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THE DECOMPOSITION OF BIS(PENTAFLUOROBENZOYL) PEROXIDE IN DILUTE SOLUTION

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Abstract—The decomposition of bis(pentafluorobenzoyl) peroxide in benzene at 60° has been studied by radiotracer methods. By using low concentrations of the peroxide, the induced decomposition previously observed has been eliminated. The mechanism of the decomposition is found to be fundamentally similar to that for benzoyl peroxide under the same conditions. The rate constant for the decomposition ($7 \cdot 4 \times 10^{-6}$ sec^{-1}) is considerably larger than that for benzoyl peroxide, although the energy of activation for the dissociation (about 120 kJ mole^{-1}) is of similar magnitude.

THE THERMAL decomposition of benzoyl peroxide in benzene has been the subject of a large number of papers. Most of the work has been carried out at moderately high concentrations, where induced decomposition becomes fairly significant.(1) Studies with radiotracers(2,3) showed that such induced decomposition is considerably reduced when sufficiently low concentrations are used. It was concluded that the primary step in the decomposition is the formation of two benzoyloxy radicals; these subsequently decompose to form phenyl radicals, with the evolution of carbon dioxide.

More recently, the preparation of the fluorocarbon analogue of benzoyl peroxide, bis(pentafluorobenzoyl) peroxide, has been reported.(4) The decomposition at moderate concentrations in benzene at 79·6° was also investigated; this showed that the decomposition was faster than that of benzoyl peroxide under the same conditions.

In the work to be described, radiotracer techniques have been applied, to compare the rate of decomposition at 60° in low concentrations of benzene with the earlier results for benzoyl peroxide under similar conditions.

EXPERIMENTAL

Materials

Bis(pentafluorobenzoyl) peroxide (carboxyl-^{14}C) was prepared from pentafluorobenzene. 0·1 mol of the latter, dried over anhydrous sodium sulphate, was dissolved in dry ether (50 ml). The solution was cooled in a Drikold/acetone bath; a solution of n-butyl lithium (0·1 mol) in dry hexane (100 ml) was added dropwise to the stirred pentafluorobenzene solution over a period of 45 min. The contents of the vessels were vented to the atmosphere via guard tubes containing silica gel and "Carbasorb". After a further 90 min of stirring, the solution was transferred to a vacuum line, frozen and degassed. The pentafluorophenyl lithium was maintained at Drikold temperature and carbonated by the action of concentrated sulphuric acid on a mixture of barium carbonate-^{14}C (1 mCi) and sodium carbonate (0·1 mol); an enclosed vacuum apparatus(5) was used for this operation, in order to contain the radioactivity. The resulting lithium pentafluorobenzoate solution was warmed to room temperature, removed from the vacuum apparatus and acidified with 6 M hydrochloric acid (600 ml). The mixture was extracted with ether (8 × 40 ml), the combined extracts being dried with anhydrous sodium sulphate and then evaporated. The pentafluorobenzoic acid (m.p. 101–102°) was recrystallized from n-hexane; 15 g were refluxed with thionyl chloride (18 ml) and dimethyl formamide (0·5 ml) for 24 hr.

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The excess thionyl chloride was distilled off and the crude pentafluorobenzoyl chloride was added dropwise, with stirring, to a mixture of 20 volume hydrogen peroxide (60 ml) and 4 M sodium hydroxide solution (10 ml) maintained at 0°; 4 M sodium hydroxide was added simultaneously to maintain alkalinity. The precipitated peroxide was filtered and recrystallized from chloroform by the addition of methanol; the white powdered product melted at 75·5–76·5°.

Diphenylpicrylhydrazyl (DPPH) (Koch-Light Laboratories Ltd.) was recrystallized from a 1:1 by volume mixture of chloroform and ether, excess solvent being removed by heating to about 75° under vacuum for 10 hr.

For the earlier experiments, A.R. benzene was dried with sodium wire, and fractionally distilled (b.p. 79°) using a column packed with glass helices. In the later experiments, this initial treatment was followed by transfer to the vacuum line; here, the benzene was further dried with calcium hydride, and distilled immediately prior to the filling of the reaction tube.

Procedure

Decompositions were carried out in break-seal tubes under vacuum. Stock solutions of the peroxide in benzene were prepared and stored in the refrigerator. These solutions were dispensed into the break-seal tubes as required, and the solvent was sublimed off under vacuum; measured quantities of dry benzene were then distilled into each tube. The sealed tubes were immersed for the required time in a water bath maintained at 60 ± 0·05°. DPPH was introduced to the break-seal tubes, when required, adopting a procedure similar to that used for introducing the peroxide.

Analyses for the products of reaction were carried out using isotope-dilution analysis;(3) tests were performed to ensure that the labelled contaminants had been removed. The relative activities of ^{14}C-labelled solids in the earlier experiments were determined by assay as carbon dioxide in a gas counter;(6) a dry catalytic combustion in a stream of oxygen was used to convert the samples to carbon dioxide. Samples of pure carbon dioxide, from the isotope-dilution of this product, were introduced directly into the gas counter. In the later experiments, the labelled solids were assayed by liquid scintillation counting; they were dissolved in scintillation grade toluene containing butyl PBD as scintillator. The counting was performed in an Intertechnique SL40 Liquid Scintillation Spectrometer; external standard ratio and channels ratio methods were used to correct for quenching.

RESULTS

The results for the formation of carbon dioxide at 60° from 2 ml of solution at initial concentrations of $2{\cdot}5 \times 10^{-3}$ mole l^{-1} are shown in Fig. 1; this is a plot of $\ln(w_\infty - w)$ against time, where w is the weight of carbon dioxide formed at a given

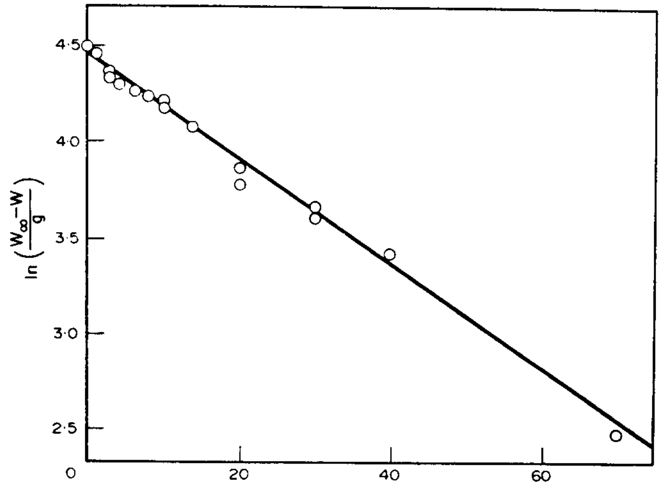


FIG. 1. A plot showing the first order dependence of the weight (w) of carbon dioxide with time.

time and w_∞ is the weight formed after a very long reaction time; it shows that the evolution of carbon dioxide follows first order kinetics, the value of the rate constant being $(7 \cdot 4 \pm 0 \cdot 4) \times 10^{-6}$ sec^{-1}. The value of w_∞ was found to represent about 29 per cent of the maximum possible yield of carbon dioxide, if all pentafluorobenzoyloxy radicals decomposed. Supplementary experiments, using benzene which had

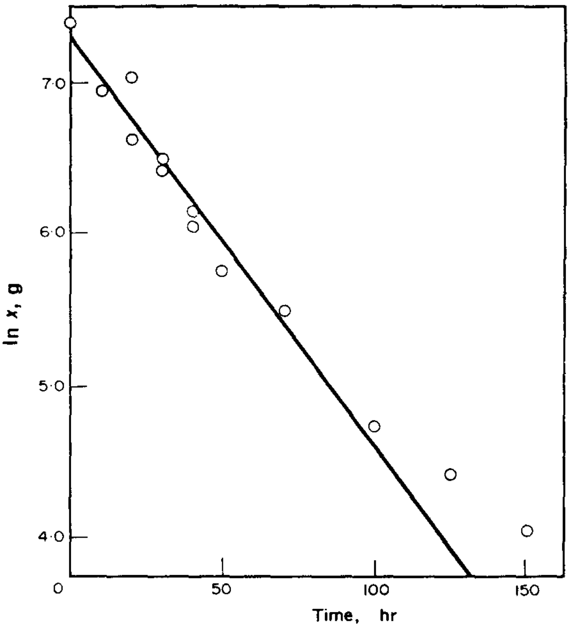


FIG. 2. A logarithmic plot of the weight (x) of bis(pentafluorobenzoyl) peroxide remaining, as a function of time.

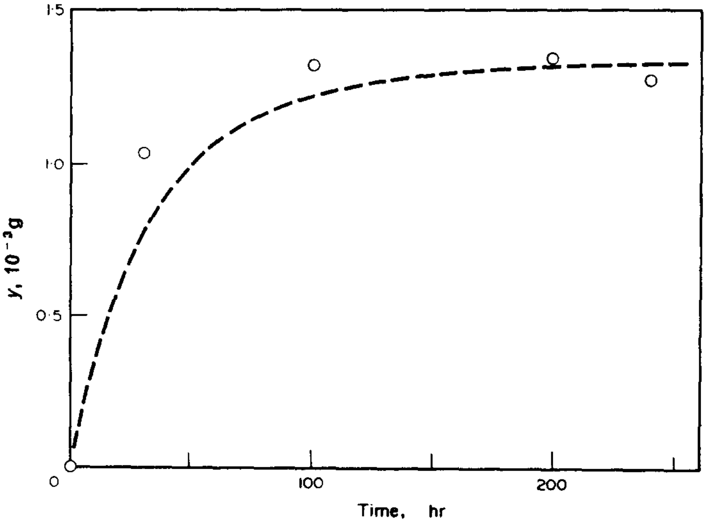


FIG. 3. A plot of the weight (y) of pentafluorobenzoic acid formed, as a function of time.

undergone a further purification step, produced an increased yield of carbon dioxide, about 33 per cent of the maximum possible yield being formed.

Figure 2 shows the weight (x) of bis(pentafluorobenzoyl) peroxide remaining after decomposition, plotted logarithmically as a function of time; 2 ml of peroxide solution at an initial concentration of $2\cdot 0 \times 10^{-3}$ mol l^{-1} were decomposed in each experiment. The kinetics are again first order, the rate constant being $(7\cdot 5 \pm 1\cdot 0) \times 10^{-6}$ sec^{-1}.

The weight (y) of pentafluorobenzoic acid formed is plotted as a function of time in Fig. 3; 2 ml of peroxide solution at an initial concentration of $2\cdot 5 \times 10^{-3}$ mol l^{-1} were again decomposed. The broken line in the graph represents the calculated maximum possible yield of the acid; this was obtained by subtracting the molar quantities of carbon dioxide formed from the corresponding quantities of peroxide decomposed; this curve satisfies first order kinetics, with a rate constant of $7\cdot 4 \times 10^{-6}$ sec^{-1}. Since some of the yields of pentafluorobenzoic acid lie above this curve, no significance can be attached to the apparently higher rate constant which would result from these yields. An extra purification step for the solvent was found to have an insignificant effect on the yields of pentafluorobenzoic acid.

When DPPH, at a concentration of 30 g l^{-1}, was added to the peroxide solution (initial concentration: $2\cdot 5 \times 10^{-3}$ mol l^{-1}) the yield of carbon dioxide was decreased to about 1 per cent of its former value.

To study the effect of initial concentration of peroxide, experiments were carried out in the concentration range from $0\cdot 25 \times 10^{-3}$ to $5\cdot 0 \times 10^{-3}$ mol l^{-1}. Within the precision of the results, there was no detectable change in the initial rate of decomposition; this showed that induced decomposition was unlikely under these conditions.

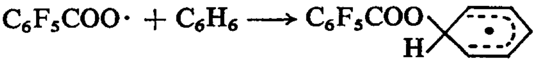
DISCUSSION

When bis(pentafluorobenzoyl) peroxide was decomposed in the presence of DPPH, the yield of carbon dioxide was suppressed virtually to zero. Thus, as with benzoyl peroxide,(2,3) carbon dioxide is not formed during the primary decomposition of the peroxide, but results from a secondary decomposition of the pentafluorobenzoyloxy radicals.

Only about 30 per cent of pentafluorobenzoyloxy radicals decompose to yield carbon dioxide and pentafluorophenyl radicals; the remainder are found in the product as pentafluorobenzoic acid. In contrast with the decomposition of benzoyl peroxide,(3) repeated purification appears to have little influence on the yield of pentafluorobenzoic acid, and it seems unlikely that this results from the interaction of pentafluorobenzoyloxy radicals with impurity in the solvent; it appears more likelv that the acid is formed through interaction with the solvent itself; thus

$$C_6F_5COO\cdot + C_6H_6 \longrightarrow C_6F_5COOH + C_6H_5\cdot.$$

Alternatively, the pentafluorobenzoyloxy radicals and the pentafluorophenyl radicals may each interact with benzene to form σ-complexes;(7)



and

these complexes may then lose a hydrogen atom to another pentafluorobenzoyloxy radical to form pentafluorobenzoic acid, and either phenyl pentafluorobenzoate or phenyl pentafluorophenyl.

The results show that the formation of carbon dioxide and the loss of bis(pentafluorobenzoyl) peroxide both follow first order kinetics, with the same rate constant; the primary decomposition into pentafluorobenzoyloxy radicals is therefore the rate controlling step. Changes in the initial concentration of peroxide also had no significant effect on the initial rate of decomposition. Thus, there is no evidence of induced decomposition being a significant factor at these concentrations. In this respect, bis(pentafluorobenzoyl) peroxide behaves similarly to benzoyl peroxide(3) for which the rate of decomposition at these low concentrations was also found to be independent of initial concentration; induced decomposition was however very significant at higher concentrations.(1,7)

The measured rate constant is some three times greater than that obtained under similar conditions with benzoyl peroxide.(3) It has been shown (8,9) that electron donating substituents increase the rate of decomposition of substituted benzoyl peroxides; this has been attributed to the effect of increased coulombic repulsion of the two dipoles within the molecule.(8) It was assumed that the latter effect was a more important factor than that resulting from the increased stability of the substituted benzoyloxy radicals.

Campbell(10) has reported a preliminary kinetic investigation of the decomposition of bis(pentafluorobenzoyl) peroxide, using the method of Gill and Williams;(1) after allowing for an induced decomposition, the first order rate constant is quoted as $7{\cdot}3 \times 10^{-5}$ sec^{-1} at 79·6°. Taking this value in conjunction with the value at 60° in the present work, an activation energy of about 120 kJ mol^{-1} is obtained; this is close to the value of 126 kJ mol^{-1} reported previously for benzoyl peroxide(8,9) and to those between 114 and 130 kJ mol^{-1} for various substituted benzoyl peroxides.(9) It provides further evidence that the basic processes of dissociation of these peroxides are similar, and suggests that the higher rate constant in the case of bis(pentafluorobenzoyl) peroxide is mainly attributable to a higher pre-exponential factor.

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Résumé—On a étudié, par des méthodes de radiotraceur, la décomposition du peroxyde de bis-(pentafluorobenzoyle) dans le benzène à 60°. En utilisant des concentrations faibles de peroxyde, on a éliminé la décomposition induite observée antérieurement. On a trouvé que le mécanisme de décomposition est fondamentalement semblable à celui de la décomposition du peroxyde de benzoyle dans les mêmes conditions. La constante de vitesse de la décomposition ($7{,}4 \times 10^{-6}$ s^{-1}) est considérablement plus grande que celle du peroxyde de benzoyle, bien que l'énergie d'activation de cette dissociation (environ 125 kJ mole^{-1}) soit d'un ordre de grandeur semblable.

Sommario—Con il metodo dei tracciatori radioattivi, si è studiata la decomposizione in benzene a 60° del bis(pentafluorobenzoil) perossido. Impiegando basse concentrazioni del perossido, è stata eliminata la decomposizione indotta precedentemente osservata. Si è trovato che il meccanismo della decomposizione è fondamentalmente simile a quello del benzoil perossido, nelle medesime condizioni. La costante della velocità della decomposizione ($7{,}4 \times 10^{-6}$ sec^{-1}) è considerevolmente maggiore di quella del benzoil perossido, sebbene l'energia di attivazione della dissociazione (circa 120 kJ mole^{-1}) sia di grandezza simile.

Zusammenfassung—Die Zersetzung von Bis(pentafluorbenzoyl)peroxid in Benzol bei 60° wurde durch radioaktive Markierungsmethoden untersucht. Bei Verwendung niedriger Konzentrationen des Peroxids wurde der induzierte Zerfall, der früher beobachtet wurde, eliminiert. Es wurde festgestellt, daß der Mechanismus des Zerfalls grundsätzlich ähnlich ist zu dem von Benzoylperoxid unter denselben Bedingungen. Die Geschwindigkeitskonstante für den Zerfall ($7{,}4 \times 10^{-6}$ s^{-1}) ist erheblich größer als die für Benzoylperoxid, obwohl die Aktivierungsenergie für die Dissoziation (etwa 120 kJ Mol^{-1}) einen ähnlichen Wert hat.