Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THERMAL DECOMPOSITION OF SOLID BENZOYL PEROXIDE IN THE PRESENCE OF SOLID ADMIXTURES

PART I. OBSERVATIONS MADE UNDER CONSTANT HEATING CONDITIONS

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(Received October 9th, 1970)

ABSTRACT

The effect of some solid admixtures on the decomposition of benzoyl peroxide in the solid state has been observed by means of differential enthalpic analysis. Admixtures which either might well participate in the radical chain process or only dilute the given reaction system have been chosen. These have been various kinds of carbon black differing from each other by free-spin concentration, chain structure and surface area, further activated charcoal and colloid silica, respectively.

INTRODUCTION

Thermal decomposition of crystalline structures of organic compounds is a complex process consisting of both the physical and chemical transformations which give rise to various solid, liquid and gaseous end products. Considerably little work has been done in this research field when compared with the study of the decomposition reactions of organic compounds in both the liquid and gaseous phases. Not until lately, with the development of high-quality measuring instruments, has the investigation of solid-state decomposition been effected. It should be noted, however, that there have been relatively more papers concerned with the decomposition of inorganic than organic compounds[1-4]. The decomposition of benzoyl peroxide in the solid state has been paid relatively little attention, although it is of major industrial importance as initiator in polymerization processes. Recently, we pointed out the possibility of studying the decomposition of solid benzoyl peroxide (Bz_2O_2) in both the absence and presence of some solid admixtures by differential enthalpic analysis (DEA)[5-7]. The present paper is a continuation of the preceding ones showing the way in which both the chemical and physical properties of the solid admixtures used might affect the decomposition of benzoyl peroxide in the solid state.

EXPERIMENTAL

Materials and method

Benzoyl peroxide was precipitated from a saturated chloroform solution by methanol. After drying, it was kept in a refrigerator at −5 °C.

Table I summarises the data concerning the series of various carbon blacks used in the present investigation (particle size, BET surface area, oil absorption and pH, respectively).

TABLE I

CHARACTERISTICS OF CARBON BLACKS USED

Type of carbon black	*Particle size (nm)*	*BET surface area (m^2/g)*	*Oil absorption (ml/100g)*	*pH*
P-1250	40–55	40–65	160–180	
MT United Carbon	470	6	35	8.5
Monarch Black	14	320	150	6.4
HAF United	31	80	150	9.2
Vulcan XC-72	12	249	145	8.5
SRF United Carbon	75	22	67	9.9
Continex ISAF	31	102–129	143	9.1
United EPC	30	116	112	4.9
65-SPF United Carbon	31	80	184	8.3
FEF Continex	80	39–43	139	9.3

Decolourizing activated "Carboraffin" charcoal was supplied by Lachema Brno(CSSR). "Aerosil Degussa" colloid silica was supplied by Degussa Co., particle size 10–20 nm, surface area determined by BET method as 175–200 m^2/g.

The carbon blacks, activated charcoal and silica used were dried for 1 h at 200 °C prior to measurements.

For measuring, a Perkin–Elmer differential scanning calorimeter Model DSC-1B was used. Since the decomposition was observed over the temperature range of 330–450 °K, the instrument was calibrated by the benzil melting point (368 °K). Covered aluminium sample pans were used. The samples were prepared in a vibration homogenizer in which mixing lasted as long as 45 sec. For measurement purposes 1–5-mg samples of mixtures were used, this weight range chosen to keep the benzoyl peroxide content therein at 1 mg. All of the measurements were carried out under a nitrogen atmosphere at a heating rate of $32\,°K \cdot min^{-1}$.

Concentration of free spins in both the carbon blacks and activated charcoal was determined by means of electron spin resonance employing simplified calculation according to the relation[8]:

$$N_x = N_n \frac{(I'_o H^2_{max})_x}{(I'_o H^2_{max})_n} \quad (1)$$

where N_x is the number of free spins in the sample, N_n the number of free spins in the standard, H_{max} the width of the derivation curve and I'_0 the height of the derivation curve, respectively.

RESULTS AND DISCUSSION

Carbon blacks and activated charcoal

The course of Bz_2O_2 decomposition in the presence of various carbon blacks and activated charcoal has been studied in relation to both surface area and free-spin concentration. The mixtures observed contained 50% (w/w) benzoyl peroxide. From DSC curves obtained the following values were evaluated: melting temperature (T_m), temperature of maximum decomposition rate right behind the melting point (T_c), temperature of maximum decomposition rate in the melt (T_{max}), overall decomposition heat (Q), and maximum decomposition rates (V_{max} and V_c) at appropriate temperatures T_{max} and T_c, respectively. The results are summarised in Table II. The course of DSC curves of some mixtures is shown in Fig. 1.

The individual sorts of admixtures (Table II, Fig. 1) affect the decomposition of the solid peroxide by suppressing both the maximum rate of the rapid chain reaction, V_c, and maximum decomposition rate, V_{max}, in the melt. Changes in the overall

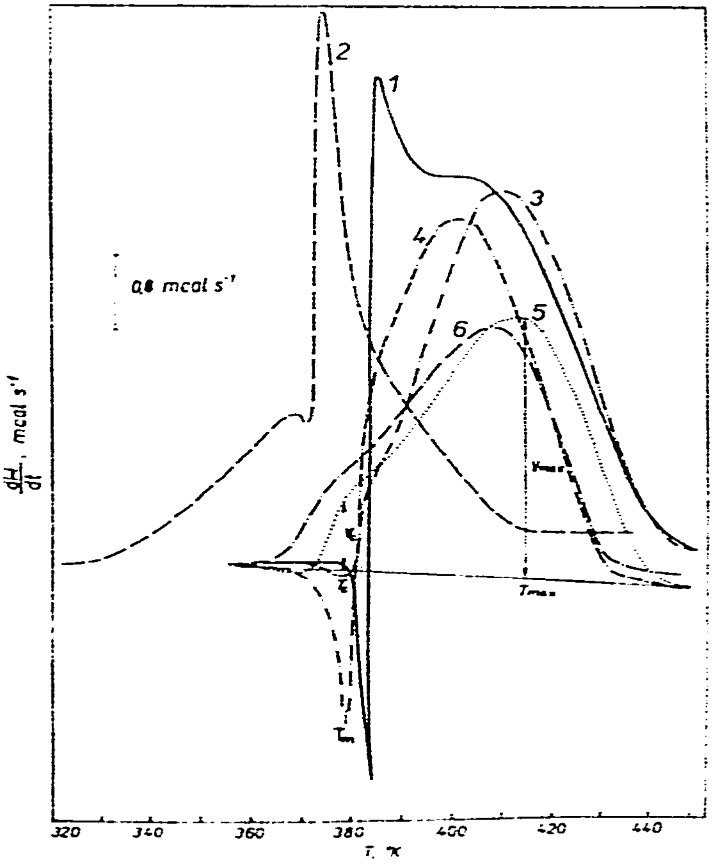

Fig. 1. DSC curves of pure Bz_2O_2 (1), 1.02 mg; and 50% (w/w) mixtures of this with activated charcoal "Carboraffin" (2); United Carbon MT black (3); P-1250 black (4); United EPC black (5); Monarch Black (6). Mixture weight 2 mg.

TABLE II

FREE-SPIN CONCENTRATIONS OF ADMIXTURES AND THERMOCHEMICAL DATA OF Bz_2O_2 DECOMPOSITION IN THEIR PRESENCE

50% (w/w) mixtures of Bz_2O_2 with	*Surface area (m^2/g)*	*Free-spin concentration per 1 g of admixture*	T_m (°K)	T_c (°K)	T_{max} (°K)	V_c (*mcal/sec*)	V_{max} (*mcal/sec*)	*Q* (*kcal/mole*)	*Oil absorption* (*ml/100g*)
Pure Bz_2O_2			384	388	408	5.2	4.1	76	
P-1250	40-65	4.6×10^{19}	379	385	403	2.0	4.0	52	160-180
MT-United Carbon	6	1.1×10^{18}	379	385	402	1.0	3.8	60	35
Monarch Black	320	6.4×10^{16}		378	408	1.0	2.6	42	150
HAF United	80	[a]	373	382	405	1.2	3.7	52	150
Vulcan XC-72	249	[a]	374	381	410	0.9	2.8	42	145
SRF United Carbon	22	2.2×10^{18}	382	388	407	3.1	3.3	59	67
Continex ISAF	102-129	[a]	374	381	407	1.1	3.2	49	143
United EPC	116	1.6×10^{19}	372	381	413	0.9	2.9	48	112
65-SPF United Carbon	80	[a]	378	383	404	1.7	3.8	57	184
FEF Continex	39-43	[a]	380	385	401	2.7	4.2	66	139
Act. charcoal "Carboraffin"		1.0×10^{19}	372	376		5.5		44	

[a] No reproducible signal (free-spin concentration less than 6.4×10^{16}).

heat of decomposition and melting temperature also take place. The dependence of the overall decomposition heat on the surface area of carbon black is a linear one (Fig. 2). Even despite the scattering observed, which might well result from the structural distribution of carbon black, the decreasing of the overall decomposition heat,

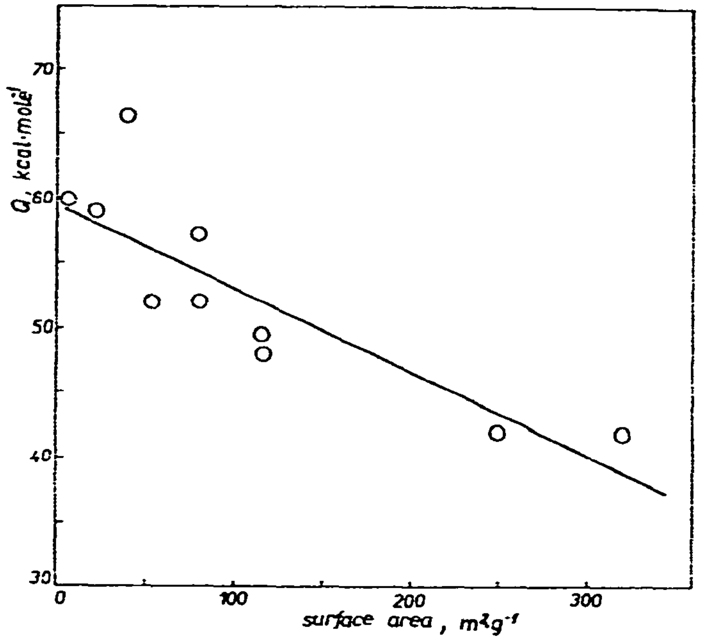

Fig. 2. Plot of overall decomposition heat of Bz_2O_2 in mixtures with the carbon blacks used *vs.* their surface area; 50% (w/w) Bz_2O_2, 2 mg.

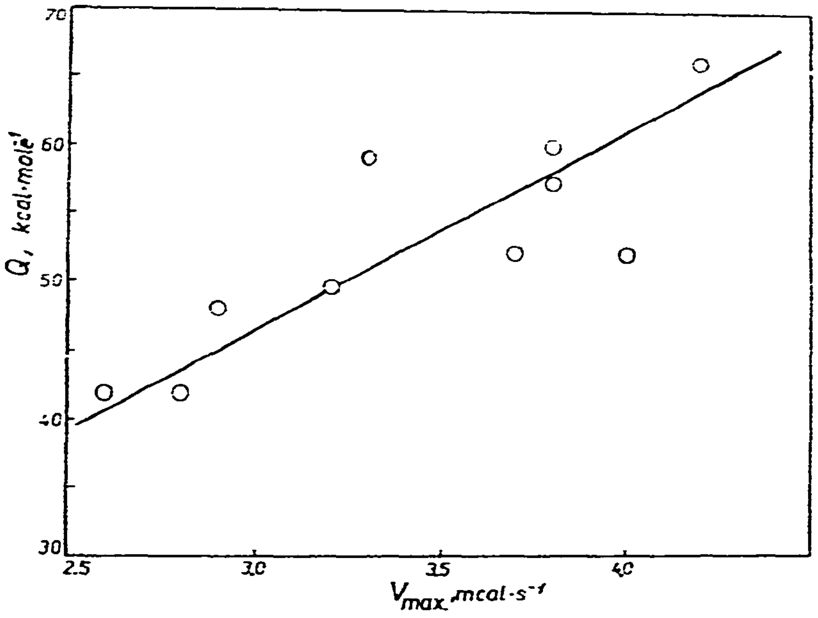

Fig. 3. Plot of overall decomposition heat of Bz_2O_2 in mixtures with the carbon blacks used *vs.* V_{max}; 50% (w/w) Bz_2O_2, 2 mg.

Q, with increasing carbon black surface may be assumed. We assume that this decrease is due to the elimination of hydrogen atoms from the carbon black surface by benzoyloxy and phenyl radicals of the decomposing Bz_2O_2. The Bz_2O_2 molecule decomposition along with hydrogen separation represents a release of about 8–10 kcal·mole^{-1} (calculated from the energies of both the forming and decaying bonds), which results in the decreasing of the overall decomposition heat, going on the presumption that the increase of chemisorbed hydrogen concentration on the carbon black surface is directly proportional to that of the surface area.

Along with the decrease in overall decomposition heat, a reduction in the maximum decomposition rate in the melt (V_{max}) is also observed (Fig. 3).

As may be seen from Table II, the effect of free-spin concentration may not be correlated. For example, the value of overall decomposition heat of Bz_2O_2 in the mixture with P-1250 carbon black exhibiting maximum free-spin concentration (4.6×10^{19} g^{-1}) almost equals that of HAF United carbon black, where free-spin concentration does not reach the 6.4×10^{16} g^{-1} limit. Likewise, *e.g.* the value of overall Bz_2O_2 decomposition heat in mixture with MT United (Carbon) carbon black exhibiting a lower free-spin concentration appears to be higher. On the other hand, in the mixture with Monarch Black carbon black exhibiting a still lower free-spin concentration than in the case of MT United Carbon, the value of the overall decomposition heat is lower than in the mixture with P-1250 carbon black.

The effect of the chain structure of carbon black on the value of the overall reaction heat, which evokes the scattering referred to in both Figs. 2 and 3, may well be expressed in the dependence of the values of oil absorption, which is the quantitative measure of chain structure[9], in particles with approximately equal surface area. When comparing the Q values of Bz_2O_2 in mixture with both the United EPC and 65-SPF United (Carbon) carbon blacks which, at considerable oil-absorption differences do not greatly differ from each other as to the value of surface area, we may see that carbon black with a higher structure produces an increase in the value of overall reaction heat. This is presumed to be due to the suppression of hydrogen elimination from the carbon black surface as a result of spherical interferences in chain structures.

As may be seen from Table II, the free-spin concentration does not affect the T_m and T_c values. Here, an influence of the value of the carbon black surface area may be observed in the sense that the larger the surface area, the lower are T_m and T_c. Thus, the commencement of Bz_2O_2 decomposition occurs at lower temperatures. This effect becomes more strikingly manifest at higher carbon black concentrations, as may well be seen in Figs. 4 and 5. Carbon black with a larger surface area in mixture with 20% (w/w) Bz_2O_2 shifts its decomposition toward considerably lower temperatures, the latter proceeding below the melting point already. The catalytic effect of greater surface area is assumed to result from sorption forces, the extent of which increases with increasing carbon black surface area. The observed decrease in overall decomposition heat in relation to an increase in carbon black concentration may again be elucidated by the elimination of hydrogen from the carbon black surface.

As may well be seen from Table II, the individual carbon-black sorts affect

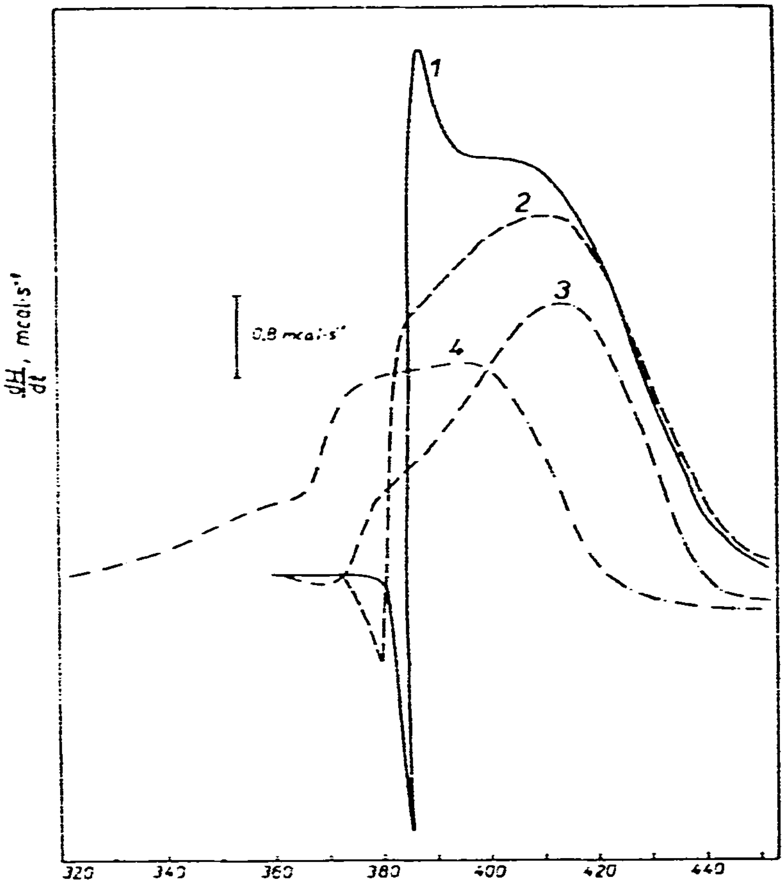

Fig. 4. DSC curves of mixtures of Bz_2O_2 with SRF United Carbon black. Concentration (%, w/w) of Bz_2O_2; 1, 100% (1.02 mg); 2, 80% (1.25 mg); 3, 50% (2.00 mg); 4, 20% (5.00 mg).

also the maximum rate of a rapid induced decomposition right behind the melting point. When starting from the assumption that the rapid chain decomposition right behind the melting point of Bz_2O_2 is due to the still ordered arrangement of the melt[5-7], the changes in V_c values will be caused by a greater or smaller disturbed arrangement of the just forming melt. This disturbance may be attributed to both the physical and chemical effects of the carbon black used. The physical effect should manifest itself in both the value of the surface area and the chain structure. In the changes of both the surface area and the chain structure even the chemical effect represented by the mentioned hydrogen elimination from the carbon black surface is included.

The influence of the surface area itself on the V_c value may well be found in comparing the specific surface at approximately equal overall Bz_2O_2 decomposition heats in mixtures with such carbon blacks and those at almost unchanging chain structure content. These conditions might be approached by the choice of the following mixtures (Table III). As may be seen, an increase of carbon black surface area causes a decrease of the V_c value and, consequently, a greater disturbance of the just

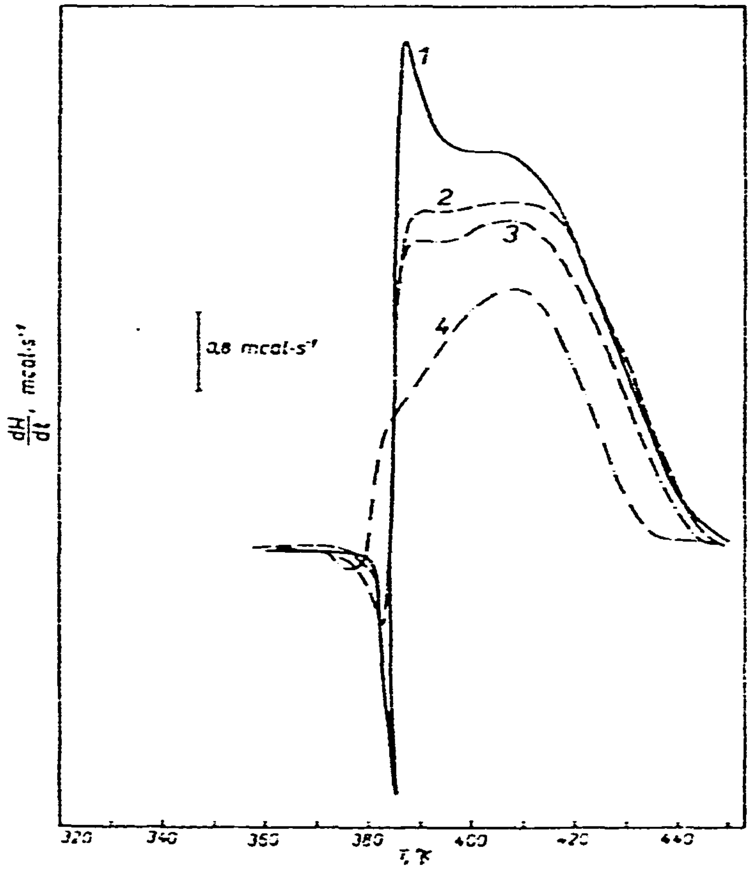

Fig. 5. DSC curves of mixtures Bz_2O_2 with United EPC black. Concentration (%, w/w) of Bz_2O_2: 1, 100% (1.02 mg); 2, 80% (1.25 mg); 3, 50% (2.00 mg); 4, 20% (5.00 mg).

TABLE III

THERMOCHEMICAL DATA OF Bz_2O_2 DECOMPOSITION IN THE PRESENCE OF SELECTED KINDS OF CARBON BLACK

50% (w/w) mixture of Bz_2O_2 with	*BET surface area (m^2/g)*	*Oil absorption (ml/100g)*	*V_c (mcal/sec)*	*Q (kcal/mole)*
P-1250	40–65	160–180	2.0	52
HAF United	80	150	1.2	52
Continex ISAF	102–129	143	1.1	49
Monarch Black	320	150	1.0	42
Vulcan XC-72	249	145	0.9	42

forming Bz_2O_2 melt. On the other hand, however, it may be seen that in comparing V_c of both HAF United and Continex ISAF carbon blacks with that of compounds with greater surface area (oil absorption being almost equal), this difference appears to be but a little one. The differences in overall decomposition heats suggest that the elimination of hydrogen atoms from the carbon black surface does not occur until a further phase of the decomposition reaction, *i.e.* within a completely disordered Bz_2O_2 melt. The fact that no effect of the chain structure on the V_c value is observed, may be seen when comparing the data of both the SRF United Carbon and FEF Continex (Table II) carbon blacks which differ considerably in oil sorption yet little in specific surface. In view of the entropy change, the low-structure carbon black should cause a larger disturbance of melt arrangement of the just melting Bz_2O_2, which should be reflected by a decrease of the V_c value.

The effect of free-spin concentration may not be gathered from the data obtained. Thus, *e.g.*, Continex ISAF and United EPC carbon black having an approximately equal surface area and differing from each other in free-spin concentration at least by a factor of 10^3, hace a close V_c value (Table II).

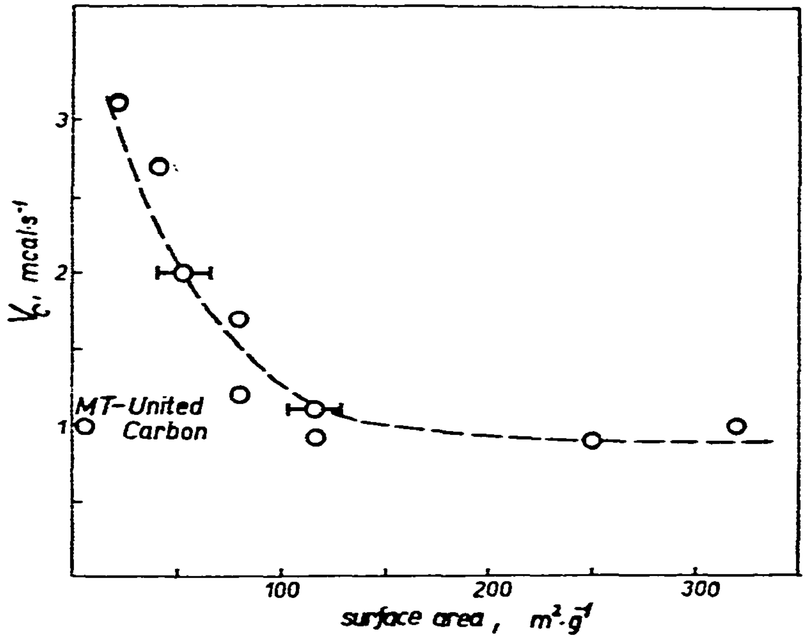

Fig. 6. Plot of Bz_2O_2 decomposition rate V_c in mixtures with the carbon blacks used *vs.* their surface area; 50% (w/w) Bz_2O_2, 2 mg.

From these considerations it is possible to correlate the effect of the surface area of the carbon blacks used with V_c value (Fig. 6). From the course of this dependence it may be deduced that V_c value rapidly decreases with increasing carbon black surface area up to about 100 m^2/g. A further increase of specific surface does not affect the V_c value. It is of interest that the thermal MT United Carbon carbon black cannot be included in this dependence. The disturbance of Bz_2O_2 melt arrangement exceeding the expected one is assumed to result from the fact that thermal carbon black does not form chain structures[10].

The course of Bz_2O_2 decomposition in the presence of activated charcoal (Fig. 1) is a considerably different one. With respect to pure Bz_2O_2 all of the decomposition course is shifted toward lower temperatures, the decomposition itself starting already at temperatures of about 330°K. Also the shape of the DSC curves differs from that of Bz_2O_2 decomposition in the presence of carbon black. To obtain a better view of the decomposition in question, mixtures with various Bz_2O_2 concentrations were prepared, whereas the weights of the mixtures were chosen so that the Bz_2O_2 content in each of them might equal 1 mg. The course of the DSC curves is shown in Fig. 7, the appropriate results being summarised in Table IV. As may be seen from Fig. 7, the change of Bz_2O_2 concentration in the given system affects the course of its decomposition in quite a marked way. Already at 20% activated charcoal concentration, decomposition below the melting point, decrease of overall decomposition heat and suppression of the rapid decomposition reaction right

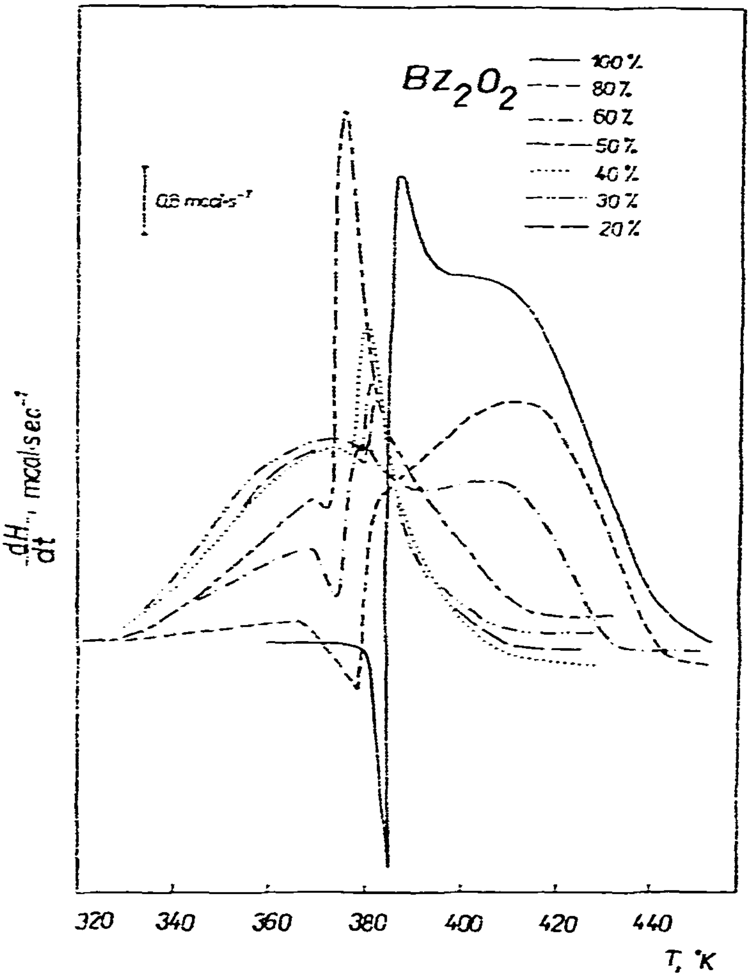

Fig. 7. DSC curves of Bz_2O_2 decomposition in mixtures with activated charcoal "Carboraffin". Sample weight: 100%, 1.02 mg; 80%, 1.20 mg; 60%, 1.60 mg; 50%, 2.10 mg; 40%, 2.50 mg; 30%, 3.33 mg; 20%, 5.00 mg (%, w/w).

TABLE IV

OBSERVED THERMOCHEMICAL DATA FOR Bz_2O_2 DECOMPOSITION IN MIXTURES WITH ACTIVATED CHARCOAL "CARBORAFFIN"

Bz_2O_2 concentration (%, w/w)	T_m (°K)	T_c (°K)	V_c (mcal/sec)	Q (kcal/mole)
100	384	388	5.3	76
80	377	383	1.8	54
60	374	379	2.4	50
50	372	376	5.5	44
40	376	381	4.5	46
30	377	381	2.8	43
20	381	386	2.7	41

behind the melting point may be observed. With increasing activated charcoal concentration, the decomposition occurring below the melting point continues shifting toward lower temperatures under simultaneous increase of the Bz_2O_2 amount decomposed in this region. This effect exhibits a growing tendency until the activated charcoal concentration reaches about 70% (w/w), whereupon any further addition of activated charcoal has little effect. Likewise as in the case of carbon black, the overall decomposition heat decreases (Fig. 8) with increasing activated charcoal concentration. Even here one may assume that the observed decrease can be attributed to the growing reaction role of hydrogen separation from the activated charcoal surface with increasing concentration of this admixture. It may be seen from Table IV that

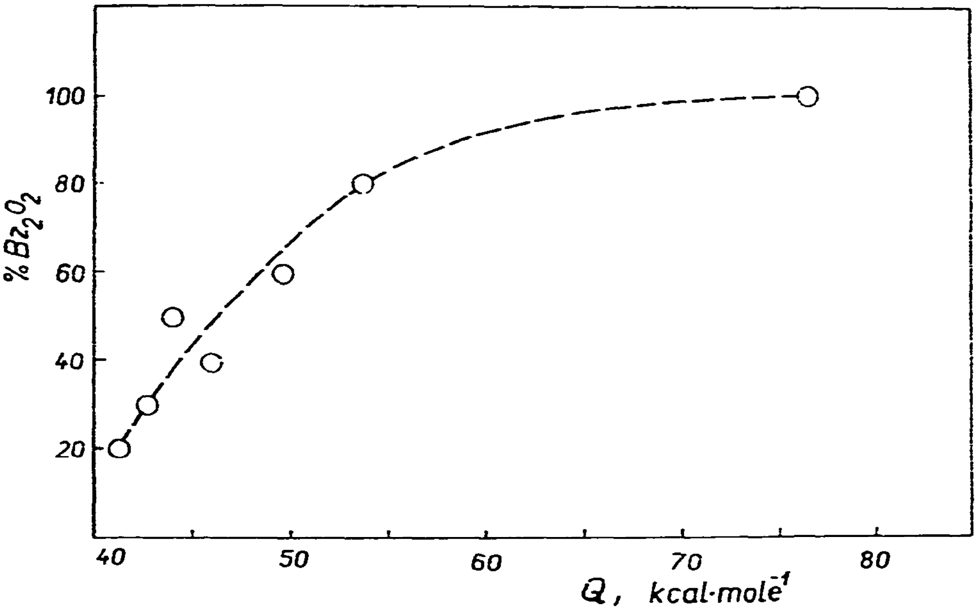

Fig. 8. Plot of overall decomposition heat of Bz_2O_2 in mixtures with activated charcoal "Carboraffin" vs. Bz_2O_2 concentration (%, w/w).

primarily (from 0 to 20% activated charcoal) the V_c value decreases, followed by an increase up to 50% of Bz_2O_2 in mixture. With a further decrease of the Bz_2O_2 concentration, the V_c value decreases down to 30% of Bz_2O_2, below which we may observe that any further decrease in Bz_2O_2 content can almost no more affect the V_c value. Apart from this, we may observe (Fig. 7), that starting with 60% BzO_2 content in mixture, a further decrease of Bz_2O_2 content leads to the disappearance of the maximum on the DSC curve corresponding to Bz_2O_2 decomposition in disordered melt. The observed decomposition course might well be explained in this way: with increasing concentration of activated charcoal in mixture with Bz_2O_2, always thinner layers of solid Bz_2O_2 form on the activated charcoal surface thus enabling the sorption forces already contributing to solid Bz_2O_2 decomposition below the melting point to exert themselves to a greater extent. Provided that in the course of decomposition below the melting point, also the sorption of decomposition products occurs, the sorption efficiency of active centres on the activated charcoal surface decreases and the decomposition rate, V_c, right behind the melting point is increased. The decrease of the V_c value with increasing activated charcoal concentration is probably caused by the continually decreasing value of overall decomposition heat as well as

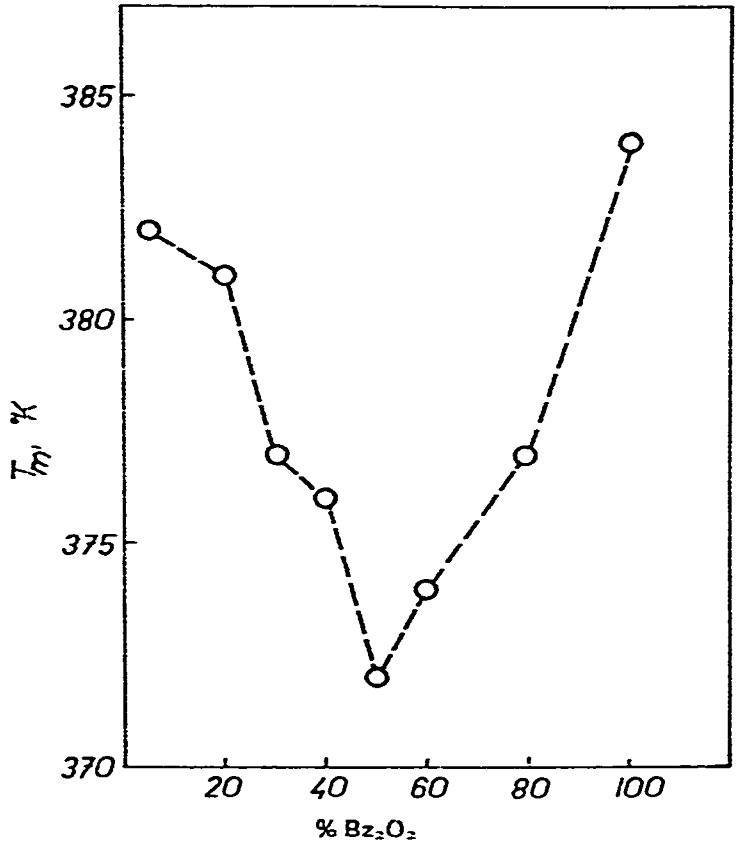

Fig. 9. Plot of Bz_2O_2 melting point vs. its concentration (%, w/w) in mixtures with activated charcoal "Carboraffin".

by a greater portion of Bz_2O_2 decomposed below the melting point. In considering the concept of solid Bz_2O_2 decomposition in the presence of activated charcoal, even the observed T_m melting point changes (Fig. 9) may well be elucidated.

A strong catalytic effect of "Carboraffin" activated charcoal on solid Bz_2O_2 decomposition was found also in studying the influence of mixing time in the homogenizer (Fig. 10). Both the observed decrease of overall decomposition heat and the maximum decomposition rate with the prolongation of mixing time suggest that the decomposition probably does already take place owing to a longer term duration of the mixing process due to the greater contact of Bz_2O_2 with coal and, consequently, to the decrease of the decomposition in pure Bz_2O_2 domains. Bz_2O_2 loss had to be determined in dependence of the mixing time by the iodometric method. This measurement was, however, made impossible by the fact that in the presence of activated charcoal the decomposition in solution is a rapid one[11].

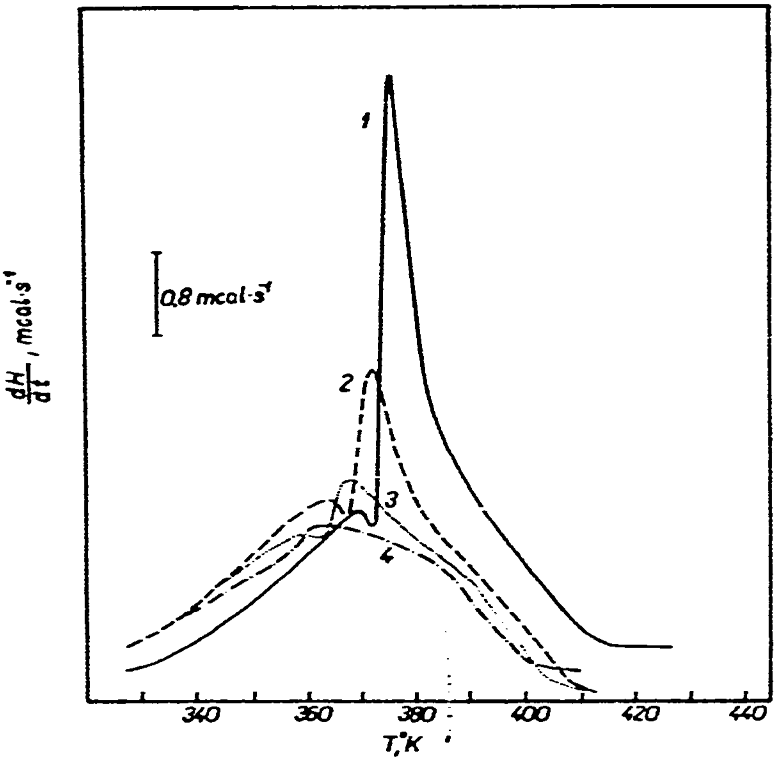

Fig. 10. DSC curves of Bz_2O_2 decomposition in mixture with activated charcoal "Carboraffin" [50% (w/w) Bz_2O_2]. Mixing time: 45 sec (1); 3 min (2); 10 min (3); 20 min (4).

Colloid silica

Aerosil of Degussa Co. was used for the preparation of mixtures with 50 and 5% (w/w) of Bz_2O_2, whereas in the case of the mixture, the mixing time was changed (45 sec and 20 min). DSC registrations were obtained under identical measuring conditions as in the case of Bz_2O_2 mixtures with both carbon black and activated charcoal (Fig. 11). Only in the case of 5% mixture were other conditions applied (heating was unchanged) to prevent the use of a mixture weight exceeding 5 mg. When comparing the course of Bz_2O_2 decomposition DSC curves in 50% mixture with Aerosil (mixing time 45 sec), V_c, V_{max} values and overall reaction heat (Table V) with the course and values referred to for 50% mixtures with both carbon black and activated charcoal (Fig. 1, Table II), we may see that some changes occur. In the case of Aerosil, the decrease in the V_c value is considerably less and may well be compared with the values obtained for carbon blacks with small surface area (except the thermal ones). Also the values of overall decomposition heat and V_{max} are higher. The observed increase of overall decomposition heat may be elucidated by the suppression of the reaction of hydrogen atom elimination from the surface. The higher V_c value, compared to

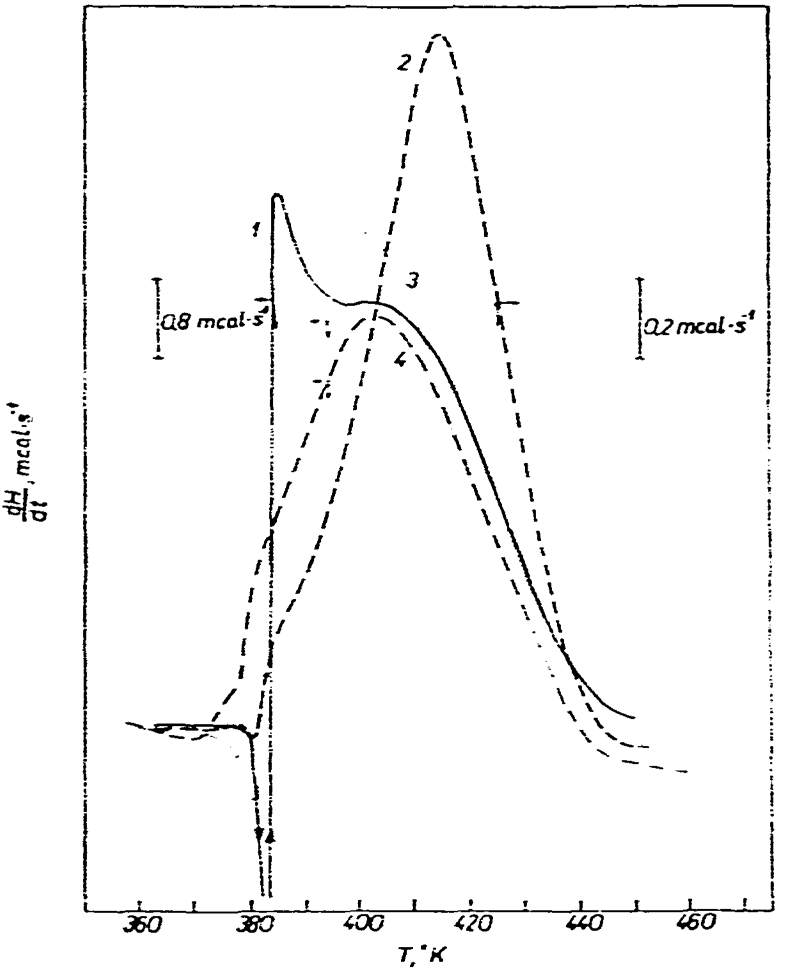

Fig. 11. DSC curves of Bz_2O_2 decomposition in mixtures with colloidal silica "Aerosil Degussa". Pure Bz_2O_2, 1.02 mg (1); 95% (w/w) Aerosil, 5 mg, mixing time 45 sec (2); 50% (w/w) Aerosil, 2 mg, mixing time 45 sec (3); 50% (w/w) Aerosil, 2 mg, mixing time 20 min (4).

carbon blacks of a surface area approximately equal to that of Aerosil, proves that the physical effect of Aerosil on Bz_2O_2 decomposition is considerably lower, the given reaction system probably being only diluted by the admixture. Smaller affinity of Bz_2O_2 molecules to Aerosil surface is the consequence of both the physical and chemical structure of the substance.

TABLE V

THERMOCHEMICAL DATA FOR Bz_2O_2 DECOMPOSITION IN THE PRESENCE OF COLLOIDAL SILICA "AEROSIL DEGUSSA"

Mixture	Q *(kcal/mole)*	T_m *(°K)*	V_c *(mcal·sec^{-1}·mg $Bz_2O_2^{-1}$)*	V_{max} *(mcal·sec^{-1}·mg $Bz_2O_2^{-1}$)*
Pure Bz_2O_2	76	383	5.2	4.1
Bz_2O_2 + Aerosil (50%, w/w), mixing time 45 sec, 2 mg	74	380	2.7	4.8
Bz_2O_2 + Aerosil (50%, w/w) mixing time 20 min, 2 mg	70	371	1.6	4.1
Bz_2O_2 + Aerosil (5%, w/w), mixing time 45 sec, 5 mg	89	380.5	0.9	6.9

From Table V it may further be seen that upon longer mixing there is a less decrease in the V_c value. Also the higher concentration of Aerosil due to the greater disturbance of Bz_2O_2 melt arrangement leads to a decrease of V_c whereas the overall decomposition heat appears to be higher compared to pure Bz_2O_2. The decomposition is slightly shifted toward higher temperatures. We assume that the observed increase of reaction heat may be the result of a more important role of the decarboxylation reaction in the decomposition of solid Bz_2O_2.

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