568. *The Effect of Water on the Decomposition of Benzoyl Peroxide.*

By C. F. H. Tipper.

The effect of water on the decomposition of benzoyl peroxide between 70° and 100° in four solvents has been investigated. When phenol is used, the water acts as an inert diluent, but in dry or aqueous benzyl alcohol, acetic acid, or pyridine the reaction appears to be complex, the results being difficult to interpret. In dry acetic acid and pyridine the decomposition is retarded by oxygen, owing probably to the formation of a secondary reaction product, which reduces the induced chain decomposition. Addition of water increases the rate in these solvents considerably. However, the effect of water on the yield of carbon dioxide and non-volatile acid formed, and on the efficiency of the peroxide as a polymerisation catalyst, shows evidence of only a small amount of ionic decomposition.

The products and kinetics of the decomposition of benzoyl peroxide under various conditions have been frequently investigated (see Barnett and Vaughan, *J. Phys. Chem.*, 1947, **52**, 926, for references). It is now generally considered that, in most solvents, the first step is a unimolecular fission into free radicals, followed by a chain decomposition of the peroxide (Bartlett and Nozaki, *J. Amer. Chem. Soc.*, 1946, **68**, 1686; 1947, **69**, 2299). However, Bartlett and Leffler (*ibid.*, 1950, **72**, 67) found that some acid-catalysed ionic decomposition can probably occur, since addition of acetic, dichloroacetic, or trichloroacetic acid increases the rate of decomposition in benzene at 70° in that order, and addition of sulphuric acid increases the rate in acetic acid, though the effect is very much smaller than for *p*-anisoyl *p*-nitrobenzoyl peroxide (Leffler, *loc. cit.*).

Mixtures of organic solvents and water should provide favourable media for ionic decomposition. The only mention of the effect of water on the decomposition of benzoyl peroxide is by Gelissen and Hermans (*Ber.*, 1925, **58**, 765) : addition of water to *iso*butyl alcohol used as the solvent is stated to increase the yield of aldehyde and benzoic acid. It is difficult to find suitable compounds which are miscible with water. However, the effect of water on the decomposition of benzoyl peroxide in acetic acid, pyridine, phenol, and benzyl alcohol has been investigated, iodometric titration being used for rate measurements.

In phenol and phenol–water mixtures the overall decomposition was of the first order, the rate constant increasing slightly with increased initial concentration in the dry solvent at 68·5° (k = 0·0322, 0·0351, and 0·0376 min.$^{-1}$ for 0·0165M-, 0·0331M-, and 0·0496M-solutions, respectively). Identical results, within the experimental error, were obtained on using fresh B.P. phenol directly or after further purification. Oxygen had no effect, but addition of water decreased the rate of decomposition, and k was approximately proportional to the molar fraction of phenol in the solvent mixture, as shown in the following table. The overall activation energies of decomposition in phenol and phenol + 55·5 mole-% water were practically the same, *viz.*, 19·6 and 19·8 kcal./g.-mol., respectively [Fig. 1(*b*) and (*c*)], which are much lower than the 30—32 kcal. found when relatively inert solvents are used (Barnett and Vaughan, *loc. cit.*). It seems, therefore, that the water was merely acting as an inert diluent, and that the results are in accordance with Bartlett and Nozaki's suggestion (*loc. cit.*) that in phenol the high rate is due to a very rapid induced decomposition of the peroxide by $C_6H_5O\cdot$ radicals.

Decomposition of benzoyl peroxide in phenol and phenol–water.

Temp. = 67·6°. *Initial concn.* = 0·033M.

(*a*) k (min.$^{-1}$)	0·0318	0·0274	0·0207	0·0138	0·00967
(*b*) Phenol concn. (mole %)	100	82·7	67·9	44·5	23·0
$10^4(a)/(b)$	3·2	3·3	3·0	3·1	4·2

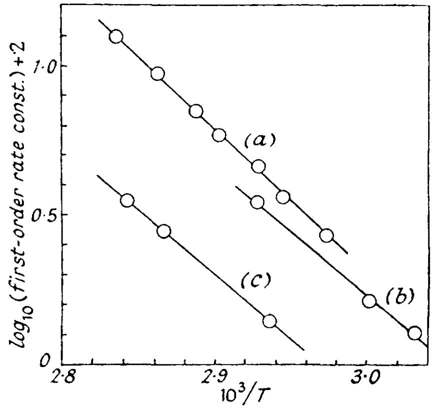

FIG. 1. *Arrhenius plots for decomposition of benzoyl peroxide in* (*a*) *pyridine* +74·7 *mole-%* H_2O, (*b*) *dry phenol,* (*c*) *phenol* +55·5 *mole-%* H_2O. *Initial concn.* = 3·31 × 10^{-2}M.

The decomposition in the other solvents, with or without added water, appears to be more complex, and the results are difficult to interpret. Under most conditions the reaction tended to a higher order than unity, although the rate again increased with increasing initial concentration (Figs. 2—5). The course of the decomposition in benzyl alcohol in an inert atmosphere was only slightly affected by the addition of up to 33 mole-% of water (Fig. 2). In the presence of oxygen the peroxide content of the solution reached a steady value, which was higher (25% compared with 52·4% apparent decomposition) in the alcohol–water mixture, and it seems likely that oxidation of the solvent was occurring, possibly to give $C_6H_5\cdot CH(OH)\cdot O\cdot OH$ (cf. Barnett and Vaughan, *loc. cit.*, pp. 945, 953). In acetic acid and pyridine, however, the rate of decomposition was considerably increased by the addition of water (Figs. 4 and 5), and so the reaction in these solvents was more extensively investigated.

Fig. 3 shows some sample results at 79·8° in dry acetic acid. The plot of $\log_{10} [Bz_2O_2]$ against time was not always reproducible at the same initial concentration in the presence of nitrogen, and depended on the specimen of acid used. Two portions from the same specimen, however, gave nearly identical curves. In freshly purified acid, the initial rate was about the same, but the curves " tailed off " at different stages in the decomposition. In the purest acid the decomposition remained approximately of first order for the longest time, and it was noticed that as the " tail off " occurred the solution began to become yellow. The difference in initial concentration being taken into account, the results agree quite well with that of Bartlett and Nozaki (*loc. cit.*). When analytical-grade glacial acetic acid from a Winchester bottle which had been opened some time previously was used directly as the solvent, the rate of reaction was greatly reduced. The decomposition became of first order and a yellow colour developed almost immediately. The presence of oxygen had exactly the same effect. The rate was reduced to the same value and was unaffected by the purity of the solvent. The decomposition was also retarded by the reaction products from the oxygen-retarded experiments. The yellow colour faded and the rate increased as the reaction proceeded. However, at 100° in the presence of nitrogen, results with different specimens of acid were identical, and even after 95% decomposition the yellow colour was very faint. Oxygen again reduced the rate, the reaction becoming of first order, but the presence of reaction products had only a slight effect.

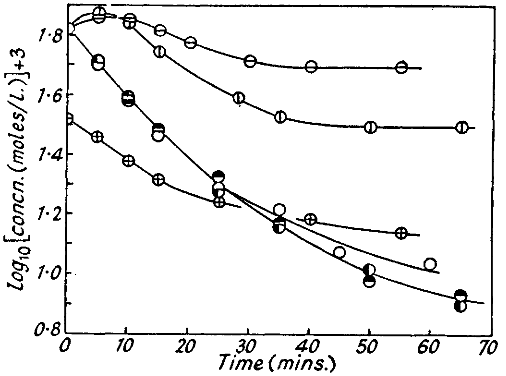

FIG. 2. *Effect of water and oxygen on the decomposition of benzoyl peroxide in benzyl alcohol. Temp.* = 79·2°. *Initial concns.* = 6·61 × 10^{-2} *and* 3·31 × 10^{-2}M.

N_2 *passed through solution*

○, ⊕, *dry benzyl alcohol.*
◐, BzOH + 19·2 *mole-%* H_2O.
◓, BzOH +33·1 *mole-%* H_2O.

O_2 *passed through solution :*

⦶, *as for* ○.
⊖, *as for* ◓.

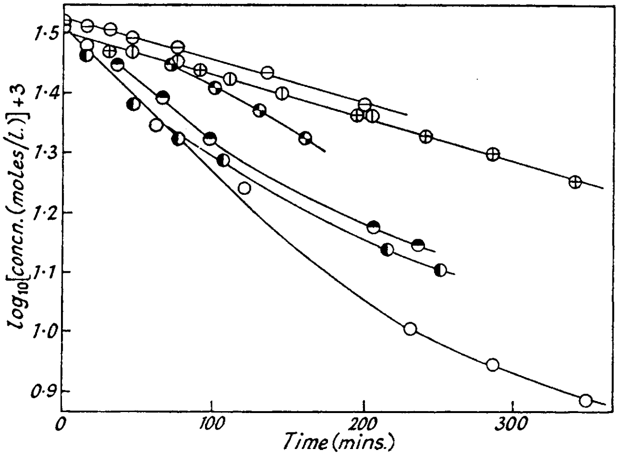

FIG. 3. *Decomposition of benzoyl peroxide in dry acetic acid. Temp.* = 79·8°. *Initial concn.* = 3·35 ± 0·05 × 10^{-3}M.

N_2 *passed through solution :*

○, *Griffin and Tatlock analytical-grade glacial acetic acid, twice fractionated and fractionally frozen.*
◐, *B.D.H. "AnalaR" glacial acetic acid, fractionated.*
◓, *as for* ◐ *but fractionally frozen.*
⊖, *G. and T. analytical-grade acid from old, opened Winchester.*
◍, *as for* ○, *but containing yellow final solution.*

O_2 *passed through solution :*

⊕, *as for* ○.
⦶, *as for* ⊖.

It seems likely that the fall off from the initial first-order rate in the later stages of the decomposition was due to the formation of a yellow secondary oxidation product, which retarded the reaction. Oxygen or a trace of impurity in the acid caused the formation of the yellow substance immediately. This substance may be a quinone, for these are known to inhibit the decomposition of benzoyl peroxide (Breitenbach and Kindl, *Monatsh.*, 1950, **81**, 1145). The retardation was probably due to partial or complete suppression of the chain reaction, since the time of half-change, ~340 mins. at 79·8° in the presence of oxygen, is roughly the same as $t_{\frac{1}{2}}$ for the fully inhibited decomposition in dioxan at 80° (Swain, Stockmayer, and Clarke, *J. Amer. Chem. Soc.*, 1950, **72**, 5426), and Bartlett and Nozaki (*loc. cit.*) found that, acetic anhydride, a solvent similar to acetic acid, being used, the decomposition was retarded by the reaction products, the chain reaction being reduced to approximately one-third of the original. Also, the overall activation energy of decomposition in the presence of oxygen, 31·8 kcal./mole (k = 0·00166 min.$^{-1}$ at 79·75° and 0·0115 min.$^{-1}$ at 100·1°), agrees quite well with the value found in the presence of a stable

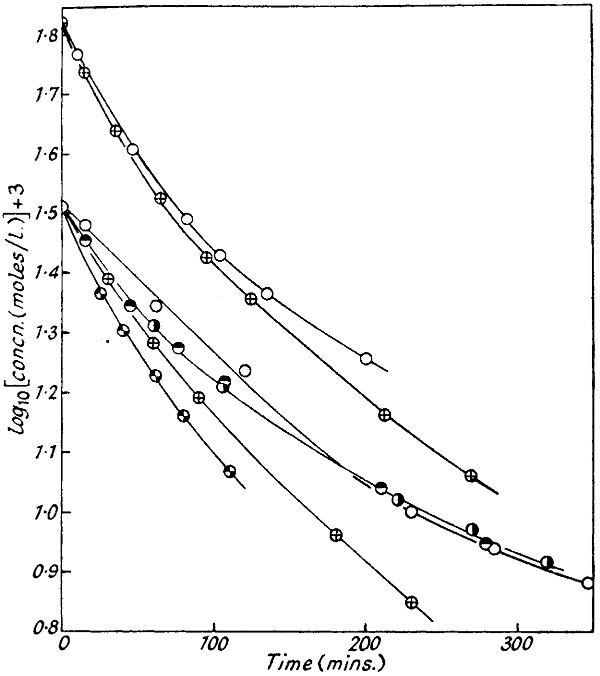

FIG. 4. *Effect of addition of water on the decomposition of benzoyl peroxide in acetic acid. Temp.* = 79·8°. *Initial concns.* = 6·71 × 10^{-2} *and* 3·30 × 10^{-2}M. N_2 *passed through solution.*

○, *dry acid as for curve* ○, *Fig.* 3.

Others : acetic acid–water.

◑, 6·1 *mole-%.*
◓, 11·7 *mole-%.*
⊕, 44·2 *mole-%.*
◍, 67·9 *mole-%.*

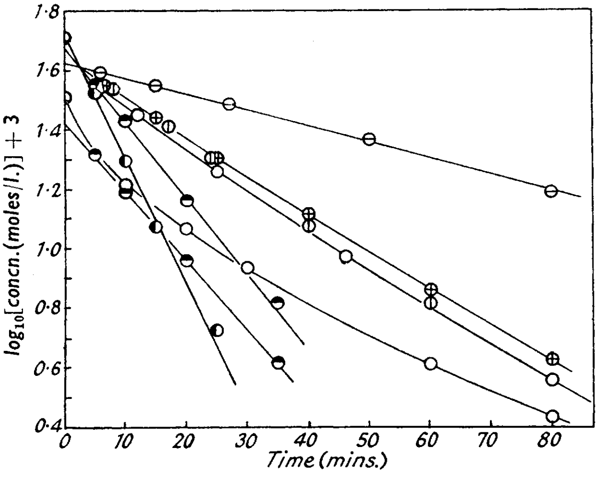

FIG. 5. *Decomposition of benzoyl peroxide in pyridine and pyridine–water. Temp.* = 79·7°. *Initial concns.* = 5·29 × 10^{-2} *and* 3·31 × 10^{-2}M.

N_2 *passed through solution :*

○, *pure pyridine.*
⦶, *pyridine containing products of decomposition.*
⊕, *pyridine* +15·6 *mole-%* H_2O.
◓, *pyridine* +53·0 *mole-%* H_2O.
◐, *pyridine* +74·7 *mole-%* H_2O.

O_2 *passed through solution :*

⊖, *pure pyridine.*

free radical in a number of solvents (Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216). At 100° the stability of the inhibitor seems to have been less than at 80°.

Since, when the acetic acid contained 67·9 mole-% of water, neither the purity of the acid nor the presence of oxygen had any marked effect on the rate of decomposition, and the solution never became more than faintly yellow, the water must largely have prevented the formation of the retarding product. The increase in the rate on the addition of water cannot have been entirely due to this because the initial rates were also increased.

The influence of water and oxygen on the rate of decomposition in pyridine is shown in Fig. 5. In dry pyridine and an atmosphere of nitrogen, after a short period the reaction became of nearly first order. A dark brown colour developed in the solution, but the rate was not affected by reaction products. Bartlett and Nozaki (*loc. cit.*) found a somewhat slower rate of decomposition, owing possibly to a difference in purity of the pyridine used. Oxygen retarded the decomposition, causing it to become of first order, probably for the same reason as in acetic acid. The overall activation energy, 31·9 kcal./mole ($k = 0{\cdot}0123$ min.$^{-1}$ at 79·65° and 0·155 min.$^{-1}$ at 100·4°), was again approximately that for unimolecular fission.

Addition of a small amount of water decreased the rate slightly, but a greater quantity increased it considerably, the overall reaction becoming of first order. The overall activation energy of decomposition in pyridine + 74·7 mole-% of water was 22·0 kcal./mole [Fig. 1(*a*)]. Under these conditions k decreased slightly, rather than increased, with increasing initial concentration ($k = 0{\cdot}125$, 0·112, and 0·112 min.$^{-1}$ for 0·0331, 0·0527, and 0·0870M-solutions respectively at 79·7°). Thus, although oxygen had a small retarding effect ($k = 0{\cdot}0927$ min.$^{-1}$ for a 0·0527M-solution), the value of 22·0 kcal. probably refers to a side reaction, rather than to any rapid chain decomposition.

It is unlikely that the increase in the rate of decomposition on the addition of water was due to an increased induced decomposition by solvent radicals, since the dissociation energy of the first O–H bond in water is very high, ~118 kcal. (Szwarz, *Chem. Reviews*, 1950, **47**, 75). Two other possibilities are that some ionic decomposition or hydrolysis of the peroxide in the presence of the acid or base was occurring :

$$[\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}}]_2 + \mathrm{H_2O} = \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}OH} + \mathrm{Ph{\cdot}CO_2H}\ *$$

If perbenzoic acid was formed it would have decomposed very rapidly at the temperatures used, probably giving a high proportion of benzoic acid, since at 0° Meyer (*J. Biol. Chem.*, 1933, **103**, 25) found that it was unstable in the presence of water and acids or pyridine. A study of the variation on addition of water, in the final yield of carbon dioxide and non-volatile acid, produced in the decomposition, and in the efficiency of the peroxide as a polymerisation catalyst, was made in the hope of finding whether the increase in rate was due to either possibility. It would be expected that any ionic decomposition would have led to a decrease in the polymer formed, whereas hydrolysis would probably have led to an increased yield of acid and a decreased yield of carbon dioxide. The following table shows the results. These do not conflict with those obtained by Barnett and Vaughan (*loc. cit.*) by using acetic acid, and by Overhoff and Tilman (*Rec. Trav. chim.*, 1929, **48**, 993) by using pyridine as solvent, since increase of temperature is known to lead to an increased yield of carbon dioxide. The very high yield of carbon dioxide in acetic acid, despite the high yield of non-volatile acid, suggests that acetoxy-radicals were formed from the solvent and decarboxylated to some extent on reaction.

Some hydrolysis was probably occurring in aqueous pyridine, and possibly the activation energy of 22·0 kcal. refers to this. If some ionic decomposition and hydrolysis were occurring in aqueous acetic acid, both of which caused a decrease in the carbon dioxide yield but influenced the acid yield in opposite direction, this might account for the results. On the other hand, the peroxide appeared to be, if anything, more efficient as a catalyst for the polymerisation of acrylonitrile in the aqueous acid. However, it can be said that, even

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* A referee has pointed out that other equilibria, *e.g.*,

$$[\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}}]_2 + \mathrm{AcOH} \rightleftharpoons \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}OAc} + \mathrm{Ph{\cdot}CO_2H}$$

might have occurred, giving other per-compounds, and might possibly explain the more anomalous decomposition rates.

under very favourable conditions, the amount of heterolytic fission of benzoyl peroxide was small. The increase in the rate of decomposition in aqueous acetic acid and pyridine was probably due to a combination of three factors—the partial suppression of the formation of a retarding secondary product, together with some hydrolysis and a little ionic decomposition. More elaborate methods are probably needed, however, to disentangle the complex side-reactions which seem to occur during the decomposition of the peroxide in many solvents.

			Yield of products :		
Temp.	Solvent	Initial concn. of Bz_2O_2, M	Moles CO_2/ mole Bz_2O_2	Equivs. acid/ mole Bz_2O_2	G. of polymer from solvent + 8 vol.-% acrylonitrile
100·0°	AcOH	0·0165	—	—	0·516
		0·0331	1·42	1·51	0·731
		0·0496	1·34	1·63	—
	AcOH + 67·9 mole-% H_2O	0·0165	—	—	0·659
		0·0331	1·19	1·55	0·783
		0·0496	1·12	1·50	—
79·7	C_5H_5N	0·0165	—	—	0·117
		0·0331	0·51	1·18	0·526
		0·0496	0·54	1·19	—
	C_5H_5N + 74·7 mole-% H_2O	0·0165	—	—	0·160
		0·0331	0·39	1·32	0·326
		0·0496	0·46	1·41	—

EXPERIMENTAL

An all-glass apparatus was used. A very slow stream of nitrogen or oxygen was passed through 25 ml. of peroxide solution, heated at constant temperatures (±0·05°) by the vapours of refluxing liquids. Samples were withdrawn at suitable intervals and analysed by Skellon and Wills's iodometric method (*Analyst*, 1948, **73**, 78). Blank titres were less than 0·1 ml.

B.D.H. Benzoyl peroxide was precipitated twice from hot chloroform solution by methanol. The dry product (m. p. 103·1—103·3°) released 98—99·5% of the theoretical amount of iodine from acidified potassium iodide. B.P. Phenol from freshly opened bottles was used directly or fractionally melted. Pyridine and benzyl alcohol were dried and fractionally distilled twice. "Analar" or analytical-grade acetic acid was used directly or fractionally distilled with 1% of acetic anhydride, and then sometimes fractionally frozen. The solvents contained <0·01—0·1% water determined by the Karl Fischer method as modified by Smith, Bryant, and Mitchell (*J. Amer. Chem. Soc.*, 1939, **61**, 2407). B.D.H. Acrylonitrile was distilled under a high vacuum and then redistilled before each experiment. Nitrogen from a cylinder was passed over red-hot copper and through a liquid-oxygen trap to remove oxygen, carbon dioxide, and water vapour. Oxygen from a cylinder was passed through a liquid-oxygen trap.

To estimate carbon dioxide and non-volatile acids formed in the decomposition, samples were not removed, and the issuing gases were passed through a calcium chloride tube, a phosphoric oxide tube and a soda-lime tube, until the weight of the last became constant. Blank experiments showed a very small increase in weight (<1 mg.) and this was allowed for. The final solutions were allowed to evaporate slowly, and the solids left were dried *in vacuo* over phosphoric oxide for 2 hours. Each dry product was taken up in 10 ml. of aclohol and titrated with 0·1N-sodium hydroxide with phenolphthalein as indicator. Parallel experiments with known amounts of benzoic acid showed that 94—95% was recovered in this way.

Solutions of benzoyl peroxide in 2 ml. of acrylonitrile and 23 ml. of solvent, in the presence of nitrogen, began to form fluffy insoluble polymer almost immediately. When decomposition of the peroxide was known to be complete, the mixture was transferred to a beaker and 25—50 ml. of water were added. The polymer was filtered off through a sintered-glass crucible, washed thoroughly with water, and dried to constant weight at 100°.

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