Thermal Decomposition of Benzoyl Peroxide in Solid State

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The course of decomposition reaction in different solid media has been investigated by differential calorimetry.

The decomposition of benzoyl peroxide in solid state differs from the decomposition in solution by a notable autocatalytic effect of decomposition reaction. The autocatalytic character of benzoyl peroxide decomposition remains in dilute solid media, too. But the induction times are shortened in the presence of different admixtures.

The effect of temperature on the isothermal decomposition of benzoyl peroxide in solid medium shows that the presence of other molecules decreases the apparent activation energy of benzoyl peroxide decomposition both in the stage of initiation and in the stage of fast branched chain decomposition.

The results obtained are discussed and interpreted from several points of view. The present knowledge supports the idea that the crystal lattice of benzoyl peroxide is responsible for the rate decrease of spontaneous decomposition in comparison with reaction rates in solutions. On the other hand, the ordered regions of benzoyl peroxide molecules enable a fast induced chain decomposition of peroxide. The admixtures accelerate the spontaneous but slow down the induced decomposition of benzoyl peroxide owing to irregularities in crystal lattice.

The present research of reactions of organic substances in solid phase is mainly aimed at polymerization reactions. Recently, we disclosed the possibility of studying the reactions in solid phase even in the case of benzoyl peroxide or 2,2'-azobis-isobutyronitrile decomposition in the absence of solvents [1]. This study was pursued with the intention of achieving other experimental information which could show the differences between the course of decomposition reactions in solid phase and in solution. In the first place, we tried to investigate the effect of those admixtures which can either affect the radical chain process of peroxide decomposition or dilute the reaction system only.

Experimental

Chemicals

Benzoyl peroxide was precipitated in chloroform by methanol. After drying it was stored in dark at −5°C. 2,2'-Methylene-bis(4-methyl-6-*t*-butylphenol), m.p. 401°K was recrystallized in hot *n*-heptane. Anthracene, analytical grade, m.p. 491°K as well as 2,6-di-*t*-butyl-4-methylphenol, m.p. 332°K, were not purified.

Aluminium oxide was heated at about 1000°C for 10 minutes approximately before using.

Preparation of mixtures

Powdered mixtures were prepared by homogenization of used substances in a vibration homogenizer; duration of homogenization 45 sec.

Isothermal measurements and differential enthalpic analysis

The differential calorimeter (Differential Scanning Calorimeter), Perkin—Elmer Model DSC-1B was used. This instrument records the variations of the rate of heat release (or absorption) with temperature or time, respectively. Scaled aluminium pans with covers were used. The weight of sample changed according to the concentration of initiator. 1 mg of pure benzoyl peroxide or 5 mg of a mixture with 5 weight % of peroxide or 2 mg of a mixture with 20 weight % or 50 weight % of peroxide was used.

Dryed nitrogen obtained from the electric bulb industry passed through the sample holder of the instrument at a rate of 20 ml/min during all measurements.

The device was calibrated for particular measurements of differential enthalpic analysis (DEA) by means of melting point of pure indium at all scan speeds (0.5—64°C/min). The melting point of indium (429.3°K) agreed with the temperature axis of record only at scan speed 4°C/min or less. For higher scan speeds we have applied a correction, *i.e.* the difference between the measured melting point of indium and its real value.

Isothermal curves were determined after the manual adjustment of a chosen temperature.

Results

Peroxide decomposition during a programmed temperature rise

The rate of reaction heat release during benzoyl peroxide decomposition in solid systems (reaction rate of decomposition) is affected very significantly by the physical character of medium (Fig. 1). As far as benzoyl peroxide is in solid state the existence of decomposition reaction is not observed under given experimental conditions. This case can be demonstrated in a differential enthalpic curve for the mixture of benzoyl peroxide with anthracene (curve *2*) as well as for pure benzoyl peroxide (curve *1*) in the temperature region under the melting point of peroxide. The rate of reaction heat release in molten systems (curve *3* and *4*) is considerably higher for benzoyl peroxide decomposition at the same temperature. These results hint that some types of crystal structure are able to inhibit the reaction of benzoyl peroxide decomposition initiated by temperature at least in the time necessary for measurement that is 2—3 minutes. It may be noted that the decomposition in melted 2,6-di-*t*-butyl-4-methylphenol has a rather similar character as the decomposition of benzoyl peroxide in solutions of different liquid solvents [2].

At the same time, it is evident from these measurements (Fig. 1) that the influence of physical structure of medium is quite considerable in the opposite direction, too. Thus the most intense rise as well as the highest rates of decomposition can be observed at temperatures close over the melting point of the mixture of peroxide with alkyl substituted methylene bis-phenol or of pure benzoyl peroxide. It is interesting to compare the temperatures at maximum decomposition rates in the two substituted phenols. The

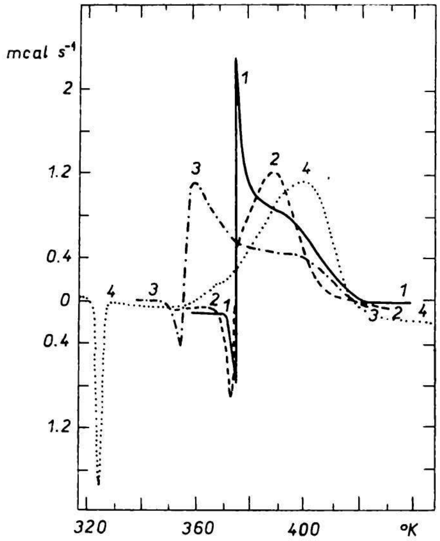


Fig. 1. Relationship between the rate of reaction heat release and temperature. Decomposition of pure benzoyl peroxide (*1*); in the presence of anthracene (*2*); in the presence of 2,2′-methylene-bis(4-methyl-6-*t*-butylphenol) (*3*); in the presence of 2,6-di-*t*-butyl-4-methylphenol (*4*). In all cases scan speed 8°C/min and weight ratio of system components 1 : 1 were used. Sample weights were 2 mg for mixtures and 1 mg for pure benzoyl peroxide.

difference between the temperatures of maximum decomposition is as much as 50°C. The phenol with a lower melting point (m.p. 332°K) behaves in a similar way as another liquid solvent while the doubled phenol with a similar structure but a higher melting point (m.p. 401°K) considerably accelerates the benzoyl peroxide decomposition at lower temperatures.

In contrast to alkylmethylene bis-phenol no marked influencing of benzoyl peroxide melting point is observed in case of anthracene addition.

This addition still manifests itself in a distinct and specific way. It is especially the suppression of the fast decomposition reaction, probably in still ordered arrangement of peroxide just melting, and the shift of maximum decomposition rate towards higher temperatures (Fig. 1) that takes place. This trend becomes more explicit by increasing scan speed of sample while the relation between the decomposition rate close after melting the peroxide and the maximum decomposition rate in the melt does not change with further addition of anthracene (Fig. 2).

Fig. 2. Variation of logarithm of maximum rate (*1*) and logarithm of benzoyl peroxide decomposition rate close over the melting point (*2*) for the mixtures of benzoyl peroxide with anthracene with weight ratio 1 : 1. Differently marked points belong to samples with 5% of benzoyl peroxide in anthracene.

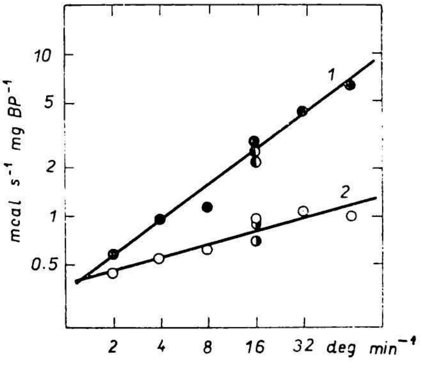


Table 1

Maximum instantaneous rates of reaction heat release [$v_{\max}$ — mcal s^{-1} (mg BP)$^{-1}$] and corresponding temperatures for benzoyl peroxide (BP) decomposition in aluminium oxide in the presence of 2,2′-methylene-bis(4-methyl-6-*t*-butylphenol) (2246) and 2,6-di-*t*-butyl-4-methylphenol (264)

Scan speed [deg min^{-1}]	5% BP in Al_2O_3		5% BP 5% 2246		5% BP 5% 264		5% BP 1% 264	
	$v_{\max}$	°K	$v_{\max}$	°K	$v_{\max}$	°K	$v_{\max}$	°K
4	2.2	378	0.6	371	0.6	393	0.5	395
8	2.6	380	1.7	375	1.1	402	1.2	403
16	3.4	381	2.7	381	2.2	408	2.1	411
32	4.2	383	4.3	385	—	—	4.4	415
64	7.4	393	7.7	398	9.1	420	9.8	425

Some changes occur in the course of decomposition reactions of system studied with varying scan speed as it has been observed previously [1] in case of the decomposition of 2,2′-azobis-isobutyronitrile or benzoyl peroxide dispersed (5 weight %) in aluminium oxide. Both the position of maximum rate of decomposition reaction on temperature axis and its absolute value are changed (Table 1 and 2). The relationship between the maximum rate and scan speed of sample (r) plotted in logarithmic coordinates is clearly linear, the slope of the linear plot varying from 0.45 to 1 (Table 3). Aluminium oxide affects the slope of straight lines or the exponent n in the relationship $v_{\max} = k\, r^n$ rather little. On the other hand, the presence of organic substances has a distinct effect.

Table 2

Maximum instantaneous rates of reaction heat release [$v_{\max}$ — mcal s^{-1} (mg BP)$^{-1}$] and corresponding temperatures for benzoyl peroxide (BP) decomposition in different media (2246 = 2,2′-methylene-bis(4-methyl-6-*t*-butylphenol), 264 = 2,6-di-*t*-butyl-4-methylphenol)

Weight ratio of reaction medium and benzoyl peroxide 1 : 1

Scan speed [deg min^{-1}]	Pure BP		2246		Anthracene		264	
	$v_{\max}$	°K	$v_{\max}$	°K	$v_{\max}$	°K	$v_{\max}$	°K
2	1.4	374	0.5	349	0.6	375	0.3	385
4	2.3	374	0.8	354	1.0	384	0.6	393
8	2.6	374	1.2	359	1.2	390	1.2	398
16	3.8	374	1.8	362	2.8	392	2.3	407
32	4.3	374	2.8	367	4.5	396	4.0	412
64	7.0	375	4.6	377	6.3	403	8.3	416

The dependence of maximum decomposition rate ($v_{\max}$) on temperature can be expressed in terms of Arrhenius relationship. The temperature coefficients thus obtained also include the influence of different scan speed and do not therefore express the true tempe-

Table 3

Data on the decomposition reaction of benzoyl peroxide (BP) in the presence of aluminium oxide, 2,2′-methylene-bis(4-methyl-6-*t*-butylphenol) (2246), 2,6-di-*t*-butyl-4-methylphenol (264) and anthracene (A)

Composition of sample and kind of admixture	Arrhenius parameters k_0 [s^{-1}]	Arrhenius parameters E [kcal $mole^{-1}$]	Reaction heat [kcal $mole^{-1}$]	% max	n
pure BP	1.2×10^{10}	21.4	72	7	0.45
5% BP in Al_2O_3	1.8×10^{8}	18.1	68	7	0.43
50% BP in 2246	1.2×10^{7}	15.3	43	15	0.63
5% BP, 5% 2246 in Al_2O_3	4.4×10^{8}	18.6	52	30	0.77
50% BP in 264	1.2×10^{11}	23.7	67	65	0.96
5% BP, 5% 264 in Al_2O_3	3.8×10^{15}	32.0	67	65	0.98
5% BP, 1% 264 in Al_2O_3	1.8×10^{8}	14.6	57	65	1.08
50% BP in A	8.7×10^{11}	24.6	47	50	0.69

n — exponent in the relationship $v_{\max} = k(\text{scan speed})^n$.

$\%_{\max}$ — % of peroxide decomposed at maximum rate of decomposition.

rature dependence of maximum rate, properly. But that is also valid for the dependence of maximum rates on the scan speed of sample. These effects coincide in both cases. The temperature coefficients equal 30 kcal $mole^{-1}$ approximately for the greater part of systems studied. A deviation can be observed in case of pure benzoyl peroxide (without Al_2O_3) which shows a substantially higher value (on the basis of the measurement series performed, it is, however, difficult to be determined exactly) and benzoyl peroxide in 2,2′-methylene-bis(4-methyl-6-*t*-butylphenol) the temperature coefficient of which has had the value of 24 kcal $mole^{-1}$ for maximum rate. For this kind of phenol, the difference between the decomposition reaction in the presence and in the absence of aluminium oxide is quite evident. Some differences manifest themselves in qualitatively different enthalpic curves, too (Fig. 3). The dilution of reaction medium with aluminium oxide

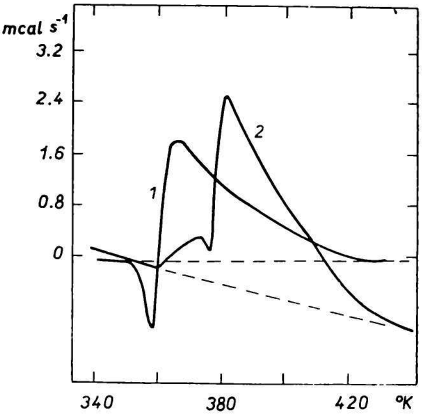


Fig. 3. Differential enthalpic curve for benzoyl peroxide in 2,2′-methylene-bis(4-methyl-6-*t*-butylphenol) (*1*) weight ratio 1 : 1, the sample weight being 2 mg. The second curve (*2*) corresponds to a sample with 5% of benzoyl peroxide and 5% of 2,2′-methylene-bis(4-methyl-6-*t*-butylphenol) in aluminium oxide; weight of sample being 5.5 mg.
Both samples were run at the scan speed 16°C/min.

suppresses the specific effect of 2,2′-methylene-bis(4-methyl-6-*t*-butylphenol) on the benzoyl peroxide decomposition and the reaction gains the character of the decomposition of pure peroxide. The first bend in the curve *2* (Fig. 3) corresponds to the melting point of the mixture containing the relevant phenol and peroxide whereas the second one corresponds to the melting point of pure benzoyl peroxide. It is also worth mentioning that the maximum decomposition rate ($v_{\max}$) of benzoyl peroxide in aluminium oxide (5% benzoyl peroxide) is dependent on the time of homogenization or grinding of the benzoyl peroxide crystals in the homogenizer.

The amount of peroxide decomposed after reaching the maximum decomposition rate is another descriptive characteristics of differential enthalpic curves. A certain value fairly little dependent on the scan speed of samples can be obtained for every system (Table 4). The deviations occur only in case of the benzoyl peroxide decomposition in aluminium oxide or in case of the decomposition of pure benzoyl peroxide. There are two distinctly separated maxima which can be observed when pure benzoyl peroxide decomposes at the highest scan speed. While 10% of decomposed peroxide approximately correspond to the maximum rate at the lower temperature the second maximum already conforms closely to the value obtained for the decomposition in solution.

Table 4

Homogenization time [min]	0.5	1.5	5	10	12
$v_{\max}$ [mcal s^{-1} (mg BP)$^{-1}$]	2.80	2.64	2.24	1.76	1.11

The scan speed of DEA measurements was 8°/min.

The differential enthalpic curves measured in different systems enable us to compute rate constants of benzoyl peroxide decomposition [2]. The computation has been carried out on the assumption that the decomposition reaction is monomolecular. The frequency factors and activation energies have been determined for particular media of benzoyl peroxide decomposition on the basis of Arrhenius equation. It may be noticed that the values of rate constants computed from individual differential enthalpic curves at various scan speed follow the Arrhenius equation very well except the rate constants for initial phases of decomposition reaction in temperature region close to the melting point of the system. Assuming that the dilution is sufficient and the concentration of chain reaction inhibitor high enough it can be seen from the values of Arrhenius parameters obtained that the benzoyl peroxide decomposition has a similar character like in dilute solution ($A = 10^{13}-10^{14}\ \mathrm{s}^{-1}$, $E = 30\ \mathrm{kcal\ mole}^{-1}$) under given conditions only in single case (Table 3).

Isothermal decomposition of peroxide under melting point

A particularly different feature of benzoyl peroxide decomposition in solid state in comparison with a decomposition in solution is an outstanding autocatalysis of decomposition reaction [1]. Since the induction period of autocatalytic decomposition involves time intervals which are long enough and sometimes even include several hours at temperatures about 10°C under the melting point of pure benzoyl peroxide or of a mixture with other crystal substance then during usual DEA runs (scan speed 4°C/min and higher) no considerable decomposition reaction is usually observed under mentioned conditions.

Table 5

Induction periods of decomposition reaction (τ_{in} (s)) and induction times (τ_{max} (s)) before reaching the maximum rate of reaction heat release [v_{max} — mcal s^{-1} (mg BP)$^{-1}$] for pure benzoyl peroxide (BP) and for its mixture with 2,2′-methylene-bis(4-methyl-6-*t*-butylphenol) (5%) at different temperatures

T [°K]	Pure BP			BP + 5% 2246		
	τ_{in}	τ_{max}	v_{max}	τ_{in}	τ_{max}	v_{max}
356	—	—	—	1920	5300	0.04
360	1400	4200	0.09	480	1800	0.10
364	360	1200	0.24	210	675	0.23
366	180	660	0.39	120	420	0.30
370	85	140	1.30	—	—	—
373	40	45	3.02	—	—	—

Table 6

Isothermal decomposition characteristics of benzoyl peroxide dispersed in 2,2′-methylene-bis(4-methyl-6-*t*-butylphenol) in solid state

τ_{in}, τ_{max} and v_{max} are defined in text to Table 5

°K	338	340	343	346	348	352
			5% BP			
τ_{in} [s]	345	—	165	100	70	40
τ_{max} [s]	1050	—	570	330	210	90
v_{max}	0.16	—	0.34	0.60	0.80	1.68
			20% BP			
τ_{in} [s]	510	420	225	120	45	—
τ_{max} [s]	1200	930	510	300	130[a]	90
v_{max}	0.17	0.22	0.34	0.45	1.1	1.30
			50% BP			
τ_{in} [s]	330	240	—	120	105	--
τ_{max} [s]	960	645	—	225	165	75
v_{max}	0.15	0.22	—	0.48	0.60	1.06
			95% BP			
τ_{in} [s]	—	300	150	—	—	—
τ_{max} [s]	660	540[b]	285[c]	180	105	—
v_{max}	0.005	0.007	0.015	0.015	0.02	—

a) at 350°K; *b*) at 342°K; *c*) at 344°K.

Table 7

Isothermal decomposition characteristics of benzoyl peroxide dispersed in anthracene at temperatures under the melting point of peroxide

τ_{in}, τ_{max} and v_{max} are defined in text to Table 5

°K	359	362	364	366	368	373
			5% BP			
τ_{in} [s]	230	120	120	75	—	—
τ_{max} [s]	630	390	300	210	—	—
v_{max}	0.10	0.24	0.34	0.44	—	—
			20% BP			
τ_{in} [s]	510	315	225	105	60	—
τ_{max} [s]	1185	630	465	240	90	—
v_{max}	0.08	0.21	0.24	0.36	0.52	—
			50% BP			
τ_{in} [s]	450	360	210	240[a]	—	—
τ_{max} [s]	1290	720	375	390[a]	105[b]	45
v_{max}	0.12	0.19	0.30	0.30[a]	0.42[b]	0.74
			95% BP			
τ_{in} [s]	900	540	280[a]	—	150	75
τ_{max} [s]	2550	1290	615[a]	—	240	100
v_{max}	0.07	0.11	0.22[a]	—	0.44	0.76

a) at 365°K; *b*) at 370°K.

During the isothermal decomposition under the melting point of pure benzoyl peroxide or in a mixture with another substance (anthracene, 2,2′-methylene-bis(4-methyl-6-*t*-butylphenol)) the induction time of decomposition reaction as well as the maximum rate of reaction heat release have been followed at various temperatures (Table 5—7). From these results it can be stated that the autocatalytic character of decomposition remains in dilute media too and the induction time as well as reaction rates can be essentially affected by the presence of other substances.

Similarly to DEA results the decomposition reaction is considerably affected by the presence of 2,2′-methylene-bis(4-methyl-6-*t*-butylphenol) which shortens the induction time of autocatalysis at 350°K about 10^3 fold in comparison to the extrapolated time for pure benzoyl peroxide. In the same way, anthracene shortens the induction period of benzoyl peroxide decomposition at all concentrations. The effect of admixture grows relatively with decreasing temperature of decomposition reaction as well as with decreasing concentration of admixture towards a definite critical value.

It is worth noticing that the samples with low content of substituted bis-phenol (5%) show two induction times with two isolated autocatalytic exothermic reactions during isothermal decomposition. It must, however, be noted that the low temperature corresponds only to 5% of over-all reaction heat in case of the low concentration of bis-phenol. Provided the concentrations of substituted bis-phenol are higher, practically all benzoyl peroxide decomposes at temperatures over 340°K.

The maximum rate of decomposition reaction at temperatures under 366°K calculated for weight unit of benzoyl peroxide present in the sample depends relatively little on the amount of anthracene added. On the other hand, the addition of anthracene in the amount of 5% only results in a considerable decrease of maximum rate of decomposition at temperatures close to the melting point of benzoyl peroxide (370—373°K). 2,2′-Methylene-bis(4-methyl-6-*t*-butylphenol) affects the maximum rates of benzoyl peroxide decompositions even more than anthracene. Like in case of other characteristics, the presence of this substance results in a shift of maximum decomposition rates by about 20°K to lower temperatures in comparison to maximum decomposition rates of pure benzoyl peroxide. The maximum specific rate rises considerably with increasing addition of bis-phenol at a definite temperature.

The amount of peroxide decomposed at maximum decomposition rate is a further descriptive datum concerning the autocatalytic decomposition reaction of benzoyl peroxide under isothermal conditions. The proportion of peroxide decomposed at maximum reaction rate decreases approximately linear with increasing temperature of isothermal decomposition. The maximum decomposition rate of pure benzoyl peroxide is at 360°K considered that the half amount of peroxide is decomposed. In case the amount of peroxide decomposed is 5% the maximum rate is at 369°K. In the presence of 2,2′-methylene-bis(4-methyl-6-*t*-butylphenol) the first temperature shifts to 335—340°K and the second one to 355—360°K whereas in the presence of anthracene it is 354—358°K and 371—372°K, respectively. The temperature ranges are given for the investigated concentration range of admixtures.

Table 8

Values of apparent activation energies of induction process (E_1, E_2) and decomposition process (E_3) for various systems

E_1 and E_2 were determined from reciprocal values of induction time (τ_{in} and τ_{max}, respectively) while E_3 was computed on basis of temperature dependence of maximum reaction rates in Arrhenius coordinates

E	Pure BP	Admixture to BP and its weight %								
		anthracene				2246				
		5	50	80	95	5		50	80	95
						a	*b*			
E_1	80	43	51	60	50	—	69	30	45	95
E_2	96	42	64	66	64	43	69	42	45	52
E_3	72	50	31	50	52	39	53	32	35	39

BP — benzoyl peroxide; 2246 — 2,2′-methylene-bis(4-methyl-6-*t*-butylphenol).
a) temperature range 338—355°K; *b*) temperature range 356—373°K.

The effect of temperature on the isothermal benzoyl peroxide decomposition in solid state, expressed by apparent activation energy (Table 8) shows that the presence of other molecules reduces the activation energy of benzoyl peroxide decomposition in solid state both in the induction stage and in the stage of fast chain decomposition.

Discussion

The diffusion of reactants as well as of original molecule fragments is an integral part of many chemical reaction so that every interference with diffusion conditions influences the chemical process. In this point, the cage effect is well known which was found by comparing the analogous decomposition reactions (kinetic parameters, composition of reaction products) in gaseous and liquid phase. Besides the idea of hindered diffusion, the considerable influence of crystal medium on the course of thermal decomposition of benzoyl peroxide can be interpreted by the energy transfer and desactivation of excited benzoyl peroxide. That is to say, the partial melting of crystal regions and their recrystallization may compete with the accumulation of vibrational energy owing to fluctuation. Assuming the idea of energy transfer to be true it should be expected that the benzoyl peroxide decomposition might be not only slower but also faster in some media. Though the influence of structural parameters on the decomposition reaction is evident from the obtained results a deeper understanding of internal relations, however, claims a broader study of decomposition reactions in various, chemically and structuraly different media. It is rather possible that the different reactivity with respect to decomposition reaction need not be due only to a different energy transfer from the medium and its accumulation on the substance which decomposes but also to geometrical structural features of medium which play an important part in the formation and decomposition of transition complex. In the case of benzoyl peroxide decomposition a radical-induced decomposition is highly probable, *i.e.* free radicals generated during spontaneous benzoyl peroxide decomposition attack molecules of benzoyl peroxide. A similar acceleration of decomposition reaction by the effect of regular configuration of reactant molecules was observed also in the case of the radiolysis of crystal choline hydrochloride [3]. In many studies it was found that the decomposition of this substance in crystalline form has a chain mechanism with the radiation yield being 10^4 fold higher than in solution.

Regarding the bimolecular character of mentioned induced decomposition it may be assumed that the rise of activated complex is possible only for a certain position of molecules reacting in space what involves that two kinds of condensed phase media may be expected [4]:

a) Assuming that the life time of activated particle is much greater than the relaxation time of the existence of definite medium structure, the structure of condensed phase does not have an essential influence on the course of reaction. For this reason, a great deal of chemical reactions in low-molecular liquids follows the same kinetic laws as in gaseous phase.

b) In the opposite case involving mainly reactions in viscous systems, the course of reactions is affected not only by the chemical characteristics of reaction centres but also by physical pecularities of medium (space arrangement, intermolecular interactions, *etc.*).

In an ordered condensed phase, such a structural arrangement may be assumed that should be similar to the structure of activated complex and *vice versa*. The observed acceleration or retardation of bimolecular decomposition reactions in crystal phase can be interpreted in this way.

The induced decomposition of pure benzoyl peroxide is speeded in comparison with that in dilute solutions by a higher concentration of reacting peroxide without respect to structural parameters. On the basis of rate constants of spontaneous and induced decomposition measured in a number of solvents [5] at 353°K, it can be deduced respecting the changed concentrations that the induced decomposition in pure benzoyl peroxide may be about 10 fold greater than the spontaneous one. Since the activation energy of induced decomposition is obviously lower than that of spontaneous, the differences of reaction rates at higher temperature shall be less. It follows from this calculation that a considerable effect of structural factors on the decomposition reaction should be assumed in the event of induced benzoyl peroxide decomposition. The idea that a simple induced decomposition not affected by the physical structure of decomposing peroxide does not take place is supported by the fact that the decomposition rate is susceptible to temperature changes and that the reaction gets slower suddenly and assumes the characteristics of decomposition reaction in solution after a short period of fast reaction leading to failures in ordered structure (probably nematic or smectic). The important role of ordered domains in this decomposition reaction can be confirmed by the evident decrease of maximum rate of benzoyl peroxide decomposition in aluminium oxide due to increasing grinding time of peroxide crystals.

The influence of admixtures upon the course of benzoyl peroxide decomposition reaction investigated by DEA method may be meanwhile interpreted either on the basis of transfer and accumulation of active states and eventually their desactivation in crystal lattice or from point of view of various possibilities of transition complex formation. Because of the autocatalytic character of decomposition and its influencing by admixtures the second interpretation seems to be more suitable for clearing up the effect of heating rate on the decomposition reaction rate and other observed phenomena as well.

The significant effect of scan speed on the absolute value of maximum rate of benzoyl peroxide decomposition reaction as well as the observed approximately square root relationship thus show that the over-all decomposition reaction depends on the level of intermediary products (probably radicals) in system. At the same time it is evident that the autocatalytic character of isothermal decomposition cannot be interpreted only as an induced decomposition involving the benzoyl peroxide decomposition in solution. In this case an unbranched chain reaction takes place and for this reason the maximum reaction rate should be observed at the beginning of reaction and not after a certain, in some cases rather long time (until an hour). The concentration increase of radicals in system may be interpreted either as an energetic branching or as rate increase of spontaneous benzoyl peroxide decomposition in places where the defects of crystal lattice have been gradually formed owing to decomposition products. This second alternative should be preferred since the admixtures studied shorten the induction period of autocatalysis what could be interpreted by the rise of initiation rate owing to damage of benzoyl peroxide crystal lattice. This case is especially topical for anthracene as admixture. Besides the physical effect of benzoyl peroxide crystal structure damage, it is the bimolecular reaction under formation of phenoxy radical, benzoyloxy radical and benzoic acid which can play an important part in case of crystalline bis-phenol. A simple interpretation of autocatalysis by an unstationary state owing to low rate of termination reactions in crystal substances is not acceptable as the rate increase of reaction heat release could be maximum linear in this case.

It is allowed to interpret the autocatalysis in an isothermal decomposition from the point of view of induction period formal similarity as a slowed down thermal explosion. This interpretation is opposed to the fact that the portion of peroxide which decomposes after reaching the maximum decomposition rate increases with rising temperature. An even more consequential counter-reason is the circumstance that the specific rates of decomposition reaction in pure benzoyl peroxide and in a 5% mixture of benzoyl peroxide with aluminium oxide are approximately equal (under adequate conditions).

Likewise the differences in the amount of benzoyl peroxide decomposed in various systems before reaching the maximum decomposition rate found by DEA measurements are quite conceivable from the point of view of induced and spontaneous decomposition idea. While the decomposition reaction of benzoyl peroxide in liquid 2,6-di-*t*-butyl-4-methylphenol and other solvent is quite alike, the maximum rate is reached after about 2/3 of peroxide present have decomposed what expresses the compromise between the controlled temperature rise and at the same time decreasing peroxide concentration in system. In case of bis-phenol with a higher melting point the maximum reaction rate shifts to lower temperatures (in comparison to preceding 2,4,6-alkylphenol by 50°K) and the portion of peroxide decomposed at maximum decomposition rate falls to 15%. In consideration of the chemical similarity of both phenols studied, the interpretation of differences observed is to be found in the effect of crystal lattice on the induced benzoyl peroxide decomposition. By comparing with similar characteristics of crystal benzoyl peroxide decomposition, it becomes evident that this case involves a greater stability of peroxide against spontaneous decomposition and at the same time a higher rate of induced decomposition in contrast to reactions in the presence of bis-phenol. In its presence less reactive alkylphenoxy radicals are formed which may initiate the induced decomposition in a lower degree but take part in the termination reaction of induced chain decomposition to a greater extent. From this point of view the influence of anthracene is manifested by the derangement of regular space order suitable for the realization of induced chain decomposition or energetic branching of the chain reaction. In this way the kinetic length of induced benzoyl peroxide decomposition becomes shorter.

The portion of peroxide decomposed at maximum reaction rate decreases expressively with increasing temperature during the isothermal benzoyl peroxide decomposition. It may be due to both rate increase of spontaneous decomposition which implies a higher radical generation in volume unit and mobility degree change in ordered regions what involves the acceleration of induced decomposition.

The foregoing considerations can be faced with the analysis of exponential curves in their initial part which present the relationship between the rate of reaction heat release and time of the decomposition reaction at a definite temperature. Supposing the sufficient length of induced branched chain decomposition

$$\mathrm{R}\bullet + m\,\mathrm{BP} \rightarrow (1 + n)\,\mathrm{R}\bullet + (m - n)\,\mathrm{RX} + Q,$$

then the rate of reaction heat release Q measured is directly proportional to the rate of induced decomposition. The benzoyl peroxide decomposition rate can be expressed by the equation

$$\frac{-\mathrm{d}\,[\mathrm{BP}]}{\mathrm{d}t} = k_\mathrm{a}\frac{\mathrm{d}Q}{\mathrm{d}t} = k_\mathrm{b}\,[\mathrm{R}\bullet],$$

while the rate of radical generation in initial stage is given by expression

$$\frac{\mathrm{d}\,[\mathrm{R}\bullet]}{\mathrm{d}t} = v_\mathrm{s} + \varphi\,[\mathrm{R}\bullet]\,.$$

(v_s and φ being the spontaneous decomposition rate and coefficient of chain reaction branching, respectively.)

The change of radical concentration in system is to be determined from the tangent to instantaneous rates in exponential part (as far as the exponent is greater than 1) of the relationship between the rate of reaction heat release and reaction time. The plot of acceleration of reaction against the reaction rate shows linear character (*e.g.* Fig. 4) and the initiation reaction rate is very low for pure benzoyl peroxide while an obvious intensification of initiation reaction occurs in the presence of admixtures.

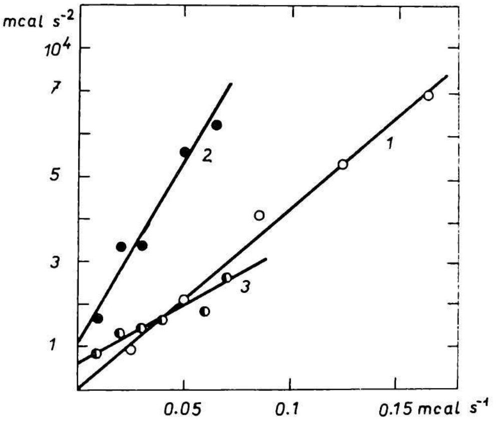
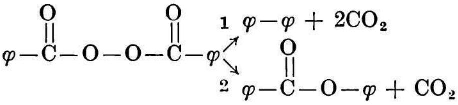


Fig. 4. Relationship between the acceleration of decomposition reaction and decomposition rate.
Pure benzoyl peroxide at 364°K (*1*); the mixture of benzoyl peroxide with 2,2'-methylene-bis(4-methyl-6-*t*-butylphenol) at 340°K (*2*); the mixture of benzoyl peroxide with anthracene at 359°K (*3*). The weight ratios of benzoyl peroxide and admixtures were 1 : 1.

The high apparent activation energy of crystal benzoyl peroxide decomposition in comparison with analogous reaction in solution seems to be conceivable as a superposition of temperature coefficient of structural transformation and dissociation energy of oxygen—oxygen bond or activation energy of induced decomposition.

It is perhaps worth trying to elucidate the differences in reaction heat under various conditions of decomposition reaction. On the basis of analysis of products obtained by pure benzoyl peroxide decomposition [6] this reaction can be expressed by two common equations in principle:



$$\varphi\text{—}\overset{\overset{\large O}{||}}{C}\text{—O—O—}\overset{\overset{\large O}{||}}{C}\text{—}\varphi \begin{cases} \xrightarrow{1} \varphi\text{—}\varphi + 2\mathrm{CO_2} \\ \xrightarrow{2} \varphi\text{—}\overset{\overset{\large O}{||}}{C}\text{—O—}\varphi + \mathrm{CO_2} \end{cases}$$

On the basis of standard bond energies it is possible to compute that 75 kcal mole^{-1} and 56 kcal mole^{-1} are released in the first and in the second reaction, respectively. Our data measured for pure benzoyl peroxide decomposition indicate a full decarboxylation of benzoyloxy radicals primarily formed. The reaction heats in the presence of alkylphenols and anthracene are difficult to evaluate because of side reactions. It may, however, be remarked that a quite great difference has been found in reaction heat for the use of investigated phenols though similar reactions can be assumed from the point of view of chemical reactivity of function groups. It seems probable that it is due mainly to the fact that the decomposition reaction takes place at a considerably lower temperature in case of alkyl bis-phenol what may suppress the fragmentation reaction of benzoyloxy radicals and thus reduce the over-all heat effect of reaction.

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