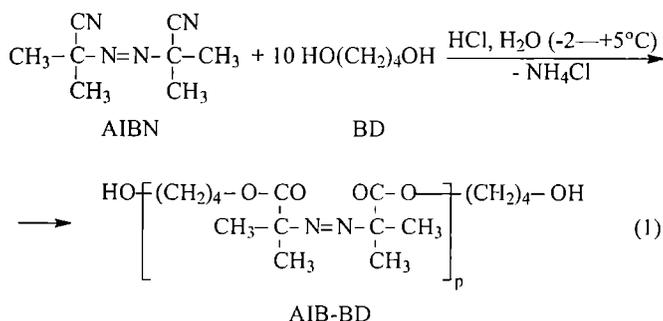
butyl)propionate (AIB-BD). The order of thermal decomposition reaction, even such a well-known initiator as AIBN has not been completely determined experimentally. Most often, the first order of the decomposition reaction of AIBN [6, 7] and its derivatives [8–11] has been assumed.

The determination of the order will enable an univocal determination of the rate constants of this reaction in pure DMF, pure MMA and in MMA/DMF mixtures over the entire range of variations of $x_M = 0-1$, that is, the determination of the dependence $k_d = f(x_M)$. Subsequently this would allow to interpret quantitatively the influence of a medium [1] on the decomposition reaction of investigated initiator.

EXPERIMENTAL

The synthesis of 2,2'-azobis(2-methyl-4-hydroxy-butyl)propionate and other materials

(AIB-BD) as azo-ester was prepared by the Pinner's method [12] in the reaction of butanediol (BD) with AIBN at the mole ratio 10:1 according to the general scheme:



The separation and purification of AIB-BD was performed similarly to the description in previous work [8].

Telechelicity of AIB-BD (the number of -OH groups per AIB-BD molecule) equal to 2, was determined by the end-groups method. The value of p was determined *via* comparison of the determined molecular weights $M_n(\text{VPO}) = 357$ and $M_n(\text{GPC}) = 380$ with calculated M (theoretical) equal to 346 and the following results were obtained: $p(\text{VPO}) = 1.03$ and $p(\text{GPC}) = 1.1$. These results indicate that an excess of BD (10:1) is sufficient for the preparation of monomeric azo-initiator ($p \approx 1$) in the reaction (1). A function of the molecular weight distribution (MWD) determined by GPC method is unimodal, symmetric and narrow ($M_w/M_n = 1.24$).

The IR analysis did not reveal the absorption band (2246 cm^{-1}) of the CN group in the prepared azo-initiator. Densities ($\text{g} \cdot \text{cm}^{-3}$) of the liquid initiator amount to $d_f^{20} = 1.0267$ and $d_f^{60} = 0.9675$ (extrapolated), and the thermal expansion coefficient $a_l = 1.58 \cdot 10^{-3} \text{ K}^{-1}$. The azo-initiator is very well soluble in the solvent (DMF), well

soluble in the mixtures DMF/MMA with any composition, and slightly soluble in the monomer (MMA).

Methyl methacrylate (Merck) and *N,N*-dimethylformamide (Fluka) were purified by standard methods. Densities of MMA ($\text{g} \cdot \text{cm}^{-3}$) were $d_M^{20} = 0.9434$ and $d_M^{60} = 0.8980$; α_{MMA} amounts $1.26 \cdot 10^{-3} \text{ K}^{-1}$. The DMF/MMA mixture ($x_M = 0.5$) is characterized by the densities ($\text{g} \cdot \text{cm}^{-3}$): $d_{x_M=0.5}^{20} = 0.9475$ and $d_{x_M=0.5}^{60} = 0.9095$ whereas $\alpha_{x_M=0.5}$ amounts $1.12 \cdot 10^{-3} \text{ K}^{-1}$. The values $d_{x_M}^{20}$ and α_{x_M} for other DMF/MMA mixtures are given in Table 2.

4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (HTEMPO) (Fluka) was used without a further purification as the inhibitor of the MMA polymerization.

Measurements

The thermal decomposition (333K) of the azo bond of the initiator in solutions was observed by recording of the volume of nitrogen evolved *via* gaseous burette [6] during the measurements, and the results were elaborated according to the previously described method [13]. The solutions (25 cm^3 , 293K) of azo-initiator in DMF, MMA and the DMF/MMA mixtures were diluted solutions (concentration AIB-BD = 0.067–0.132 mol · dm⁻³).

RESULTS AND DISCUSSION

One of the methods used to recognize the mechanism of the chemical reactions is the kinetic method. In relation to the reaction of thermal decomposition of the initiator, the kinetic equation has the form:

$$-\frac{d}{dt}[I]_t = k_d^{(x)} \cdot [I]_t^x \quad (2)$$

where: $[I]_t$ — the initiator concentration at any moment t , x — order of decomposition reaction.

The adjustment of eq. (2) to measurements of the volume of N₂ can be performed through the stoichiometric conversion factor A :

$$\begin{aligned}
 [I]_0 &= A \cdot V_\infty; [I]_0 - [I]_t = A \cdot V_t \text{ and } [I]_t = A \cdot (V_\infty - V_t) \\
 \text{thus } -\frac{d}{dt}[I]_t &= A \cdot \frac{d}{dt}V_t
 \end{aligned} \quad (3)$$

then we obtain:

$$R_{d,t} = A \cdot \frac{d}{dt}V_t = k_d^{(x)} \cdot A^x \cdot (V_\infty - V_t)^x \quad (4)$$

where: $R_{d,t}$ — rate of decomposition at the time t ; $[I]_0$ (mol · dm⁻³) — initiator concentration at t_0 ; dV_t/dt — instantaneous rate of increase of the nitrogen volume; V_t and V_∞ — respectively, the volume of N₂ evolved up to time t and the total amount of N₂ which will be evolved after the termination of decomposition ($t \rightarrow \infty$); $k_d^{(x)}$ — decomposition rate constant dependent on the reaction order as far as the numerical value and the dimension are concerned.

Equation (4) for the times t greater than that occurring in the measurements of induction time t_i , can be trans-

formed to the equation describing the stationary rate of decomposition $R_{d,s}$:

$$R_{d,s} = A \cdot \frac{d}{dt} V_t = k_d^{(x)} \cdot A^x \cdot V_\infty^x \quad (5)$$

Equations (4) and (5) can be written in the forms, respectively:

$$R'_{d,t} = \frac{d}{dt} (V_t / V_\infty) = k_d^{(x)} \cdot A^{x-1} \cdot (V_\infty - V_t)^x / V_\infty \text{ for } t < t_i \quad (6)$$

$$R'_{d,s} = \frac{d}{dt} (V_t / V_\infty) = k_d^{(x)} \cdot A^{x-1} \cdot (V_\infty)^{x-1} \text{ for } t > t_i \quad (7)$$

The rates: instantaneous ($R'_{d,t}$) and stationary ($R'_{d,s}$) are expressed in the units which are not kinetically correlated. A conclusion results from eq. (7) that for $x = 1$, the decomposition rate constant $k_d^{(x=1)}$ will not be dependent on V_∞ (thereby on the initial concentration of the initiator $[I]_0$).

The exponent x (the reaction order) in eq. (5), after finding the logarithm becomes the slope of a straight line:

$$\ln R_{d,s} = \ln k_d^{(x)} + x \ln(A \cdot V_\infty) \quad (8)$$

The course of the individual recording of $V_t = f(t)$ in pure MMA for three different initial concentrations of the initiator $[I]_0$ is shown in Fig. 1. After the induction time (t_i) which is dependent on $[I]_0$, the stationary rate ($R_{d,s}$) is established. The stationary rate implies that an increase of the volume (V_t) of N_2 becomes proportional

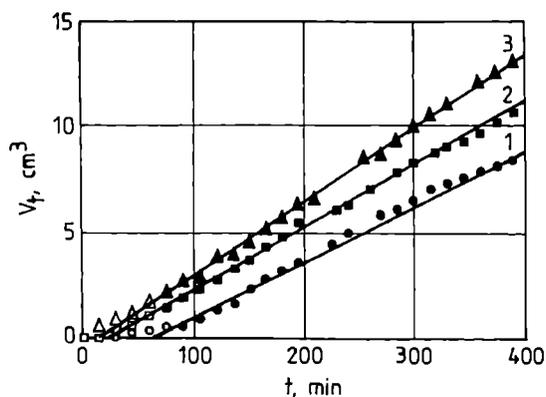


Fig. 1. Nitrogen volume (V_t) (1013 hPa, 333K) in relation to 2,2'-azobis(2-methyl-4-hydroxybutyl)propionate (AIB-BD = I) decomposition time (t) in 25 cm^3 (293K) of the monomer (MMA): 1 — $[I]_0 = 0.1 \text{ mol} \cdot \text{dm}^{-3}$, $V_\infty = 71.95 \text{ cm}^3$, $V_t = 0.0241 \cdot t - 1.1746$, $d(V_t/V_\infty)/dt = 3.34 \cdot 10^{-4} \text{ min}^{-1}$, $t_i = 49 \text{ min}$, $CF = 0.9950$; 2 — $[I]_0 = 0.117 \text{ mol} \cdot \text{dm}^{-3}$, $V_\infty = 82.11 \text{ cm}^3$, $V_t = 0.0295 \cdot t - 0.6387$, $d(V_t/V_\infty)/dt = 3.65 \cdot 10^{-4} \text{ min}^{-1}$, $t_i = 21 \text{ min}$, $CF = 0.9992$; 3 — $[I]_0 = 0.132 \text{ mol} \cdot \text{dm}^{-3}$, $V_\infty = 95.64 \text{ cm}^3$, $V_t = 0.0345 \cdot t - 0.4661$, $d(V_t/V_\infty)/dt = 3.66 \cdot 10^{-4} \text{ min}^{-1}$, $t_i = 13 \text{ min}$, $CF = 0.9994$; $\blacktriangle, \blacksquare, \bullet$ — experimental points used for plotting of equation of the straight line $V_t = f(t)$; $\triangle, \square, \circ$ — experimental points not considered for determination of this equation

to the length of time. The correlation coefficient (CF) of the straight lines 1, 2 and 3 amounts to 0.9950, 0.9992 and 0.9994, respectively.

Two independent courses of $V_t = f(t)$ were recorded for five initial concentrations of the initiator in the solvents DMF, MMA, and DMF/MMA mixture for $x_M = 0.5$ (Table 1, column 2). The linear dependences for $V_t = f(t)$ were obtained analogously as in Fig. 1, which allow to determine a single straight line by the method of arithmetic averaging. Such averaged equations (Table 1, column 4) enable the calculations of $R_{d,s}$ (Table 1, column 8) and subsequently allow to plot the courses of the dependence (8) (Fig. 2). As can be seen, they are the straight lines for all solvents (DMF, DMF/MMA mixture, and MMA) with the slopes of straight lines close to unit (0.9673, 0.9495 and 0.9951 respectively). This means that the order of AIB-BD thermal decomposition can be recognized as 0.97 ± 0.02 over the whole system DMF/MMA.

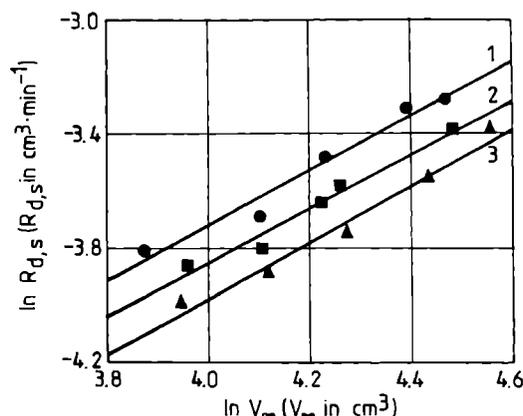


Fig. 2. Determination of the reaction order of AIB-BD decomposition according to eq. (8): 1 — decomposition in DMF: $x = 0.9673$; $k_d = 4.94 \cdot 10^{-4} \text{ min}^{-1}$; 2 — decomposition in the DMF/MMA mixture ($x_{AN} = 0.5$): $x = 0.9495$; $k_d = 4.31 \cdot 10^{-4} \text{ min}^{-1}$; 3 — decomposition in MMA: $x = 0.9951$; $k_d = 3.84 \cdot 10^{-4} \text{ min}^{-1}$

The determination of the order (x) of decomposition reaction allows to determine unambiguously the decomposition rate constant $k_d^{(x)}$, through the integration of eq. (5), which leads to the general result for $x > 1$:

$$\frac{1}{x-1} \left[\left(\frac{V_\infty}{V_\infty - V_t} \right)^{x-1} - 1 \right] = k_d^{(x)} \cdot V_\infty^{x-1} \cdot t \quad (9)$$

as well as to a detailed solution for $x = 1$:

$$\ln \frac{V_\infty}{V_\infty - V_t} = k_d \cdot t \quad (10)$$

The values of k_d determined from eq. (10) are given in Table 1 (column 10). These values, in accordance with the previous conclusion [eq. (7)] practically are not dependent on $[I]_0$ for the respective solvents.

Table 1. Thermal decomposition of the initiator AIB-BD at 333 K in the solvents: DMF, DMF/MMA mixture and MMA

No	$[I]_0, \text{mol} \cdot \text{dm}^{-3}$	V_∞, cm^3	$V_t = f(t), \text{cm}^3$	$t_i^a), \text{min}$	$10^4 \cdot \frac{d}{dt} \left(\frac{V_t}{V_\infty} \right) \text{min}^{-1}$	$\Delta^b)$	$\ln R_{d,s}^c)$	$\ln V_\infty$	$10^4 \cdot k_d^{(x=1)d) \text{min}^{-1}}$
Solvent: DMF ($x_M = 0$)									
1.1	0.067	48.12	0.0222t-1.7121	77.12	4.6012	0.1972	-3.81	3.87	5.2878
1.2	0.085	60.53	0.0247t-1.8393	74.46	4.1266	-0.2774	-3.69	4.10	4.6215
1.3	0.097	68.98	0.0306t-3.1117	101.69	4.4503	0.0463	-3.48	4.23	4.9455
1.4	0.114	80.88	0.0372t-2.4745	66.51	4.5062	0.1022	-3.31	4.39	5.1006
1.5	0.123	86.98	0.0380t-2.7785	73.12	4.3356	-0.0684	-3.28	4.47	4.7449
					average: 4.4040				average: 4.9401
Solvent: MMA/DMF ($x_M = 0.5$)									
2.1	0.073	52.35	0.0210t-0.4904	23.35	4.0207	0.1680	-3.86	3.96	4.4370
2.2	0.084	60.78	0.0222t-0.5386	24.26	3.6732	-0.1795	-3.80	4.11	4.0345
2.3	0.095	68.32	0.0262t-0.4927	18.80	3.8363	-0.0164	-3.64	4.22	4.3190
2.4	0.099	70.91	0.0266t-1.5704	59.04	3.9169	0.0642	-3.58	4.26	4.4319
2.5	0.123	88.55	0.0338t-0.7258	21.47	3.8165	-0.0362	-3.39	4.48	4.3242
					average: 3.8527				average: 4.3093
Solvent: MMA ($x_M = 1$)									
3.1	0.072	51.71	0.0185t-0.4472	24.17	3.5840	0.1489	-3.99	3.95	4.0671
3.2	0.086	61.61	0.0206t-0.4433	21.52	3.3389	-0.0962	-3.88	4.12	3.7052
3.3	0.100	71.82	0.0235t-0.7258	30.88	3.2934	-0.1417	-3.74	4.27	3.6038
3.4	0.117	84.20	0.0284t-0.5644	19.87	3.4000	-0.0351	-3.55	4.43	3.9000
3.5	0.132	95.41	0.0338t-0.6566	19.42	3.5591	0.1240	-3.38	4.56	3.9171
					average: 3.4351				average: 3.8386

a) $t_i = -a_1/a_0$ for $V_t = a_0 \cdot t - a_1$.

b) $\Delta = \frac{d}{dt} \left(\frac{V_t}{V_\infty} \right)_i - \frac{d}{dt} \left(\frac{V_t}{V_\infty} \right)_m$ deviation of measurement (i) from the average taken from all measurements.

c) $\ln R_{d,s} = \ln V_\infty \cdot \frac{d}{dt} \left(\frac{V_t}{V_\infty} \right)$.

d) $k_d^{(x=1)} = \frac{d}{dt} \ln \frac{V_\infty}{V_\infty - V_t}$.

In Fig. 3 we used eq. (5) with assumed $x = 1$, eq. (10) for $x = 1$ experimentally determined in this work and eq. (9) for assumed $x = 3/2$ and $x = 2$. These equations utilize the values of V_t and V_∞ from equation of the straight line



Fig. 3. The influence of the reaction orders in the eqs. (5), (9) and (10) on the kinetic relation of the decomposition of AIB-BD in MMA: \diamond — $f(V_t) = V_t/V_\infty \cong 3.62 \cdot 10^{-4} \cdot t - 0.89 \cdot 10^{-4}$; CF = 1.0000; $x = 1$; $k_d^{(x=1)} = 3.62 \cdot 10^{-4} \text{min}^{-1}$; Δ —

$f(V_t) = \ln \frac{V_\infty}{V_\infty - V_t} \cong 3.72 \cdot 10^{-4} \cdot t - 0.9314 \cdot 10^{-4}$; CF = 0.9999;

$x = 1$; $k_d^{(x=1)} = 3.72 \cdot 10^{-4} \text{min}^{-1}$; \square — $f(V_t) = 2 \left(\sqrt{\frac{V_\infty}{V_\infty - V_t} - 1} \right)$

$\cong 3.77 \cdot 10^{-4} \cdot t - 0.9523 \cdot 10^{-4}$; CF = 0.9998; $x = 3/2$; $k_d^{(x=3/2)}$

$= 3.77 \cdot 10^{-4} \text{mol}^{-1/2} \cdot \text{dm}^{3/2} \cdot \text{min}^{-1}$; \circ — $f(V_t) = \frac{V_t}{V_\infty - V_t} \cong 3.83 \cdot 10^{-4} \cdot t - 0.9372 \cdot 10^{-4}$; CF = 0.9996; $x = 2$;

$k_d^{(x=2)} = 3.83 \cdot 10^{-4} \text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{min}^{-1}$ [$f(V_t)$ was calculated on the basis of the straight line $V_t = 0.0297 \cdot t - 0.7316$ presented in Fig. 1 (curve 2)]

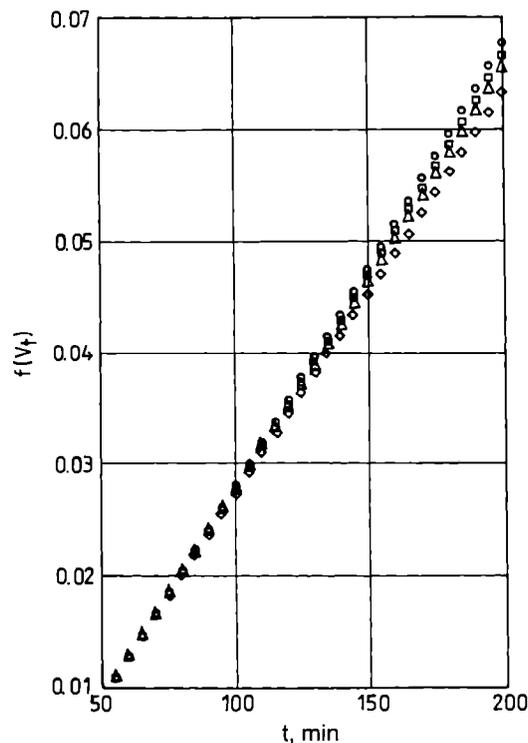


Table 2. Thermal decomposition rate constant (k_d) of the initiator AIB-BD in relation to monomer mole fraction (x_M) in DMF/MMA system at 333K

x_M	$[I]_0^{60}$, mol · dm ⁻³	V_∞^a , cm ³	$10^4 \cdot k_d^{b)}$, min ⁻¹	$10^4 \cdot k_{d,calc}^c)$, min ⁻¹	Error ^{d)} , %	DMF/MMA mixtures	
						$d_{x_M}^{20}$, g · cm ⁻³	$10^3 \cdot \alpha_{x_M}$, K ⁻¹
0.00	0.067	47.68	5.2878	5.1853	1.94	0.9475	1.03
0.05	0.074	52.68	5.1053	5.0730	0.63	0.9479	1.04
0.11	0.067	47.70	4.6736	4.9523	-5.96	0.9482	1.04
0.16	0.073	51.99	4.9073	4.8618	0.93	0.9483	1.05
0.21	0.072	51.30	4.9782	4.7791	4.00	0.9484	1.06
0.27	0.075	53.46	4.6248	4.6889	-1.39	0.9484	1.07
0.30	0.071	50.62	4.4749	4.6471	-3.85	0.9484	1.08
0.41	0.074	52.80	4.7005	4.5097	4.06	0.9481	1.10
0.52	0.073	52.13	4.4370	4.3933	0.98	0.9475	1.12
0.63	0.076	54.34	4.1558	4.2939	-3.32	0.9468	1.15
0.73	0.074	52.97	4.1731	4.2161	-1.03	0.9460	1.18
0.84	0.073	52.31	4.2504	4.1438	2.51	0.9450	1.21
0.95	0.074	53.11	4.0783	4.0952	-0.41	0.9439	1.25
1.00	0.072	51.69	4.0671	4.1170	-1.23	0.9434	1.26

a) V_∞ (cm³) = $[I]_0^{60} \cdot 683.5 \cdot (1 + \alpha_{x_M} \cdot \Delta T)$.

$$b) k_d = -\frac{d}{dt} \ln \left(1 - \frac{V_t}{V_\infty} \right)$$

c) Calculated for the solvation type IM-SIS-SIM according to eq. (13); $H^{II} = 1.56$, $H_M = 3.19$, $k_{SM} = 4.05 \cdot 10^{-4} \text{ min}^{-1}$ and $k_M = 4.12 \cdot 10^{-4} \text{ min}^{-1}$, $k_{SS} = 5.19 \cdot 10^{-4} \text{ min}^{-1}$.

d) Relative error = $10^2 \cdot (k_d - k_{d,calc}) / k_d$.

presented in Fig. 1 (curve 2). Based on Fig. 3 it can be clearly seen, that all the dependences $[f(V_t)]$ are the straight lines with high and similar CF value, thereby, the linearity of any of the straight lines cannot be a criterion of selection of the order x , as it was assumed in works [6, 9, 11, 14] for $x = 1$.

Clearness of determination $x = 1$ and $k_d^{(x=1)}$ is the base for the interpretation of the dependence $k_d = f(x_M)$. The results in Table 1 indicate that a decline of the constant $k_d^{(x=1)}$ was found starting from DMF ($x_M = 0$) through the DMF/MMA ($x_M = 0.5$) to MMA ($x_M = 1$).

Table 2 presents the average values of $k_d^{(x=1)}$ from several measurements (analogously to Fig. 1) over the whole range of x_M variations obtained for practically constant concentration of the initiator. It results from Table 2 that the thermal decomposition rate constant (k_d) of the initiator decreases monotonically with the increase of the monomer concentration (x_M). The random errors are within the relative error boundary $\pm 5\%$.

The explanation of the observed dependence of k_d on a change of the environment is plausible on the basis of the solvation model of the initiator by monomer and a solvent [1]. According to this model the k_d is presented as expression:

$$k_d = \frac{k_M \cdot K_M \cdot [M] + k_S \cdot K_S \cdot [S] + k_{MM} \cdot K_{MM} \cdot [M]^2 + k_{SS} \cdot K_{SS} \cdot [S]^2 + k_{SM} \cdot K_{SM} \cdot [S] \cdot [M]}{K_M \cdot [M] + K_S \cdot [S] + K_{MM} \cdot [M]^2 + K_{SS} \cdot [S]^2 + K_{SM} \cdot [S] \cdot [M]} \quad (11)$$

or after the division of numerator by denominator:

$$k_d = k_M \frac{K_M \cdot [M]}{B} + k_S \frac{K_S \cdot [S]}{B} + k_{MM} \frac{K_{MM} \cdot [M]^2}{B} + k_{SS} \frac{K_{SS} \cdot [S]^2}{B} + k_{SM} \frac{K_{SM} \cdot [S] \cdot [M]}{B} = k_M \cdot [IM]_r + k_{MM} \cdot [MIM]_r + k_S \cdot [IS]_r + k_{SS} \cdot [SIS]_r + k_{SM} \cdot [SIM]_r \quad (12)$$

where: $B = K_M \cdot [M] + K_S \cdot [S] + K_{MM} \cdot [M]^2 + K_{SS} \cdot [S]^2 + K_{SM} \cdot [S] \cdot [M]$; $k_M, k_S, k_{MM}, k_{SS}, k_{SM}$ (min^{-1}) — thermal decomposition rate constants of the respective solvated forms IM, IS, MIM, SIS and SIM (the concentration of these forms in the system amounts $[IM] + [IS] + [MIM] + [SIS] + [SIM] = [I]_0$, whereas the relative content is $[IM]_r + [IS]_r + [MIM]_r + [SIS]_r + [SIM]_r = 1$); K_S, K_M, K_{SS}, K_{MM} and K_{SM} represent the stability of the physical interaction of a solvent and a monomer with the initiator, which is proportional to the duration time of the respective solvated forms; $[M], [S]$ and $[I]_0$ — initial concentrations of the monomer, solvent and initiator ($\text{mol} \cdot \text{dm}^{-3}$), respectively.

The single solvated forms IM, IS denote the physical interaction of short-range, and the double forms MIM, SIS and SIM denote the interaction of long-range. The model [1] of initiator solvation excludes the simultaneous occurrence of single and double solvated forms of the same type (e.g. IM and MIM).

This assumption simplifies the eqs. (11) and (12). Thus, the thermal decomposition constant k_d (Table 2) for pure solvent ($x_M = 0$) can mean, according to the solvation model [1], that this is the constant k_S or k_{SS} and similarly in the pure monomer ($x_M = 1$) it can mean the constant k_M or k_{MM} . The remaining data in Table 2 and known initial concentrations of the monomer, solvent

Table 3. Determination of K_M , K_S , K_{MM} , K_{SS} , K_{SM} and k_{SM} constants from eq. (11) by Levenberg—Marquardt's algorithm [15]

No	Initial stability constants	0.1	1	10	100	1000
Calculated stability constants and k_{SM}						
1 ^{a)}	K_S	-576.34	-7897.40	-45 923.25	680 620.80	-6 822 241.94
	K_M	-29.53	-404.70	-2354.37	34 870.57	-349 532.62
	K_{SM}	-30.04	-411.55	-2393.04	35 469.62	-355 531.19
	$10^4 \cdot k_{SM}$	1.63	1.63	1.63	1.63	1.63
2 ^{a)}	K_S	0.32	-0.44	-7.04	283.59	3256.21
	K_{MM}	0.00	2.42	39.05	1.62	18.59
	K_{SM}	0.02	0.91	14.64	15.94	183.07
	$10^4 \cdot k_{SM}$	1.81	5.30	5.30	1.81	1.81
3 ^{a)}	K_{SS}	0.26	1.14	10.00	-30.29	934.82
	K_{MM}	0.02	0.08	0.71	1157.98	66.47
	K_{SM}	0.53	2.37	20.88	378.23	1952.66
	$10^4 \cdot k_{SM}$	4.05	4.05	4.05	5.41	4.05
Stability constants (calculated and relative) and k_{SM}						
4a ^{a)}	K_M	0.01	0.15	0.64	6.76	306.61
	K_{SS}	0.01	0.23	1.00	10.59	479.35
	K_{SM}	0.02	0.47	2.03	21.57	976.66
	$10^4 \cdot k_{SM}$	4.05	4.05	4.05	4.05	4.05
	$H'' = K_{SS}/K_M$	1.56	1.56	1.57	1.57	1.56
	$H_M = K_{SM}/K_M$	3.19	3.19	3.19	3.19	3.19
4b ^{b)}	K_M	0.10	2.15	3.05	113.83	2857.75
	K_{SS}	0.16	3.37	4.77	178.25	4472.49
	K_{SM}	0.32	6.87	9.71	363.20	9112.91
	$10^4 \cdot k_{SM}$	4.05	4.05	4.05	4.05	4.05
	$H'' = K_{SS}/K_M$	1.57	1.57	1.56	1.57	1.57
	$H_M = K_{SM}/K_M$	3.19	3.19	3.19	3.19	3.19
4c ^{c)}	K_M	11.84	117.97	925.91	12 631.08	102 641.37
	K_{SS}	18.55	184.54	1450.10	19 789.55	160 514.71
	K_{SM}	37.80	376.00	2954.70	40 323.56	327 045.06
	$10^4 \cdot k_{SM}$	4.05	4.05	4.05	4.05	4.05
	$H'' = K_{SS}/K_M$	1.57	1.56	1.57	1.57	1.56
	$H_M = K_{SM}/K_M$	3.19	3.19	3.19	3.19	3.19

^{a)} Initial $k_{SM} = 5 \cdot 10^{-4} \text{ min}^{-1}$.

^{b)} Initial $k_{SM} = 4 \cdot 10^{-4} \text{ min}^{-1}$.

^{c)} Initial $k_{SM} = 3 \cdot 10^{-4} \text{ min}^{-1}$.

and initiator allow to calculate the stability constants of the type K and the thermal decomposition rate constant of mixed solvated form k_{SM} from eq. (11).

As a result, the four cases are possible:

— The constants $k_d(x_M = 1) = k_M = 4.12 \cdot 10^{-4} \text{ min}^{-1}$ and $k_{MM} = 0$ (the MIM form does not occur) and $k_d(x_M = 0) = k_S = 5.19 \cdot 10^{-4} \text{ min}^{-1}$ and $k_{SS} = 0$ (the SIS form does not occur); this case simplifies the eqs. (11) and (12) bringing the system to the solvation type IM-IS-SIM (Table 3, No 1).

— The constant $k_d(x_M = 1) = k_{MM} = 4.12 \cdot 10^{-4} \text{ min}^{-1}$ and then $k_M = 0$ and $k_d(x_M = 0) = k_S = 5.19 \cdot 10^{-4} \text{ min}^{-1}$ and then $k_{SS} = 0$; this case implies the solvation type MIM-IS-SIM (Table 3, No 2).

— The constant $k_d(x_M = 1) = k_{MM} = 4.12 \cdot 10^{-4} \text{ min}^{-1}$, $k_M = 0$ and the constant $k_d(x_M = 0) = k_{SS} = 5.19 \cdot 10^{-4} \text{ min}^{-1}$ and $k_S = 0$; this is the solvation type MIM-SIS-SIM (Table 3, No 3).

— The constant $k_d(x_M = 1) = k_M = 4.12 \cdot 10^{-4} \text{ min}^{-1}$, $k_{MM} = 0$ and the constant $k_d(x_M = 0) = k_{SS} = 5.19 \cdot 10^{-4} \text{ min}^{-1}$ and $k_S = 0$; this is the solvation type IM-SIS-SIM (Table 3, No 4).

The calculations of simplified eq. (11) for data given in Table 2 were performed by the nonlinear least-squares method according to the Levenberg—Marquardt's algorithm [15]. This algorithm requires the assumption of initial (starting) values for calculated parameters. The starting values of stability parameters (K) were imparted from the range 0.1—1000, whereas the starting value of the decomposition constant k_{SM} was assumed as $5 \cdot 10^{-4} \text{ min}^{-1}$. The calculation result is recognized as correct when the values of determined parameters are independent on the starting values. The compilation of calculation results is presented in Table 3.

As it results from Table 3 (No 1—4), a criterion of constancy of the stability parameters (type K) does not

fulfil either of cases. On the other hand, the ratios $K_{SS}/K_M = H''$ and $K_{SM}/K_M = H_M$ for the solvation type IM-SIS-SIM (Table 3, No 4) are independent on the assumed starting values since they have been univocally established. Also, a change of $k_{SM} = 5 \cdot 10^{-4} \text{ min}^{-1}$ to other arbitrary accepted values does not change both the values H'' , H_M and a value of the constant $k_{SM} = 4.05 \cdot 10^{-4} \text{ min}^{-1}$ (Table 3, No 4a, 4b, 4c).

Thereby, $K_{SM} = 3.19 > K_{SS} = 1.56 >$ for $K_M = 1.0$ and $k_{SM} = 4.05 \cdot 10^{-4} \text{ min}^{-1}$.

In such way, the eq. (11) takes the form:

$$\begin{aligned} k_d &= \frac{k_M \cdot K_M \cdot [M] + k_{SS} \cdot K_{SS} \cdot [S]^2 + k_{SM} \cdot [S] \cdot [M]}{K_M \cdot [M] + K_{SS} \cdot [S]^2 + K_{SM} \cdot [S] \cdot [M]} = \\ &= \frac{k_M \cdot [M] + k_{SS} \cdot H'' \cdot [S]^2 + k_{SM} \cdot H_M \cdot [S] \cdot [M]}{[M] + H'' \cdot [S]^2 + H_M \cdot [S] \cdot [M]} = \\ &= k_M \cdot [IM]_r + k_{SS} \cdot [SIS]_r + k_{SM} \cdot [SIM]_r, \end{aligned} \quad (13)$$

which contains the experimentally determined values of $k_d(x_M)$, k_M and k_{SS} , and calculated H'' , H_M and k_{SM} (Table 3, No 4a, 4b, 4c). The determination of the relative contents of the solvated forms as a function of the monomer/solvent composition is possible from the following equations:

$$[IM]_r = \frac{[M]}{[M] + H'' \cdot [S]^2 + H_M \cdot [S] \cdot [M]} \quad (14)$$

$$[SIS]_r = \frac{H'' \cdot [S]^2}{[M] + H'' \cdot [S]^2 + H_M \cdot [S] \cdot [M]} \quad (15)$$

$$[SIM]_r = \frac{H_M \cdot [S] \cdot [M]}{[M] + H'' \cdot [S]^2 + H_M \cdot [S] \cdot [M]} \quad (16)$$

The numerical values H'' , H_M and k_{SM} can be also confirmed by the linearization of eq. (13):

$$H'' = \frac{H_M \cdot (k_{SM} - k_d) \cdot [S] \cdot [M] + (k_M - k_d) \cdot [M]}{(k_d - k_{SS}) \cdot [S]^2} \quad (17)$$

The dependences of H'' on the consecutively assumed values of H_M for various compositions of the monomer/solvent mixture and different values of k_{SM} form the pencil of the straight lines. The intersection points of these straight lines determine a value pair H'' and H_M at a given k_{SM} . Figure 4. illustrates this method. The results obtained according to the algorithm [15] (Table 3, No 4) and by the method of the pencil of the straight line (Fig. 4) are in a complete agreement for the IM-SIS-SIM solvation.

An established type of the initiator solvation in MMA/DMF system correlates with the experimental observation of initiator (AIB-BD) solubility, which is very good in DMF, good in the DMF/MMA and poor (incomplete) in MMA.

The relative contents of solvated forms $[IM]_r$, $[SIS]_r$ and $[SIM]_r$ according to eqs. (14)–(16) as a function of x_M are shown in Fig. 5. The courses of these functions $[IM]_r = f(x_M)$, $[SIS]_r = f(x_M)$ and $[SIM]_r = f(x_M)$ determine a character of variability of the following products: $k_M \cdot [IM]_r = f(x_M)$, $k_{SS} \cdot [SIS]_r = f(x_M)$ and $k_{SM} \cdot [SIM]_r = f(x_M)$,

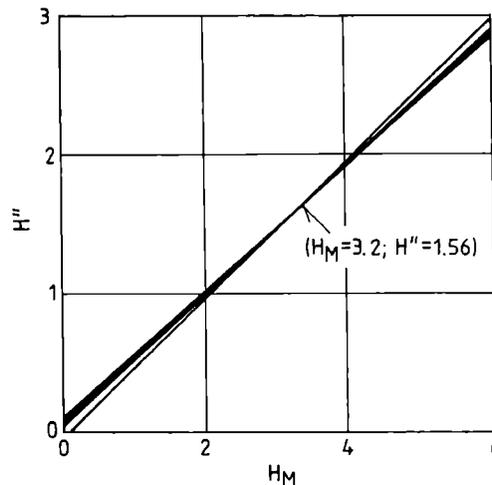


Fig. 4. Determination of constants H'' and H_M from eq. (17) for $k_{SM} = 4.05 \cdot 10^{-4} \text{ min}^{-1}$; solvation type IM-SIS-SIM

which are the components of eq. (13) ($k_M = 4.12 \cdot 10^{-4} \text{ min}^{-1}$, $k_{SS} = 5.19 \cdot 10^{-4} \text{ min}^{-1}$ and $k_{SM} = 4.05 \cdot 10^{-4} \text{ min}^{-1}$). These components represent the variable fractions of the respective solvated forms in the global dependence $k_d = f(x_M)$ (eq. 13).

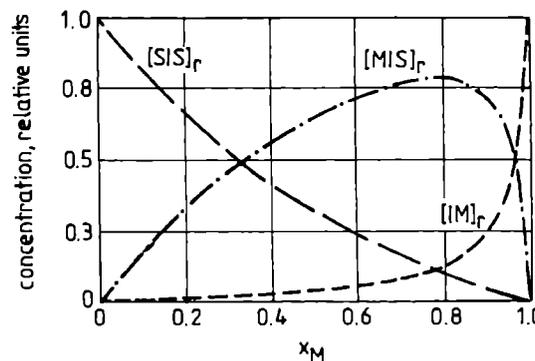


Fig. 5. Dependence of the relative content of solvated forms $[IM]_r$, $[SIS]_r$ and $[SIM]_r$ on the monomer mole fraction (x_M) according to eqs. (14)–(16) for $H'' = 1.56$, $H_M = 3.19$, $k_{SM} = 4.05 \cdot 10^{-4} \text{ min}^{-1}$, $k_M = 4.12 \cdot 10^{-4} \text{ min}^{-1}$ and $k_{SS} = 5.19 \cdot 10^{-4} \text{ min}^{-1}$

A comparison of the experimentally determined dependences of $k_d = f(x_M)$ (Fig. 6, experimental points) with the dependences calculated according to the solvation model (IM-SIS-SIM) (Fig. 6, full lines) demonstrates a complete agreement of both investigated systems: DMF/MMA/AIB-BD/60°C (Fig. 6a) and the previously described system [3, 4] DMF/MMA/AIBN/60°C (Fig. 6b).

This comparison reveals that a replacement of the AIBN by AIB-BD as initiator changes a character of the dependence of the thermal decomposition rate constant (k_d) on the composition of the DMF/MMA mixture. In the DMF/MMA/AIBN system the relationship $k_d = f(x_M)$ is characterized by a distinct minimum for $x_M =$

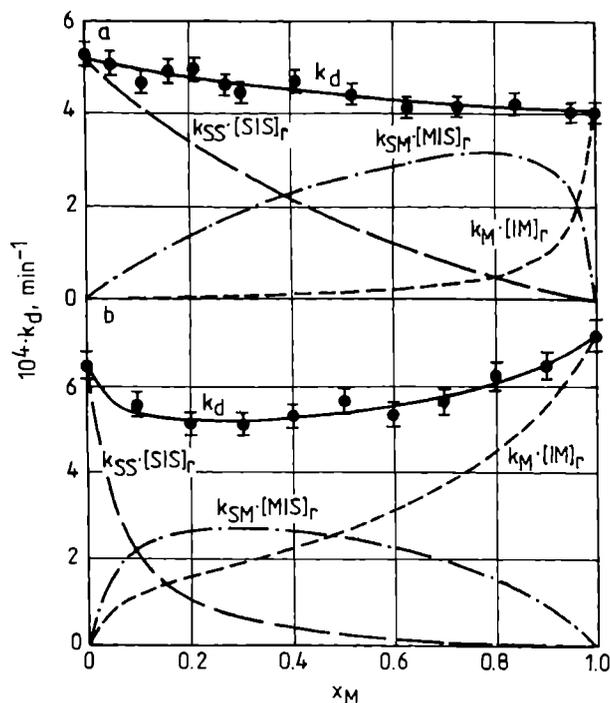


Fig. 6. Solvation model of the IM-SIS-SIM type. The dependences of the global rate constant (k_a) calculated from eq. (13) (full lines) and the partial decomposition rate constants of the solvated forms according to eqs. (14)–(16) (dashed lines) on the composition of the monomer – solvent mixture (x_M) (● — experimental points): a — DMF/MMA/AIB-BD/60°C: $H^{\parallel} = 1.56$, $H_M = 3.19$, $k_{SM} = 4.05 \cdot 10^{-4} \text{ min}^{-1}$, $k_M = 4.12 \cdot 10^{-4} \text{ min}^{-1}$, and $k_{SS} = 5.19 \cdot 10^{-4} \text{ min}^{-1}$; b — DMF/MMA/AIBN/60°C: $H^{\parallel} = 0.02$, $H_M = 0.31$, $k_{SM} = 4.2 \cdot 10^{-4} \text{ min}^{-1}$, $k_M = 7.2 \cdot 10^{-4} \text{ min}^{-1}$ and $k_{SS} = 6.45 \cdot 10^{-4} \text{ min}^{-1}$ [3, 4]

0.15–0.25, whereas for the DMF/MMA/AIB-BD system this relationship declines monotonically from the value $k_a(x_M = 0) = k_{SS} = 5.19 \cdot 10^{-4} \text{ min}^{-1}$ to the value $k_a(x_M = 1) = k_M = 4.12 \cdot 10^{-4} \text{ min}^{-1}$. The same type of solvation occurs in both systems, that is the SIM solvation forms exist besides IM and SIS. For the DMF/AIB-BD/60°C system in spite of the presence of the SIM form, the dependence $k_a = f(x_M)$ (Fig. 6a) does not show the minimum usually occurring in such cases [3, 4] (Fig. 6b). The solvation forms of the AIBN initiator in the DMF/MMA mixture have higher values of the thermal decomposition rate constants ($k_{SS} = 6.45 \cdot 10^{-4} \text{ min}^{-1}$, $k_M = 7.2 \cdot 10^{-4} \text{ min}^{-1}$ and $k_{SM} = 4.2 \cdot 10^{-4} \text{ min}^{-1}$) in comparison with the forms of the initiator AIB-BD, for which $k_{SS} = 5.19 \cdot 10^{-4} \text{ min}^{-1}$, $k_M = 4.12 \cdot 10^{-4} \text{ min}^{-1}$ and $k_{SM} = 4.05 \cdot 10^{-4} \text{ min}^{-1}$.

A change of the initiator also causes the differences in the stability constants (relative). Hence, in the DMF/MMA/AIBN system $H^{\parallel} = K_{SS}/K_M = 0.02$, $H_M = K_{SM}/K_M = 0.31$, whereas in the DMF/MMA/AIB-BD system $H^{\parallel} = K_{SS}/K_M = 1.56$ and $H_M = K_{SM}/K_M = 3.19$. These results reveal that the solvation form (SIS) of the AIB-BD initiator with DMF is about of two orders of magnitude more

stable, whereas the solvation form (SIM) with the mixed solvent is of one order of magnitude more stable than the analogous forms formed with AIBN.

CONCLUSION

The reaction of thermal decomposition of the AIB-BD initiator in various solvents (DMF, MMA, and DMF/MMA mixtures) proceeds according to the kinetics of the first order (Fig. 2) what can mean that a homolytic, pseudo-monomolecular decomposition of the azo bond takes place, similarly as in AIBN [16].

The establishment of the decomposition order allows to determinate unambiguously by the constant k_a for all compositions of the DMF/MMA mixtures (Table 2).

The linearity of eqs. (9) and (10) takes place for any order within the range $1 \leq x \leq 2$ (Fig. 3). The effect of a change of the initiator in the monomer/solvent/initiator system promotes the investigations concerning the influence of the environment on the thermal decomposition of other initiators.

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