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THERMAL DECOMPOSITION OF AZO-BIS-ISOBUTYRONITRILE IN THE SOLID PHASE

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The thermal decomposition of solid azo-bis-isobutyronitrile (AIBN) has been studied below its melting point by means of differential scanning calorimetry. The two-step nature of the decomposition is explained by different mechanisms of formation of active growth nuclei. The apparent activation energy of the formation of the active growth nuclei for the decomposition initiation is nearly three times higher than the activation energy of the decomposition of AIBN in solution. The initiation process of the decomposition depends on the history of the AIBN and on the nature of the mixture.

It is well known from numerous studies that the thermal decomposition of azo-bis-isobutyronitrile (AIBN) proceeds at practically equal rates in all solvents, the decomposition not being affected by inhibitors of radical chain reactions. It can be concluded from this that the decomposition of AIBN is a spontaneous reaction:

$$\mathrm{AIBN} \rightarrow 2\mathrm{R}^{\cdot} + \mathrm{N}_2 \rightarrow \mathrm{R}_2 + \mathrm{N}_2 \tag{1}$$

without radical-induced chain decomposition

$$\mathrm{AIBN} + \mathrm{R}^{\cdot} \rightarrow \mathrm{Rx} + \mathrm{R}'^{\cdot} \tag{2}$$

This simplifies the kinetic evaluation of the decomposition. Certain complications in the decomposition of AIBN are due to the recombination of cyanopropyl radicals with formation of tetramethylsuccinonitrile and dimethyl-[N-(2-cyano-2-propyl)] ketenimine [1]. Tetramethylsuccinonitrile is a stable product (m.p. 442 °K), whereas the ketenimine $(CH_3)_2(CN)C-N=C(CH_3)_2$ (m.p. 286–289 °K) undergoes decomposition. The rate constant of this process is approximately equal to that of the reaction of the original AIBN. The main product of the decomposition process is tetramethylsuccinonitrile, together with 2,3,5-tricyanohexane, isobutyronitrile and methacrylonitrile [2].

There is considerably less knowledge on the decomposition of AIBN in the solid phase than in solution. The decomposition of AIBN is an autocatalytic process below the melting point in the absence of solvents [3, 4].

The activation energy of the initiation of this process is 2–3 times [4] that of the spontaneous decomposition in solution.

The activation energy of the decomposition above the melting point of AIBN is 37 kcal.mole^{-1}, which is 7 kcal.mole^{-1} more than that for decomposition in solution [3]. The study of the decomposition of AIBN in the solid phase and in the melt of the decomposition products suggests that the decomposition is faster in the solid phase in a given temperature range. From this result a greater possibility of activation of the surrounding undecomposed reactant molecules by "hot" molecules formed in the final process can be assumed in the solid phase as compared to that in solution.

The knowledge acquired so far suggests that a more detailed study of the decomposition of AIBN in the solid phase may bring about further interesting results and contribute to the determination of laws governing reactions in the solid phase.

Experimental

In studying the kinetics of the decomposition of AIBN a Perkin–Elmer differential scanning calorimeter, Model DSC-IB, with covered sample pans was used. Both the measuring method and the preparation of samples have been described previously [4, 5]. The reproducibility of the measurements was within ±10%. All reagents used were of analytical grade.

Results

The first information on the decomposition of AIBN in a medium of alumina was acquired earlier [4]. In the present study, however, we found that in the decomposition of AIBN alumina does not behave as indifferently as in the case

Table 1

Maximum specific rates [release of reaction heat (v_{max}), and activation energies (E)] for the isothermal decomposition of AIBN in various mixtures

Temperature, °K	v_{max} mcal.s^{-1}.mg^{-1}							
	Al_2O_3			Anthracene			2246	
	5	50	95	5	50	95	95*	100% w/w AIBN
360	0.07	0.08	0.07	—	0.08	0.07	0.07	0.07
362	0.08	0.12	0.10	0.08	0.10	0.10	0.08	0.09
364	0.12	0.11	0.12	0.14	0.14	0.15	0.12	0.12
366	0.14	0.17	0.14	0.17	0.21	0.20	0.14	0.16
367	0.18	0.20	0.19	0.19	0.23	0.24	0.14	0.18
E, kcal.mole^{-1}	36	32	33	40	41	46	31	37

* Two other concentrations [5 and 50% (w/w) of AIBN in 2,2'-methylene-bis-(4-methyl-6-tert-butyl)phenol] were studied in a different temperature interval.

of benzoyl peroxide [4, 5]. The thermal decomposition of AIBN exhibits two exothermic peaks (Fig. 1). The decomposition close to the melting point is influenced markedly by the presence of alumina, whereas that in the melt is practically unaffected. The maximum specific rate of the decomposition expressed by

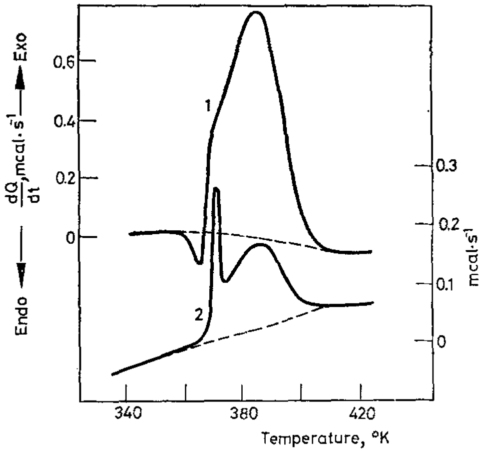


Fig. 1. DSC curve of (1) pure AIBN (1 mg) and (2) AIBN-alumina mixture (10%): 90% w/w (2 mg); heating rate: 4°K.min^{-1}

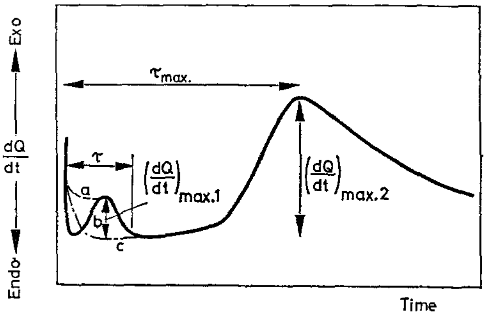


Fig. 2. Characteristic dependence of the rate of release of reaction heat in the isothermal decomposition of AIBN in various media as a function of time (t). (a) pure AIBN; (b) AIBN in the presence of alumina or anthracene; (c) 5—50% (w/w) AIBN in a mixture with 2,2′-methylene-bis-(4-methyl-6-tert-butyl)phenol

the rate of release of reaction heat per unit weight of AIBN does not change substantially over the wide concentration range of the decomposing compound (Table 1). The influence of alumina also appears to be evident in the course of isothermal decomposition of AIBN; the induction times are prolonged (Table 2) but, at the same time, the first exothermic reaction is preferred. The correlation between the exothermic process, referred to as *a* in Fig. 2, in the isothermal de-

Table 2

Values of induction times necessary to obtain maximum reaction rate in isothermal decomposition of AIBN (τ_{max}; s) and reaction times (τ; s) of the process preceding the main decomposition reaction for various AIBN contents in alumina (induction times are defined in Fig. 2)

Temperature, °K	5		50		95		100% w/w AIBN	
	τ	τ_{max}	τ	τ_{max}	τ	τ_{max}	τ	τ_{max}
360	1320	2000	270	1350	230	1350	530	1350
362	670	1340	210	900	170	880	340	840
364	470	760	220	700	120	620	290	660
366	330	550	120	330	120	390	170	300
367	250	390	120	270	120	280	120	240
E, kcal.mole^{-1}	62	62	30	62	28	57	57	64

composition and the decomposition close to the melting point of AIBN recorded by differential scanning calorimetry, was confirmed by a combination of the isothermal decomposition with DSC measurements. In samples with the time of isothermal decomposition exceeding τ, no fast reaction is observed in the vicinity of the melting point. The extent of the fast reaction at 371 °K increases with the reduction in the time of isothermal decomposition. For the subsequent heating a scanning rate of 4°K.min^{-1} was chosen.

By addition of anthracene the induction times of isothermal decomposition are first shortened but, in addition, there is an apparent prolongation in the induction period of the autocatalytic decomposition of the compound (Table 3). In the case of programmed heating and excess anthracene the decomposition pro-

Table 3

Values of induction times (τ_{max}), and reaction times (τ; s) in isothermal decomposition of AIBN in anthracene

Temperature, °K	5		50		95		100% w/w AIBN	
	τ	τ_{max}	τ	τ_{max}	τ	τ_{max}	τ	τ_{max}
360	—	—	210	1070	260	1230	530	1300
362	760	1180	190	720	150	850	340	840
364	440	680	140	390	140	470	290	660
366	230	420	100	250	80	210	170	300
367	140	490	100	225	80	200	120	240
E,* kcal.mole^{-1}	87	56	33	62	45	72	57	64

* The activation energies for individual induction processes of the decomposition reaction were calculated from the reciprocal values of τ and τ_{max}. In some values of E_τ the doubts result from short induction times decreasing the exactness of their reading with respect to the possible contribution of the initial instability of the equipment (about 40 s).

ceeds catalytically close to the melting point on the solid surface of the mixture. The rate of release of reaction heat with increasing temperature is very similar to that observed in the case of alumina (curve 2 in Fig. 1).

Unlike alumina, the presence of anthracene increases the value of the maximum decomposition rate at higher temperature (Table 1).

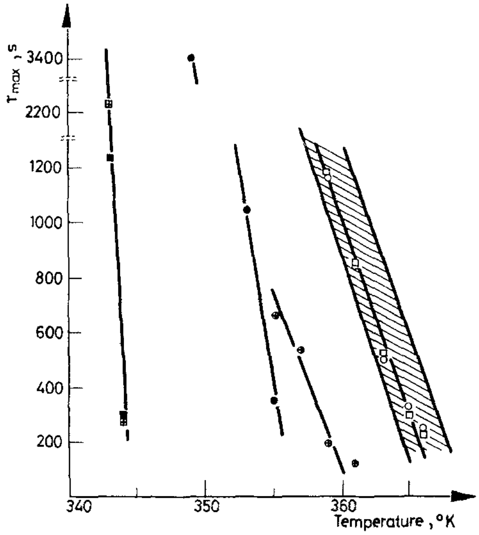


Fig. 3. Chart of induction times (τ_{max}) vs. temperature of AIBN in the presence of various amounts of organic admixtures: □ 5%; ■ 50% benzyl; ⊞ 95%; ○ 5%; ● 50% 2246; ⊕ 95%; The hatched region corresponds to induction times τ_{max} for pure AIBN and in the presence of various amounts of anthracene or alumina, respectively

Whereas neither anthracene nor alumina reduces the melting temperature of AIBN, some other compounds, such as 2,2′-methylene-bis(4-methyl-6-tert-butyl)phenol (2246) or diphenyl α,β-diketone (benzyl) do reduce the melting point markedly. In the presence of substituted phenol the melting temperature decreases to 360 °K, and in the presence of benzyl to 347 °K. The considerable effect of benzyl on the temperature shift in comparable induction times (Fig. 3) and comparable rates of autocatalytic AIBN decomposition (Fig. 4) can be similarly explained. The melting temperature of the mixture found from DSC measurements corresponds approximately to the point of intersection of the straight lines with the temperature axis in Fig. 3.

Although the reproducibility of decomposition measurements on equal portions of the same AIBN sample was relatively good after repeated preparation (recrystallization) of the sample, striking differences were observed in the decomposition. This led us to check the influence of various recrystallization methods on the course of the decomposition (Table 4). Slow crystallization resulting in bigger

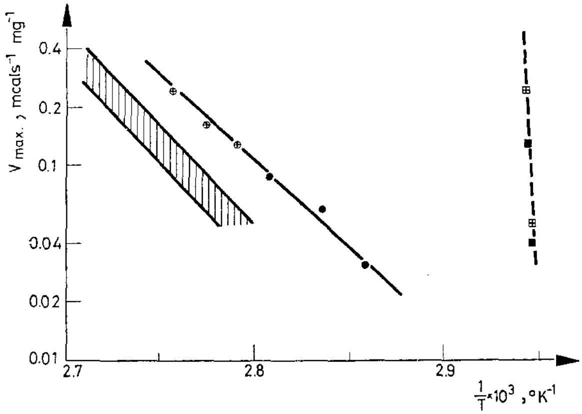


Fig. 4. Dependence of logarithm of the maximum specific rate of release of reaction heat (mcal.s^{-1}.mg^{-1} (AIBN)) in the isothermal decomposition of AIBN on the reciprocal of absolute temperature in the presence of various admixtures: □ 95% (w/w) benzyl; ■ 50% (w/w) benzyl; ⊕ 95% (w/w) 2246; ● 50%(w/w) 2246. The hatched region corresponds to reaction rates of the decomposition of pure AIBN proceeding in the presence of both alumina and anthracene (5—95%) and two other admixtures (benzyl and 2246), for low admixture content (5% (w/w) only

Table 4

Induction times and appropriate rates of release of reaction heat (see Fig. 2) in the isothermal (362 °K) decomposition of AIBN crystallized from various solvents. Sample weight 2 mg, covered sample pan

Solvent		τ, s	$\left(\frac{dQ}{dt}\right)_{\max 1}$, mcal. s^{-1}	$\tau_{\max}$, s	$\left(\frac{dQ}{dt}\right)_{\max 2}$, mcal. s^{-1}
Chloroform	a	180	0.06	1530	0.15
	b	330	0.04	1890	0.14
Benzene	a	240	0.05	1540	0.12
	b	540	0.02	2080	0.16
Ethanol	a	250	0.06	1590	0.12
	b	570	0.01	2310	0.08
Ethyl ether	a	210	0.13	660	0.25
	b	510	0.02	2190	0.14

Crystallization of AIBN from various solvents was carried out in two ways:

a) by rapid cooling of saturated solution heated to about 50 °C;

b) by gradual crystallization from saturated solution.

After crystallization the samples were dried in vacuum.

and more regular crystals leads to the prolongation of the induction period and suppression of the first exothermic process of the decomposition.

The first exothermic process is not only affected by the nature of the mixtures and by various crystallization methods, but particularly by the sample size of AIBN in the covered sample pan (Table 5).

Table 5

Characteristics of AIBN decomposition for different sample sizes of the decomposing compound (362 °K). The induction times and the appropriate rates of release of reaction heat are defined in Fig. 2

Charge, mg	τ, s	$\left(\frac{dQ}{dt}\right)_{\max 1}$, mcal. s^{-1}	$\tau_{\max}$, s	$\left(\frac{dQ}{dt}\right)_{\max 2}$, mcal. s^{-1}
0.5	1200	0.03	2400	0.03
1	810	0.03	2170	0.06
2	550	0.04	2100	0.16
4	220	0.07	a	a
6	180	0.09	a	a

a) Measurements are disturbed by the sudden release of gaseous reaction products from the sample pan.

The connection of the first process with the overall decomposition is demonstrated by the correlation of the induction times at various temperatures $\tau_{\max} = k\tau$, where the proportionality constant (2–5) depends on the nature and amount of the admixture or the method of crystallization of AIBN.

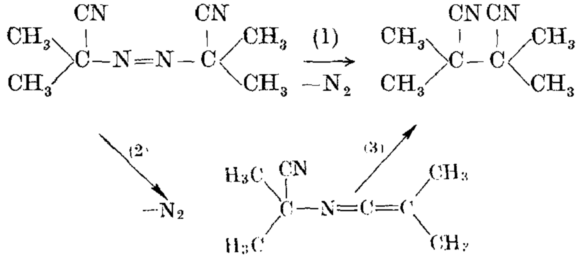
The activation energy for maximum rates of autocatalytic decomposition below the melting temperature of AIBN is similar to that of the decomposition calculated from DSC measurements [4], i.e. in the melt of AIBN itself. On the other hand, the activation energy of the initiation of autocatalytic decomposition, found from induction processes, is considerably higher (Tables 2, 3).

Discussion

The first phases of the decomposition are interesting primarily because the decomposition and formation of the first active sites begin in the solid phase, i.e. in that stage of the decomposition where the effects of the decomposition products on the melting point depression cannot be taken into account.

Measurements of the released reaction heat show that of the overall reaction heat of the decomposition about 5% is due to the first exothermic process. As a first approximation it appeared acceptable that the first exothermic process corresponded to the decomposition of ketenimine accumulated in the sample due to the gradual decomposition of AIBN.

The possible two-stage character of decomposition reaction (1) even in the absence of solvents



might become evident in the rate of release of reaction heat. When assessed from standard bond energies of the bonds forming and breaking in the individual reactions, both reaction (1) and reaction (3) are exothermic.

A similar acceleration and repeated retardation of the process at the outset of the decomposition were also observed, however, in the study of nitrogen from AIBN decomposing below its melting point [3]. This phenomenon was attributed to decomposition in the solid phase, whereas only about 10% of AIBN is assumed to exhibit a favourable crystal-modification for solid-phase decomposition. The above-mentioned gradual release of nitrogen and a similar release of reaction heat suggest that, in the present case, the first exothermic process corresponds to decomposition of AIBN since decomposition of the ketenimine is not accompanied by nitrogen release. Ketenimine may act as decomposition initiator. Following its exhaustion the decomposition slows down, to reaccelerate gradually in its further course due to another initiation mechanism. From our results it can further be seen that the first exothermic peak becomes more evident compared to the second one, not only in the presence of alumina and anthracene but also when the sample size of the reactant is reduced. The same effect may also be observed in the samples prepared by fast crystallization compared to the slow one. On the other hand, the first exothermic process is suppressed by the presence of benzyl and 2246 in concentrations exceeding 50% (w/w). A common feature of the factors leading to the appearance of the first exothermic peak is the relative increase of the surface of the decomposing compound. It seems probable that in surface crystal layers as well as at the sites of crystal defects the individual molecules of the decomposing AIBN exhibit a greater freedom of intramolecular motion than those inside the crystal lattice. This may then result in a faster decomposition of molecules at the defect sites, since less physical bonds have to be broken for the reaction to proceed.

The observed two-stage character of the decomposition suggests that in the process of AIBN decomposition, under certain conditions two kinds of nuclei arise from which the decomposition starts. Although the mechanism of the formation of nuclei has so far not been elucidated, the results obtained show that it requires a relatively high activation energy, considerably higher than in the case of the spontaneous decomposition of the same compound in solvent.

A high activation energy of nucleation (60 – 80 kcal.mole^{-1}) also results from the measurements of nitrogen release in the course of heating AIBN [3]. The activation energy was calculated from the initial phases (induction periods) of the two courses of nitrogen release at 358 and 363 °K, respectively.

The high activation energy of the initiation in the solid-phase decomposition was assumed to be the superposition of the heat coefficient of the structural change of the compound decomposing close to its melting point onto the energy of dissociation of the weakest chemical bond in the compound. The high activation energy of the reaction may also be regarded from the viewpoint of the proper nucleation mechanism of the decomposition in the solid phase. According to Bagdasarjan [6], in the decomposition of barium azide active growth nuclei are formed only by multiple consecutive activation steps at the same site. This leads to the conclusion that the number of active growth nuclei with "i" products in initial reaction phases is proportional to the i-th power of the rate constant of the decomposition. Considering that the decomposition of AIBN in the melt of the decomposition products is similar to that in solvents, the activation energy of the formation of active nuclei of the decomposition should be at least twice (suppose $i = 2$) the activation energy of the spontaneous decomposition.

Another approach to the problem of active site formation consists in the trapping of mobile active particles on crystal lattice defects [7]. The motion of activated particles does not require any material transport, but it may consist in the transport of the energy of excitation (e.g. exciton). The trapped excitons may either cause AIBN decomposition or be deactivated by phonon radiation.

Similarly, the results of the study of autocatalytic AIBN decomposition admit more possibilities of elucidation. One may be considered to be the decomposition acceleration due to gradual AIBN dissolution in the decomposition products [3]. Though this idea has been used relatively often in accounting for the similar course of other solid-phase reactions, there are at present no experimental results for AIBN to delineate the influence of the decomposition products on its melting point depression. In this case the role of the decomposition products may not consist in homogeneous AIBN dissolution. Should the AIBN dissolution in the decomposition products be of such character, it would be difficult to account for the various maximum rates of decomposition in differently crystallized AIBN samples. This discrepancy may well be explained by various numbers of nuclei per unit volume of AIBN and, consequently, by various sizes or differently sized interphase surfaces of the nucleus of the decomposition. This is in quite good agreement with the generally observed tendency (Table 4) that with shortening of induction times, i.e. with increasing rate of reaction centre formation, an increase occurs in the appropriate exothermic reaction (v; $v_{\max}$).

The elucidation of the reaction acceleration due to AIBN solubility in the reaction products need not, however, be an unambiguous and only cause of the phenomenon observed. This standpoint is supported by the evident difference in the rate of AIBN decomposition in its mixture with benzyl when compared with pure AIBN decomposition, or in the presence of anthracene or 2246. The observed maximum rate, which is about 100 times higher at a comparable temperature than for other media, confirms the major influence of the physical structure of the medium on the decomposition. Since AIBN decomposes at comparable rates in various solvents, the rate differences observed have to be attributed to different decomposition rates at the phase boundary of physically interacting, chemically different molecules. Other causes of the acceleration of the decomposition may also be considered. In the present state of knowledge of the observed phenomenon it might be stated that the acceleration of the decomposition of AIBN is not necessarily due to the more rapid decomposition in the solution of the decomposition products than in the AIBN crystal lattice.

A similar conclusion may also result from the evaluation of the curves showing acceleration in the decomposition step with the maximum rate for the exothermic reaction. The idea of decomposition in the solution of the decomposition products is contradicted by the fact that, after reaching the maximum rate, a stronger decrease occurs in the rate of the decomposition than would correspond to that for the concentration of undecomposed AIBN in the system.

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Résumé — On a étudié la décomposition thermique de l'azo-bis-isobutyronitrile solide (AIBN) au-dessous de son point de fusion, par analyse calorimétrique différentielle (DSC). Les deux étapes de la réaction de décomposition s'expliquent par le mécanisme différent de la formation des centres actifs de croissance. En comparant l'énergie d'activation de la décomposition de l'AIBN dans un solvant à l'énergie d'activation apparente de la formation des centres actifs de croissance dans le premier stade de la réaction de décomposition, on trouve que cette dernière est presque trois fois élevée. Le processus d'initiation de la réaction de décomposition dépend de l'histoire antérieure de l'AIBN et de la nature des additions.

Zusammenfassung — Die thermische Zersetzung von festem Azo-bis-Isobutyronitril (AIBN) wurde unterhalb seines Schmelzpunktes mittels Differential-Abtastkalorimetrie studiert. Die Zweistufigkeit der Zersetzungsreaktion wird durch die verschiedenen Mechanismen der Entstehung aktiver Wachstumskerne erklärt. Im Vergleich zur Aktivierungsenergie der AIBN-Zersetzung in Lösungsmitteln ist die scheinbare Aktivierungsenergie der Bildung aktiver Wachstumskerne der anfänglichen Zersetzungsreaktion beinahe dreifach. Der Auslösungsvorgang der Zersetzungsreaktion hängt von der Vorgeschichte des AIBN und der Art der Mischung ab.

Резюме — С помощью дифференциального сканнирующего калориметра изучен термораспад твердого азо-бис-изобутиронитрила (АИБН) ниже его температуры плавления. Двухступенчатый характер реакции распада объяснен различным механизмом активного роста ядрообразования. По сравнению с энергией активации распада АИБН в растворителе, кажущаяся энергия активации активного роста ядрообразования реакции начального распада примерно в три раза выше. Начальный процесс реакции распада зависит от приготовления АИБН и от характера примеси.