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THERMAL DECOMPOSITION OF p-METHYL-p′-NITROBENZOYL AND BIS-p-NITROBENZOYL PEROXIDES

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ABSTRACT

Differential enthalpic analysis was carried out below the melting point as well as at regular increases of temperature over the melting point of peroxides. From these measurements it follows that the thermal stabilities of peroxides in the solid state increase with their melting points. The rise in the melting point of the peroxide due to changed chemical structure is accompanied by a rise in the melting points of products which in turn affects the isothermal autocatalytic decomposition. The common feature of the thermal decomposition of the peroxides studied below their melting points is a very high apparent activation energy of the initiation of a chain decomposition reaction which is several times higher than that of a spontaneous thermal decomposition of peroxide in solution or in a melt of peroxide.

From the study of the decomposition of nitro derivatives of benzoyl peroxide in solution it is known[1] that the electron attracting nitro-substituents have a retarding effect on the spontaneous decomposition of peroxides. The introduction of nitro groups into benzoyl peroxide increases the induced decomposition which accompanies its thermal decomposition in solution[2]. However not only the substitution of nitro groups in the molecule but also the presence of nitro compounds accelerates the decomposition of benzoyl peroxide[3]. This indicates that the decomposition reaction may be influenced not only by an intramolecular rearrangement of electrons but also by an intermolecular interaction of nitro compounds with the peroxidic compounds or radicals generated by them. The substitution of methyl groups for hydrogen in aromatic rings does not produce any marked changes in the decomposition reactions of benzoyl peroxide[2].

Among other changes produced by substitution, the physical changes—in particular, the changes in the melting points of investigated substances—are of importance to our study of the thermal decomposition of nitro derivatives of benzoyl peroxide. These data are interesting mainly because the decomposition of peroxides is influenced by the state of aggregation of the decomposing substances.

EXPERIMENTAL

The measurements were carried out with a differential calorimeter (Perkin–Elmer DCS-1B). During measurement nitrogen flowed through the gauging head of instrument (ca. 30 ml per minute). For the measurement 2 mg of sample were weighed and closed in gas-tight aluminium dishes. Some measurements were repeated three times but no important change in the shape of thermograms was observed.

Benzoyl peroxide was purified by precipitation with methanol from a saturated chloroform solution.

p-Methyl-p'-nitrobenzoyl peroxide was prepared according to the following procedure[4]: Into a solution of 5 g of di-p-tolyl peroxide in 55 ml of dry toluene a solution of 0.5 g of Na in 18 ml of dry methanol was dropped while the temperature was held at −5°C. Using an ice/water mixture sodium p-methyl perbenzoate was extracted from the reaction mixture. A solution of 3.4 g of freshly distilled p-nitrobenzoyl chloride in 20 ml of toluene was dropped into this aqueous solution. Then the crystals of mixed peroxide separated. Another portion of the crystals of peroxide was obtained after adding methanol into a toluene layer.

Thus 2.6 g of peroxide were obtained after repeated precipitation with methanol from a chloroform solution; the melting point of peroxide was 134°C. Analysis revealed:

calculated	59.80% C, 3.68% H, 4.65% N
found	59.62% C, 3.92% H, 4.76% N

p-Nitrobenzoyl peroxide was prepared from p-nitrobenzoyl chloride and sodium peroxide[5].

RESULTS

Isothermal decomposition below the melting point of peroxides

The heating of the peroxides under investigation up to melting point results in their rapid exothermal decomposition. However decomposition occurs even below the melting point and is obviously of autocatalytic character (Figs. 1 and 2). On the basis of isothermal reaction it is possible to determine the induction periods of thermal decomposition (τ_i) as well as the data characterizing the period of time before the attainment of the maximum rate of decomposition (τ_{max}) and the maximum rate of decomposition (v_{max}). See Table 1. The data given in this table characterize the rate of decomposition and the Arrhenius coordinates yield linear relationships from which the corresponding apparent energies of activation have been estimated (Table 2). The initation of decomposition reaction is very sensitive to a change of temperature which manifests itself by a rapid decrease in the induction periods of autocatalytic reaction with increasing temperature and by high apparent activation energies when compared with the relations in solution. For the decomposition of benzoyl peroxide and its derivatives in solution the energy of activation of the monomolecular (spontaneous) decomposition reaction is 30 kcal mol^{-1}, which is about a third or even a fourth of the value which should be assigned to the decomposition of crystalline peroxide. The activation energy of the processes which take place in the presence of the decomposition products of peroxides and, as a matter of fact, in their melt is considerably lower (Table 2).

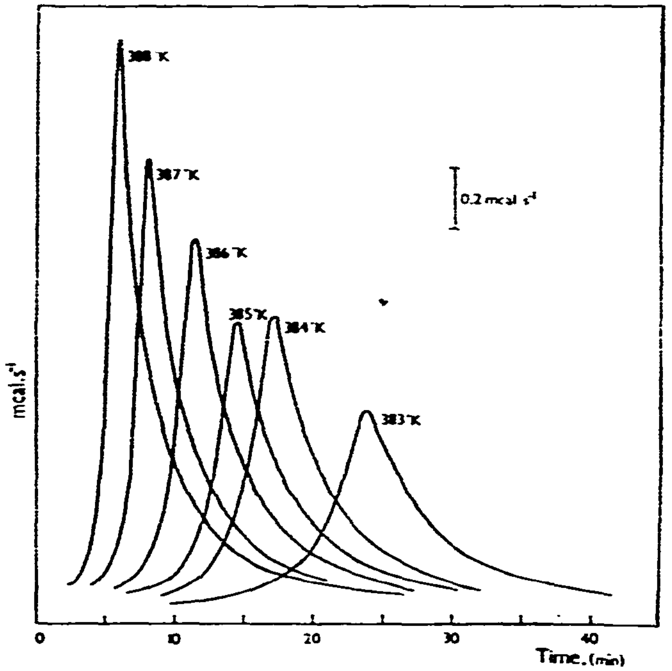

Fig. 1. Isothermal decomposition of p-methyl-p′-nitrobenzoyl peroxide below its melting point. The rate of the liberation of reaction heat as a function of temperature.

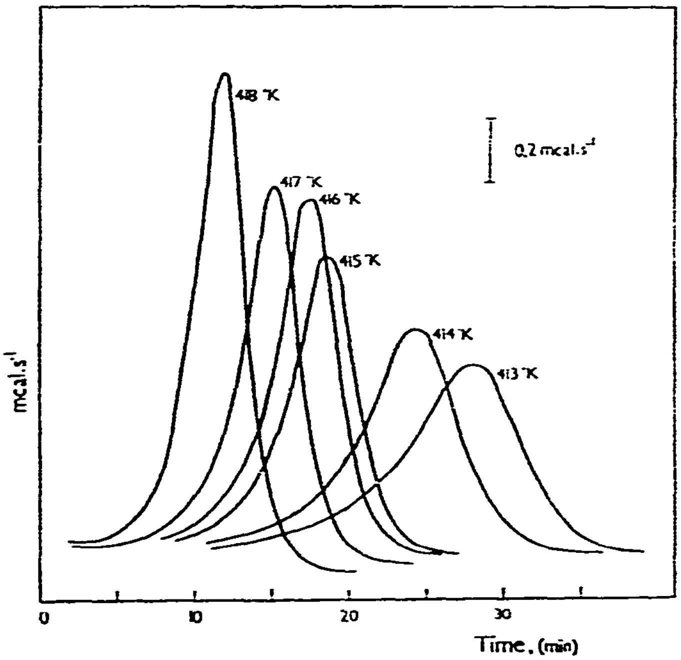

Fig. 2. Isothermal decomposition of bis-p-nitrobenzoyl peroxide below its melting point. The rate of the liberation of reaction heat as a function of temperature.

TABLE 1

THERMAL DECOMPOSITION OF BENZOYL PEROXIDE AND SOME OF ITS DERIVATIVES AT DIFFERENT TEMPERATURES

τ_i, induction period; τ_{max}, time before the attainment of maximum rate of decomposition; r_{max}, maximum rate of decomposition; %, amount of peroxide decomposed before the attainment of maximum rate of decomposition. r_{max} was calculated for initial amount of 1 mg peroxide. Corrected value r_{max} was obtained by calculation taking into account non-decomposed peroxide at the attainment of maximum rate.

Temperature (°*K*)	τ_i (*s*)	τ_{max} (*s*)	r_{max} (*mcal* s^{-1} mg^{-1})	%	r_{max} (*mcal* s^{-1} mg^{-1})
p-Methyl-p′-nitrobenzoyl peroxide					
383	505	1360	0.33	36	0.52
384	415	945	0.49	30	0.71
385	320	820	0.48	32	0.71
386	240	630	0.61	27	0.83
387	150	400	0.74	17	0.89
388	105	300	0.93	20	1.16
Bis-p-benzoyl peroxide					
413	640	1615	0.29	57	0.67
414	570	1405	0.34	59	0.82
415	315	1060	0.46	62	1.23
416	230	980	0.55	55	1.23
417	205	865	0.57	59	1.40
418	120	675	0.75	59	1.84
Benzoyl peroxide					
363	1570	4300	0.11	43	0.19
364	898	2930	0.17	40	0.28
365	645	2610	0.17	39	0.28
366	283	1300	0.27	30	0.39

TABLE 2

ACTIVATION ENERGIES OF THE DECOMPOSITION OF BENZOYL PEROXIDE, BIS-p-NITROBENZOYL PEROXIDE, AND p-MEHTYL-p′-NITROBENZOYL PEROXIDE IN THE ABSENCE OF SOLVENTS FOR DIFFERENT DEGREES OF DECOMPOSITION

Peroxide	*Temperature interval* (*K*)	*E* (*kcal/mol*)			
		τ_i	τ_{max}	v_{max}	v_{max}
Benzoyl peroxide	363–375	130	100	72	45
p-CH_3 p′-NO_2	383–388	96	85	57	44
p-NO_2 p′-NO_2	413–418	111	62	64	62

The shapes of the thermochemical isotherms of both peroxides (Figs. 1 and 2) seem to be similar. But some differences may be observed from a more detailed analysis. There are different amounts of peroxide decomposed before the maximum rate of decomposition has been attained, as well as the fact that this amount does not depend on temperature in the case of dinitro derivative whereas it decreases with increasing temperature in the case of p-methyl-p′-nitro-derivative (Table 1). A qualitatively similar but quantitatively more marked decrease in the amount of peroxide decomposed before the attainment of the maximum rate of decomposition was observed with benzoyl peroxide itself[6].

The shape of kinetic thermochemical isotherms as well as the amount of the peroxide decomposed indicates the autocatalytic character of the decomposition reaction starting from the idea that the acceleration of reaction is due to a partial melting or solvation of peroxide in decomposition products. The decrease in decomposing substance may in this case[7] be expressed by the expression

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_x x + k_y xy \tag{1}$$

where x is the concentration of decomposing substance and y the concentration of arising substance which effects the liquefaction of substance x. The solution of eqn (1) on condition that $y = x_0 - x$ yields the expression

$$\ln\left(\frac{1}{x} - 1\right) = (k_x + k_y)\, t + \mathrm{const} \tag{2}$$

Regarding the reaction heats (a) measured at different time intervals and the overall reaction heat (A) expression (2) may be expressed

$$\log \frac{a}{A-a} = kt + \mathrm{const.} \tag{3}$$

The representation of the measured kinetic thermochemical isotherms in a system of coordinates according to eqn (3) (Fig. 3) shows very clearly the differences in the course of the decomposition reaction of individual peroxides. At the same time it is obvious from this figure that the whole course of decomposition reaction of the three peroxides studied cannot be described by similar concepts of gradual liquefaction of the reacting system. The courses do not differ only in the rate constants of decomposition at equal temperature but also in a qualitative way. The relative rates of the decomposition of benzoyl peroxide and methylnitro derivative decrease at a certain conversion while it increases in the case of dinitro derivative (Fig. 3, Table 3). In addition to the rate constants k_1 (before maximum rate) and k_2 (after maximum rate) evaluated from relation (3), the constants of the decomposition of peroxides were also calculated from the following expression

$$\log \frac{A}{A-a} = k_3 t. \tag{4}$$

The data obtained by isothermal measurements comply very well with this relation, of course, merely in the case of higher degrees of the decomposition of peroxides (from 40 to 99%).

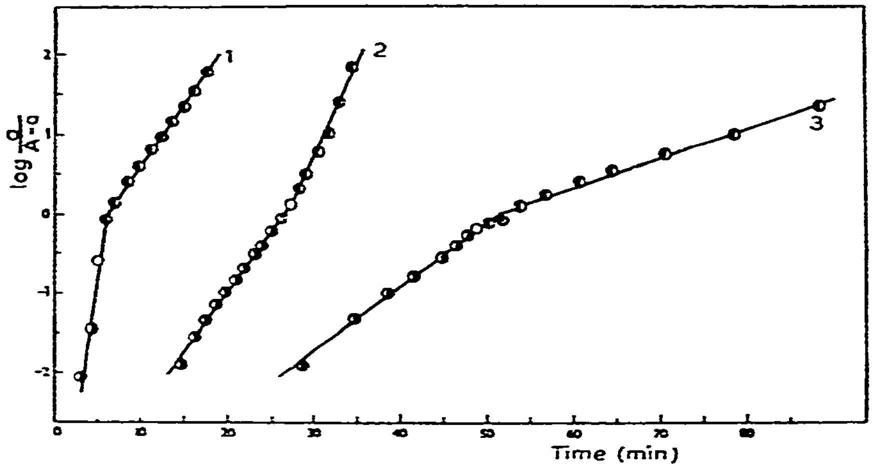

Fig. 3. Log $a/(A-a)$ as a function of time [expression (3)] for isothermal decomposition of :1, p-methyl-p′-nitrobenzoyl peroxide at 388 K; 2, bis-p-nitrobenzoyl peroxide at 413 K; 3, benzoyl peroxide at 365 K. ◑, values before the maximum of isothermal DEA curve; ○, values in the maximum of isothermal DEA curve; ◐, values behind the maximum of isothermal DEA curve.

The reaction heat released at the isothermal decomposition of benzoyl peroxide and investigated nitro derivatives below the melting point of these substances lies in the interval from 49 to 57 kcal mol^{-1}. Similar values are also obtained by differential enthalpic analysis.

Decomposition of peroxides at a programmed temperature increase

The effect of the structure of benzoyl peroxide derivatives on the course of their thermal decomposition is illustrated by the curves of differential enthalpic analysis (DEA) (Fig. 4). Though the above peroxides decompose in solution at equal temperature with comparable rate (Fig. 5), the temperatures of initiation differ in the absence of solvent in the extreme case even by 70 °C. This difference corresponds to a 400-fold retardation of the decomposition reaction of this type at equal temperature.

From the DEA curves of the decomposition of benzoyl peroxide derivatives we calculated the rate constants for the decomposition in the melt (or solution) of peroxide according to the following relationship[8]

$$k = \frac{\mathrm{d}H/\mathrm{d}t}{(A-a)} \tag{5}$$

where A is the overall reaction heat of decomposition reaction (total area under the DEA curve), a denotes the reaction heat liberated at a certain degree of advancement of reaction (at a certain temperature) and $\mathrm{d}H/\mathrm{d}t$ is the rate of the liberation of heat at a certain temperature.

TABLE 3

RATE CONSTANTS OF THE ISOTHERMAL DECOMPOSITION OF BENZOYL PEROXIDE (BP) AND ITS DERIVATIVES EVALUATED ACCORDING TO EXPRESSION (3) (Fig. 3) FOR INITIAL AUTOCATALYTIC STAGE OF REACTION (k_1) AND FOR THE STAGE AFTER ATTAINMENT OF MAXIMUM RATE OF DECOMPOSITION (k_2)

Rate constants k_3 were calculated from expression (4).

Peroxide	*Temperature* (°*K*)	$10^3 \times k_1$ (s^{-1})	$10^3 \times k_2$ (s^{-1})	$10^3 \times k_3$ (s^{-1})
BP	363	1.04	0.50	1.08
	364	1.52	0.57	1.11
	365	1.71	0.57	1.01
	366	2.84	0.71	1.50
	368[a]	2.40	0.96	1.94
	372[a]	6.68	3.15	5.10
	375[a]	6.60	3.75	7.24
E (kcal/mol)		45	45	45
p-NO_2-p′-CH_3 BP	383	3.95	2.04	1.55
	384	4.45	2.11	1.71
	385	5.37	2.10	1.56
	386	5.92	2.21	1.82
	387	9.34	2.53	2.05
	388	12.50	2.56	2.08
E (kcal/mol)		68	16	20
p-NO_2-p′-NO_2 BP	413	2.47	3.25	4.08
	414	3.19	4.38	4.44
	415	3.65	5.56	6.02
	416	3.78	5.96	5.43
	417	4.40	7.41	7.44
	418	5.25	7.57	6.57
E (kcal/mol)		49	53	43

[a] Isothermal measurements were carried out with 1 mg of benzoyl peroxide and 2 mg of other peroxides.

The relationships between the rate constants of the decomposition of peroxides in the melt of themselves or in the melt of decomposition products and the reciprocal value of absolute temperature give relatively low values of activation energies (18–20 kcal mol^{-1}) for benzoyl peroxide and p-methyl-p′-nitrobenzoyl peroxide. In both cases the values of frequency factors ($\sim 10^7$ s^{-1}) are also not conform with the values (10^{13}–10^{15} s^{-1}) which are usually observed in the case of peroxide decomposition in dilute solutions of common low-molecular solvents. The low values of activation energy, as well as the low value of the frequency factor, must be due to the simultaneous occurrence of the decomposition induced by radicals and the spontaneous decomposition of peroxide. Furthermore, the Arrhenius plot (Fig. 6) is similar in the case of benzoyl peroxide and its methyl-nitro derivative while it shows a deviation in the case of the dinitro derivative which resembles the results obtained with isothermal decomposition below the melting points of peroxides.

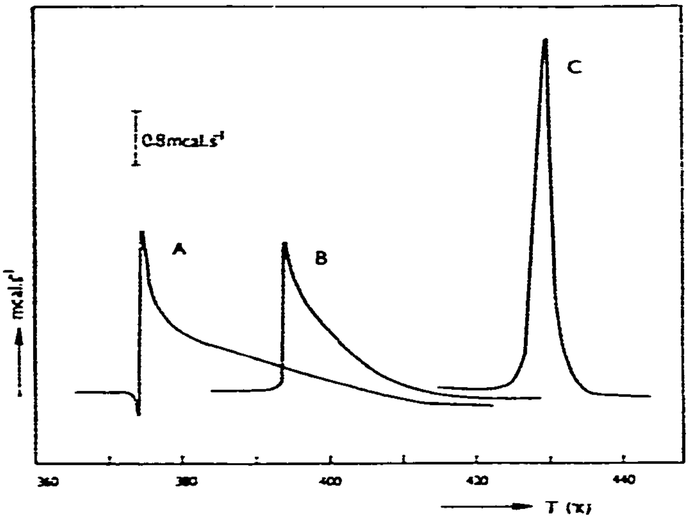

Fig. 4. Differential enthalpic analysis curves at a programmed temperature rise 4°/min for: A, benzoyl peroxide; B, p-methyl-p′-nitrobenzoyl peroxide; C, bis-p-nitrobenzoyl peroxide.

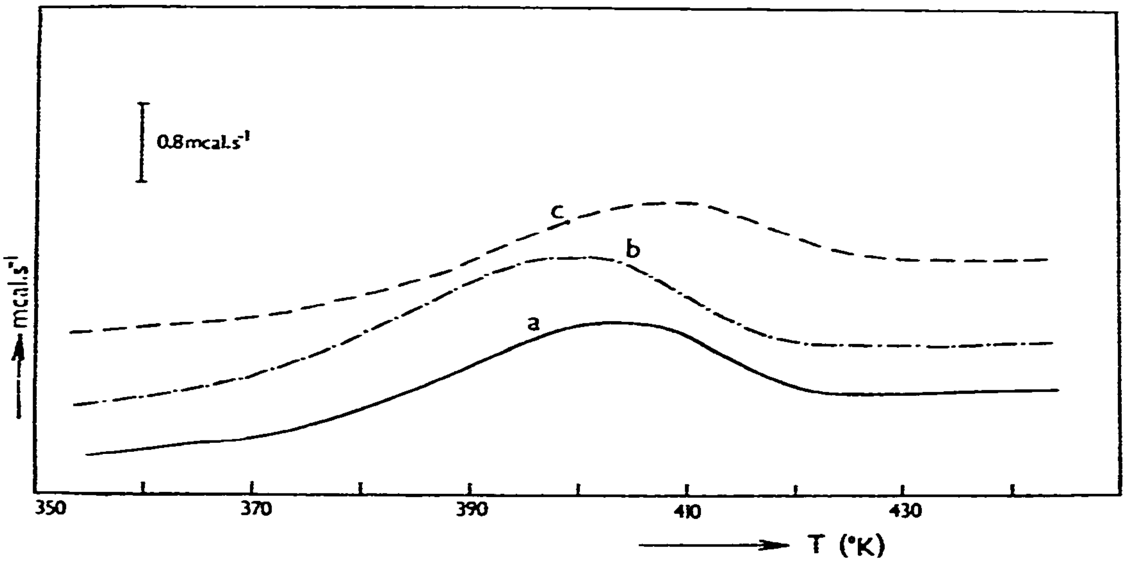

Fig. 5. Differential enthalpic analysis curves at a programmed temperature rise 8°/min for the solutions (20 weight %) in phenyl benzoate of: a, benzoyl peroxide (weight of sample = 4.6 mg); b, p-methyl-p′-nitrobenzoyl peroxide (weight of sample = 4.8 mg); c, bis-p-nitrobenzoyl peroxide (weight of sample = 4.8 mg).

From the character of the DEA curve obtained for benzoyl peroxide decomposition it is obvious that the decomposition proceeds in two stages. The first stage corresponds to the decomposition in the regions of melt which are still arranged and occurs in the proximity of the melting point of benzoyl peroxide. With a further increase in temperature (and degree of decomposition) the decrease in the rate of decomposition reaction is greater than is to be expected from the amount of benzoyl

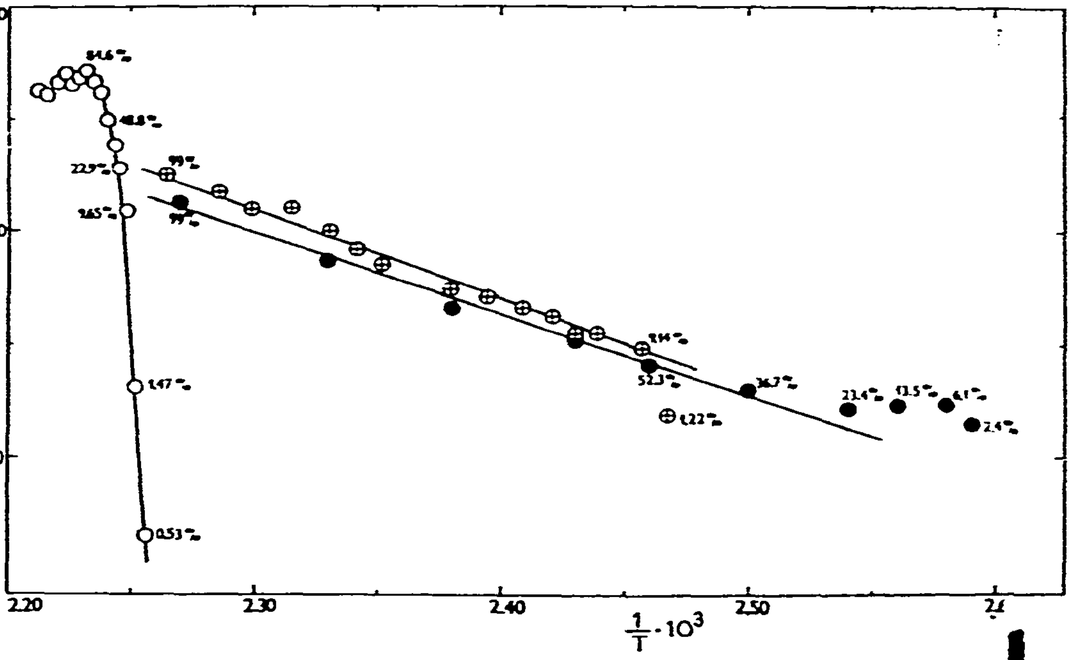

Fig. 6. Logarithm of the rate constants of decomposition as a function of reciprocal temperature for: ●, benzoyl peroxide; ⊖, p-methyl-p′-nitrobenzoyl peroxide; ○, bis-p-nitrobenzoyl peroxide.

peroxide decomposed. Besides it seems that the contribution of induced decomposition which decreases with increasing conversion is superimposed on the above course. The shape of the DEA curve obtained for the decomposition of p-methyl-p′-nitrodibenzoyl peroxide is similar to that obtained for benzoyl peroxide, but the first part corresponding to a rapid decomposition in the proximity of the melting point of peroxide is not so distinct. A quite different character of the DEA curve appears in the case of the dinitro derivative. The curve is narrower and more symmetric. These differences manifest themselves in the relationships between rate constants and reciprocal temperature, too. In the case of the dinitro derivative the change of rate constant with temperature is so large that it should rather be ascribed to the changes in the physical state of reaction system than to the changes in the proportion of reactive molecules caused by the change of temperature. These anomalous differences disappear if the corresponding reactions take place in the presence of solvent (Figs. 5 and 7). In this case the activation energy of decomposition is 30 kcal mol^{-1} and the frequency factors vary over the range between 2×10^{14} and $6\times10^{14}\ \text{s}^{-1}$.

DISCUSSION

The general appreciation of rate constants of the decomposition of benzoyl peroxide, p-methyl-p′-nitrobenzoyl peroxide, and bis-p-nitrobenzoyl peroxide under different conditions (Fig. 8) indicates that the decomposition is inhibited where the decomposing substance is in the crystalline state. However even under these condi-

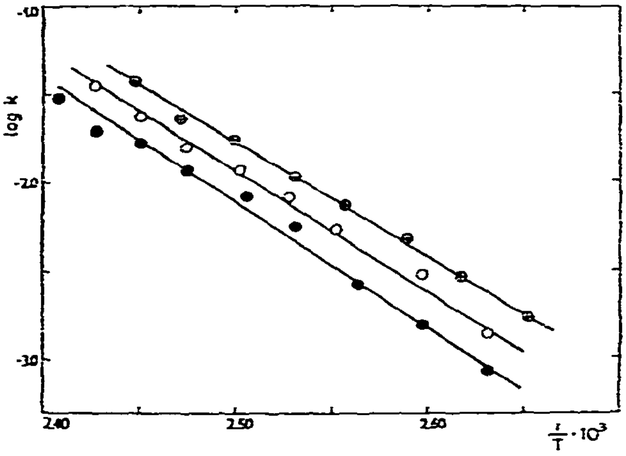

Fig. 7. Logarithm of the rate constants of decomposition as a function of reciprocal temperature for the solutions (20 weight %) in phenyl benzoate of: ○, benzoyl peroxide; ●, bis-p-nitrobenzoyl peroxide; ⊖, p-methyl-p′-nitrobenzoyl peroxide.

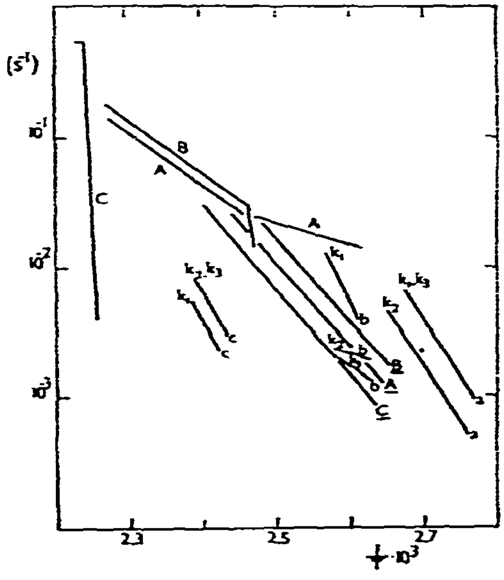

Fig. 8. Rate constants (s^{-1}) of the decomposition under isothermal conditions (small letters) and at a programmed temperature rise (capital letters) as a function of reciprocal temperature for: A, a benzoyl peroxide; B, b, p-methyl-p′-nitrobenzoyl peroxide; C, c bis-p-nitrobenzoyl peroxide. Underlined capital letters correspond to the decomposition of peroxides dissolved (20 weight %) in phenyl benzoate at a programmed temperature rise. Besides, the symbols k_1, k_2, and k_3 according to the legend of Table 3 are used for isothermal decomposition.

tions a slow autocatalytic process with a relatively very high activation energy occurs (a threefold and even fourfold dissociation energy of the weakest bond in peroxide molecule: oxygen–oxygen). The high activation energy of the initiation of decomposition process may be explained by the mechanism of the formation of reaction centres[9]. A last decomposition in reaction centre begins at that time when on the same place several molecules of peroxide have decayed spontaneously. Thus the number of active reaction centres containing "x" decomposed molecules is proportional to the x-th power of the rate constant of peroxide decomposition in crystalline phase (probable in primary defects of crystal lattice). Then the activation energy of the formation of reaction centres is an x-fold dissociation energy of unstable chemical bond, *i.e.* it is practically equal to an x-fold activation energy of the decay of peroxide in solution.

The autocatalytic decomposition of solid organic substances is usually explained by a gradual liquefaction of reaction system and a greater rate of decomposition in liquid than in solid phase[10]. If benzoyl peroxide decays in the absence of solvents, mainly diphenyl, carbon dioxide, and small amounts of phenyl benzoate and benzene are formed[11]. Assuming the reaction is analoguous in the case of the studied derivatives of benzoyl peroxide as well it may be expected that mainly p,p'-dinitrophenyl (m.p. 513 °K) and p-methyl-p'-nitrodiphenyl (m.p. 377 °K) will appear among reaction products. While diphenyl (m.p. 343 °K) as well as p-methyl-p'-nitrodiphenyl liquefy the reaction medium in the temperature region of decomposition reaction, it might not be quite unambiguous in the case of dinitro derivative. The melting point of the major reaction product is by about 100° higher than the temperature of peroxide decomposition. Though the effect of dinitrodiphenyl on the melting point of corresponding peroxide is not known it seems probable that the differences in the properties of the investigated derivatives are due not only to different melting points of decomposing peroxides but also to different physical properties of the products arisen in decomposition reaction.

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