

## THERMAL DECOMPOSITION OF SOLID BENZOYL PEROXIDE IN THE PRESENCE OF SOLID ADMIXTURES PART II. ISOTHERMAL MEASUREMENTS

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### ABSTRACT

Isothermal decomposition of solid benzoyl peroxide ( $Bz_2O_2$ ) below the melting point in the presence of various kinds of carbon blacks, activated charcoal and colloidal silica has been studied by the technique of differential scanning calorimetry (DSC). The presence of the admixtures has an influence on the decomposition both in the initiation process and in the period of a fast chain reaction. With a rising value of surface area of carbon blacks both the induction period and the time necessary to attain the maximum rate of decomposition are shortened. As compared to other admixtures the presence of activated charcoal shows the most striking effect on the decomposition of  $Bz_2O_2$ . In such a case the apparent activation energy of both the initiation process and the fast chain reaction are decreased. It has also been found that colloidal silica compared to other admixtures has the least effect on  $Bz_2O_2$  decomposition. No effect of free-spin concentration of carbon blacks on  $Bz_2O_2$  decomposition has been observed.

### EXPERIMENTAL

#### *Materials and method*

The characteristics of the materials as well as the method of sample mixing were described previously<sup>1</sup>. A Perkin-Elmer differential scanning calorimeter (DSC-1B) was used for the thermal measurements. All of the decompositions were carried out under dry nitrogen at 365°K. The concentration of the admixture was 5% (w/w). The sample weight was in all cases 2 mg. Covered aluminium sample pans were used.

### RESULTS AND DISCUSSION

The course of isothermal DSC curves of some mixtures is shown in Fig. 1. As may be seen, the decomposition of solid  $Bz_2O_2$  in the presence of the admixtures is still autocatalytic. However, each of the curves compared to that for pure  $Bz_2O_2$  differs in its position and height. From the DSC curves obtained the following quantities were evaluated: time necessary to attain the maximum decomposition rate ( $\tau_{max}$ ) and maximum decomposition rate ( $V_{max}$ ). Table I summarizes the results.

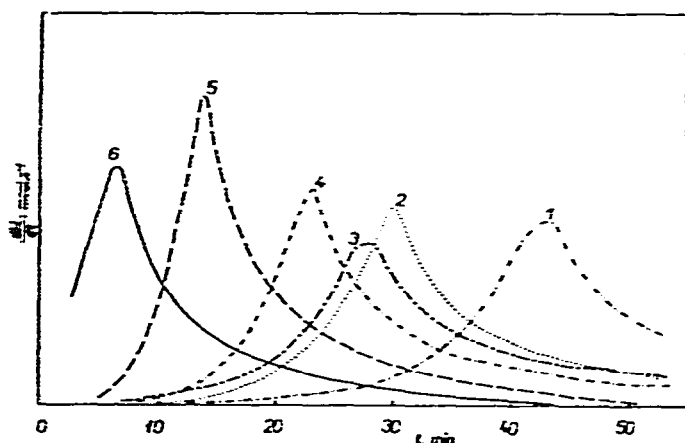


Fig. 1. Isothermal DSC curves (365 °K) of  $Bz_2O_2$  decomposition in the presence of these admixtures: 1, pure  $Bz_2O_2$ ; 2, MT United Carbon; 3, silica gel; 4, SRF United Carbon; 5, P-1250; 6, activated charcoal. 5% (w/w) concentration of the admixtures were used. Sample weight 2 mg.

With a rise in surface area of carbon blacks the time necessary to attain the maximum rate of decomposition is rapidly decreased towards values corresponding to a surface area of about  $100 \text{ m}^2/\text{g}$ , as shown in Fig. 2. Further increasing of surface area does not affect the  $\tau_{\text{max}}$  value as strikingly.

It is of interest that the acetylene black P-1250 cannot be included into this dependence. Despite its small surface area, however, this particular carbon black

TABLE I

THERMOCHEMICAL DATA FOR ISOTHERMAL DECOMPOSITION OF  $Bz_2O_2$  (365 °K) IN THE PRESENCE OF GIVEN ADMIXTURES

Mixture of $Bz_2O_2$ with 5% (w/w) of	Surface area of the admixture (BET) ( $\text{m}^2/\text{g}$ )	Free-spin concentration per mg of the admixture	$\tau_{\text{max}}$ (min)	$V_{\text{max}}$ (mcal/sec/mg $Bz_2O_2$ )
pure $Bz_2O_2$	—	—	43.5	0.17
P-1250	40–65	$4.6 \times 10^{19}$	13.9	0.31
MT United Carbon	6	$1.0 \times 10^{18}$	30.4	0.19
Monarch Black	320	$6.4 \times 10^{16}$	13.4	0.20
HAF United	80	"	16.3	0.22
Vulcan XC-72	249	"	13.2	0.25
SRF United Carbon	22	$2.2 \times 10^{18}$	23.4	0.21
Continex ISAF	102–129	"	15.5	0.23
United EPC	116	$1.6 \times 10^{19}$	16.3	0.21
Continex FEF	39–43	"	20.4	0.23
65-SPF United Carbon	80	"	17.6	0.19
Activated charcoal "Carboraffin"	—	$1.0 \times 10^{19}$	6.6	0.24
Colloidal silica "Aerosil"	175–200		28.0	0.15

\*No reproducible signal (free-spin concentration less than  $6.4 \times 10^{16}$ ).

produced a decrease in  $\tau_{\max}$  relative to  $\tau_{\max}$  for pure  $\text{Bz}_2\text{O}_2$ , which was greater than expected. In fact, such a decrease should correspond to much higher values of surface area, as may be seen in Fig. 2. We assume that this fact cannot be attributed to the high free-spin concentration of the black ( $4.6 \times 10^{19} \text{g}^{-1}$ ).

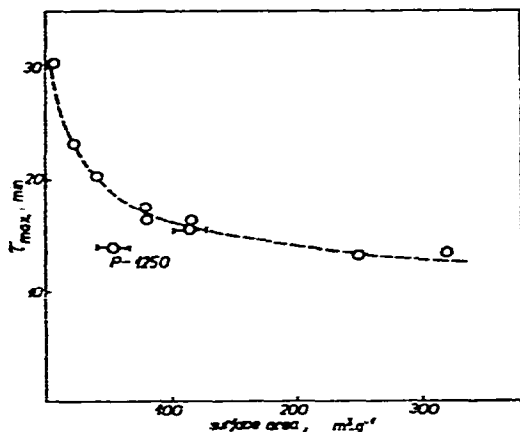


Fig. 2. Plot of time necessary to attain maximum decomposition rate of  $\text{Bz}_2\text{O}_2$  in the presence of carbon blacks *vs.* their surface area. 5% (w/w) of blacks in mixtures, 365°K. Sample weight 2mg.

Closely similar values were obtained for  $\tau_{\max}$  in the presence of Continex ISAF and United EPC blacks, which are of approximately equal surface area but differ by a factor of  $10^3$  in their free-spin concentrations (Table I).

The above mentioned decrease of the  $\tau_{\max}$  value with increasing surface area of carbon blacks shows that higher primary decomposition rate of solid  $\text{Bz}_2\text{O}_2$  is due to the increase in adsorptive power of the carbon black.

The extreme behaviour of P-1250 black, however, could be attributed to its different internal structure, for, according to the literature<sup>2</sup>, acetylene blacks possess a lower number of graphite layers in their crystallites. As can be seen in Table I the  $\tau_{\max}$  value is decreased by the activated charcoal to the greatest extent. On the other hand, colloidal silica "Aerosil" does not decrease the  $\tau_{\max}$  value to the same extent as carbon black with approximately equal surface area. This suggests that the physical effect of "Aerosil" surface area on solid  $\text{Bz}_2\text{O}_2$  decomposition below the melting point is a relatively minor one.

The  $V_{\max}$  values of  $\text{Bz}_2\text{O}_2$  mixtures with carbon blacks and activated charcoal appear to be generally higher as compared with pure  $\text{Bz}_2\text{O}_2$ . This indicates that carbon blacks as well as activated charcoal catalyse isothermal decomposition of solid  $\text{Bz}_2\text{O}_2$  below the melting point both in the initiation process and in the stage of branched chain reaction. On the other hand, the effect of colloidal silica "Aerosil" becomes evident only in the initiation stage of decomposition. As may be seen from Table I, the effect of free-spin concentration cannot be correlated with the  $V_{\max}$  values. In Fig. 3 can be seen a plot of maximum rate of decomposition,  $V_{\max}$ , *vs.* surface area of carbon blacks. Despite the points scattering and the repeated extreme behaviour of

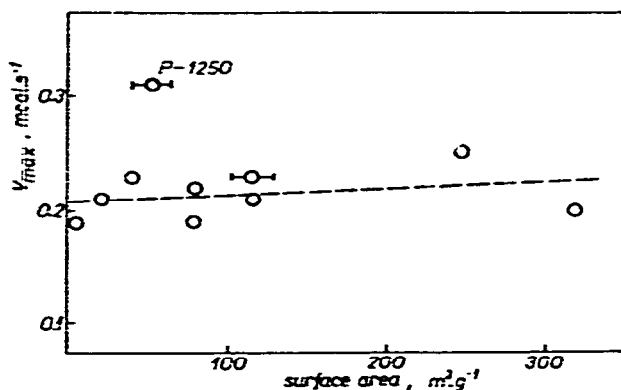


Fig. 3. Plot of maximum decomposition rate of  $Bz_2O_2$  in the presence of carbon blacks *vs.* their surface area. 5% (w/w) of blacks, 365°K. sample weight 2 mg.

P-1250 black observed, the slight increase of maximum rate of decomposition with increasing carbon black surface area may be assumed.

The rate of radical production in the initial stage of decomposition may be expressed by the equation<sup>3</sup>

$$\frac{d[R]}{dt} = r_s + \varphi[R] \quad (1)$$

where  $r_s$  = spontaneous decomposition rate and  $\varphi$  = coefficient proportionate to probability of branching.

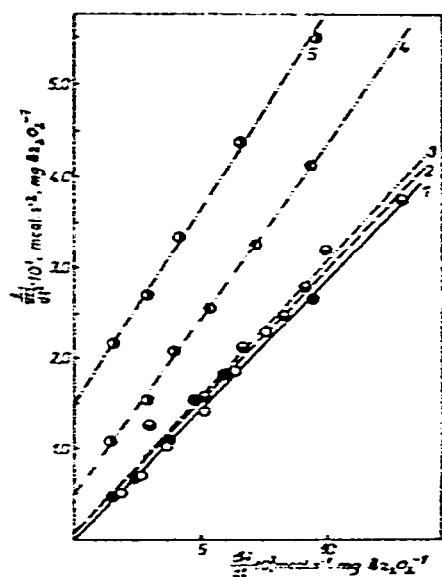


Fig. 4. Plot of acceleration of reaction as a function of reaction rate for decomposition of  $Bz_2O_2$ ; 1, pure  $Bz_2O_2$ ; 2,  $Bz_2O_2$  + colloidal silica; 3,  $Bz_2O_2$  + MT United Carbon; 4,  $Bz_2O_2$  + Monarch Black; 5,  $Bz_2O_2$  + P-1250. 5% (w/w) of the admixtures were used. Sample weight 2 mg.

The radical concentration change can be determined from the tangent of exponential part of the dependence rate of heat evolution *vs.* time. Thus, according to Eqn. (1) the plot of  $d^2H/dt^2$  *vs.*  $dH/dt$  is to be a linear one.

The above mentioned dependence for the mixtures of  $Bz_2O_2$  with some carbon blacks is shown in Fig. 4. A linear character of the dependence suggests that isothermal autocatalytic decomposition of  $Bz_2O_2$  below the melting point in the presence of the admixtures appears to be a branched chain reaction. The intercepts of the plots in Fig. 4 being proportionate to primary decomposition rates are in a good agreement with  $\tau_{max}$  values obtained for these mixtures.

Some kinetic data of  $Bz_2O_2$  decomposition in the presence of activated charcoal were obtained. Concentration of 5% (w/w) in the temperature range 363–367°K was used. The apparent activation energies of the initiation process and the fast chain reaction were determined from the plots of  $1/\tau_{max}$  *vs.*  $1/T$  and  $V_{max}$  *vs.*  $1/T$ , respectively, as shown in Fig. 5 and Fig. 6.

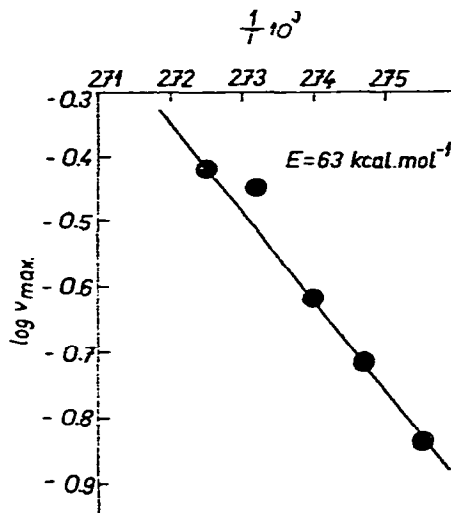
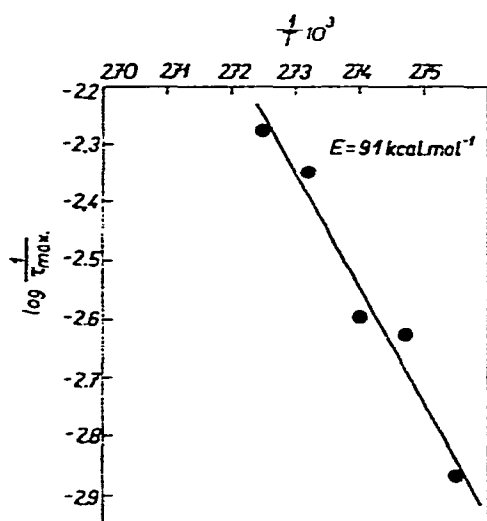


Fig. 5. Temperature dependence of the time necessary to attain maximum decomposition rate of  $Bz_2O_2$  in the presence of 5% (w/w) of activated charcoal. Sample weight 2 mg.

Fig. 6. Temperature dependence of maximum decomposition rate of  $Bz_2O_2$  in the presence of 5% (w/w) of activated charcoal. Sample weight 2 mg.

TABLE II

DATA FOR APPARENT ACTIVATION ENERGY OF  $Bz_2O_2$  DECOMPOSITION BELOW THE MELTING POINT IN THE PRESENCE OF 5% (w/w) OF ACTIVATED CHARCOAL, CALCULATED FROM ARRHENIUS PLOTS OF  $\tau_{max}$  AND  $V_{max}$ , RESPECTIVELY

Sample	$E(\tau_{max})$ (kcal/mole)	$E(V_{max})$ (kcal/mole)
Pure $Bz_2O_2$	100 <sup>a</sup>	72 <sup>a</sup>
$Bz_2O_2$ + 5% (w/w) of activated charcoal "Carboraffin"	91	63

<sup>a</sup>Ref. 4.

When comparing the values of activation energies thus obtained with those of pure  $Bz_2O_2$  (Table II) it can be seen that the presence of activated charcoal leads to the decrease in activation energy both in the initial and in the fast chain reaction stage of  $Bz_2O_2$  decomposition. The results suggest a catalytic effect of activated charcoal on the isothermal  $Bz_2O_2$  decomposition below the melting point.

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