# 560. *Aroyl Peroxides. Part I. The Decomposition of Benzoyl Peroxide in Alkylbenzenes.*

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The kinetics and products of the reactions of benzoyl peroxide with isopropylbenzene, ethylbenzene, and *p*-xylene have been studied over a range of initial peroxide concentrations. Reactions of order 1 and 1·5 occur simultaneously in all three solvents, corresponding to primary and induced decomposition of the peroxide. A mechanism for the reaction of benzoyl peroxide with alkylbenzenes is suggested, which is consistent with the kinetics and the products of the reactions. The most important reaction of chain propagation in the induced decomposition is the reaction of the σ-complex formed by addition of phenyl radicals to the nucleus of the alkylbenzene with benzoyl peroxide.

THE decomposition of benzoyl peroxide in aromatic solvents has been widely used as a source of phenyl radicals for the quantitative study of the homolytic phenylation of aromatic compounds.[1] However, although the kinetics of the decomposition have been studied, considerable uncertainty still exists concerning certain features of its mechanism.

A detailed examination of the kinetics of this reaction was made by Nozaki and Bartlett [2] who studied it in a number of aliphatic, and some aromatic, solvents and subjected the results to kinetic analysis. It was shown that, in addition to the unimolecular dissociation of the peroxide, there also took place a chain decomposition induced by radicals formed directly from the peroxide or by interaction of these radicals with the solvent. This conclusion was supported by the subsequent work of Barnett and Vaughan [3]

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[1] Hambling, Hey, and Williams, *J.*, 1962, 487, and earlier papers in that series.

[2] Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686; 1947, **69**, 2299.

[3] Barnett and Vaughan, *J. Phys. Chem.*, 1947, **51**, 926.

and of Cooper.[4] Nozaki and Bartlett also found that the induced decomposition was a reaction of order approximately 1·5, and that the total rate-equation was of the form:

$$-\mathrm{d}[\mathrm{P}]/\mathrm{d}t = k_1[\mathrm{P}] + k_{3/2}[\mathrm{P}]^{3/2}, \qquad (1)$$

where P is the peroxide, and $k_1$ and $k_{3/2}$ are first- and 1·5-order rate constants, respectively. It was also indicated that the induced decomposition, which was considered to contribute the second term to equation (1), was the main cause of the variation in the total rate of decomposition from one solvent to another, and that these rates varied in the following order: highly halogenated solvents $<$ most aromatics $<$ most aliphatics $<$ ethers, alcohols, monohydric phenols $<$ amines. While the induced decomposition was less important in the aromatic solvents investigated than in most other solvents, its contribution is still considerable, and its mechanism of great interest.

This kinetic picture of the reaction has been supported by measurements of the kinetics of the primary decomposition of benzoyl peroxide under conditions where chain reactions were inhibited by the use of " radical-traps " of various kinds.[5,6] The values of $k_1$ obtained in this way for the decomposition in several solvents agree reasonably well with those obtained from the study of the uninhibited reaction,[2,3,7] although the range of aromatic solvents studied was again not large.

It is therefore clear that free radicals are formed from benzoyl peroxide both by the unimolecular dissociation (2),

$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}Ph} \longrightarrow \mathrm{2Ph{\cdot}CO{\cdot}O{\cdot}} \qquad (2)$$

$$\mathrm{R'{\cdot}} + \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}Ph} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} + \text{Products} \qquad (3)$$

and by an induced decomposition (3). Such a process can contribute a term in $[\mathrm{P}]^{3/2}$ to the rate-equation under certain conditions of chain-termination. Various suggestions have been made from time to time concerning the nature of the radical R'• which takes part in reaction (3). Nozaki and Bartlett, for example, suggested that this radical was formed either directly from the decomposition of the peroxide, or by reaction of such a radical with the solvent. Augood and Williams,[8] however, pointed out that the formation of " solvent-radicals " by hydrogen abstraction from the *nuclei* of aromatic solvents is incompatible with the known products of these reactions.

It is therefore clear that a completely satisfactory mechanism for this reaction can be advanced only as the result of examination both of the reaction kinetics and of the products. The alkylbenzenes are particularly suited to such an investigation, since it has been clearly demonstrated that benzyl-type " solvent radicals " are formed from them by hydrogen-abstraction from their side-chains, and that these benzyl-type radicals undergo dimerisation to give easily identified products.[9-11] This dimerisation is unequivocally a chain-termination, and a knowledge of the extent to which it occurs is of great assistance in the interpretation of the kinetics.

The only alkylbenzene in which the decomposition of benzoyl peroxide has hitherto been subjected to detailed kinetic study is isopropylbenzene. This system was studied by Bailey and Godin [12] who confirmed that the kinetics were of the form expressed by equation (1). These measurements have now been repeated at one temperature, since discrepancies have previously been observed in various workers's estimates of $k_1$ and $k_{3/2}$ for the same solvent. Our results, however, agree with those obtained by Bailey and

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[4] Cooper, *J.*, 1951, 3106; 1952, 2408.
[5] Swain, Stockmayer, and Clarke, *J. Amer. Chem. Soc.*, 1950, **72**, 5426.
[6] Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216.
[7] Hartmann, Sellers, and Turnbull, *J. Amer. Chem. Soc.*, 1947, **69**, 2416.
[8] Augood and Williams, *Chem. Rev.*, 1957, **57**, 123.
[9] Dannley and Zaremsky, *J. Amer. Chem. Soc.*, 1955, **77**, 1588.
[10] Rondestvedt and Blanchard, *J. Amer. Chem. Soc.*, 1955, **77**, 1769; *J. Org. Chem.*, 1956, **21**, 229.
[11] Hey, Pengilly, and Williams, *J.*, 1956, 1463.
[12] Bailey and Godin, *Trans. Faraday Soc.*, 1956, **52**, 68.

Godin. We have also examined the kinetics of the decomposition in ethylbenzene and *p*-xylene and obtained values of $k_1$ and $k_{3/2}$ for these solvents which had not previously been studied. In addition, we have studied in detail the products of the reactions in isopropylbenzene and *p*-xylene, and the variation of the yield of the various products with initial peroxide concentration; also, in rather less detail, the products of the reaction in ethylbenzene. As a result, some suggestions concerning the mechanism of the reaction, which accommodate the main features of both the kinetics and the product distribution, can now be made.

## EXPERIMENTAL METHODS

*Kinetics.*—Before each experiment, the solvent was freed from dissolved oxygen by boiling it under reflux in a stream of oxygen-free nitrogen. It was then passed through activated alumina to remove any autoxidation products. Reactions were conducted under dry oxygen-free nitrogen (to prevent autoxidation of the solvents), in vessels equipped with reflux condensers and immersed in a thermostat-bath at 80°. Samples of the appropriate size (1—10 ml.) were withdrawn at intervals and their peroxide contents determined iodometrically. Each peroxide estimation was carried out in quadruplicate, and each run was duplicated. Satisfactory agreement was obtained among the results of the several determinations.

Apparent first-order rate constants ($k_{1(\text{obs.})}$) were obtained from the initial slopes of graphs of the logarithm of the peroxide concentration against time. These graphs were good straight lines for about two half-lives but, owing to the incursion of a reaction of higher order (the induced decomposition), deviated slightly from linearity towards the end of the reactions. Graphs were then plotted of $k_{1(\text{obs.})}$ against the square root of the initial peroxide concentration $[\text{P}]_0$. The slopes of these lines gave $k_{3/2}$, and the intercepts at $[\text{P}]_0 = 0$ gave $k_1$, since, from equation (1),

$$k_{1(\text{obs.})} = k_1 + k_{3/2}[\text{P}]_0^{1/2}. \tag{4}$$

The results obtained with the three solvents are given in Table 1, and derived rate constants are summarised in Table 2.

*Reaction Products.*—*Isopropylbenzene.* Benzoyl peroxide, at various initial concentrations, was allowed to decompose in isopropylbenzene under nitrogen, in a thermostat-bath at 80°, for 72 hr. The pale yellow reaction mixtures, after cooling, were extracted with saturated aqueous sodium hydrogen carbonate (4 × 50 ml.). The combined extracts were washed with a little isopropylbenzene, which was added to the organic layer. The alkaline extract was acidified with concentrated hydrochloric acid and extracted with methylene chloride (4 × 20 ml.). The resulting extract was dried ($MgSO_4$), filtered, and allowed to evaporate at room temperature, and the residual benzoic acid (m. p. 119—120°) was weighed.

TABLE 1.

Rate of decomposition of benzoyl peroxide in alkylbenzenes at 80·0°.

| $[P]_0$ (mole l.$^{-1}$) | $[P]_0^{1/2}$ (mole$^{1/2}$ l.$^{-1/2}$) | $10^5k_{1\,(\text{obs.})}$ (sec.$^{-1}$) | $[P]_0$ (mole l.$^{-1}$) | $[P]_0^{1/2}$ (mole$^{1/2}$ l.$^{-1/2}$) | $10^5k_{1\,(\text{obs.})}$ (sec.$^{-1}$) | $[P]_0$ (mole l.$^{-1}$) | $[P]_0^{1/2}$ (mole$^{1/2}$ l.$^{-1/2}$) | $10^5k_{1\,(\text{obs.}}$ (sec.$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| Isopropylbenzene | | | Ethylbenzene | | | *p*-Xylene | | |
| 0·168 | 0·410 | 5·75 | 0·181 | 0·425 | 5·95 | 0·168 | 0·410 | 4·78 |
| 0·138 | 0·372 | 5·45 | 0·138 | 0·372 | 5·45 | 0·138 | 0·371 | 4·40 |
| 0·111 | 0·333 | 5·11 | 0·099 | 0·314 | 4·90 | 0·104 | 0·322 | 4·14 |
| 0·082 | 0·286 | 4·72 | 0·070 | 0·264 | 4·45 | 0·070 | 0·265 | 3·69 |
| 0·064 | 0·252 | 4·35 | 0·048 | 0·218 | 3·95 | 0·054 | 0·233 | 3·41 |
| 0·048 | 0·220 | 4·00 | 0·035 | 0·186 | 3·65 | 0·035 | 0·187 | 3·10 |
| 0·029 | 0·170 | 3·50 | 0·020 | 0·140 | 3·15 | | | |
| 0·020 | 0·142 | 3·34 | | | | | | |

TABLE 2.

Rate-constants for the decomposition of benzoyl peroxide in alkylbenzenes at 80·0°.

| Solvent | $10^5k_1$ (sec.$^{-1}$) | $10^5k_{3/2}$ (mole$^{-1/2}$ l.$^{1/2}$ sec.$^{-1}$) |
|---|---|---|
| Isopropylbenzene | 1·95 | 9·50 |
| Ethylbenzene | 1·85 | 9·63 |
| *p*-Xylene | 1·75 | 7·25 |

The organic layer from the alkaline extraction was fractionally distilled, the first 20 ml. of distillate were collected and weighed, and its benzene content was determined by gas–liquid chromatography (in a Perkin–Elmer model 166 vapour fractometer). Nitrogen was used as carrier gas, and internal normalisation was used for the analysis of all mixtures except those containing less than 0·5% of benzene, for which it was inaccurate. For these mixtures, the instrument was calibrated with known mixtures of benzene and isopropylbenzene. All analyses by the method of internal normalisation were checked by the analysis of a synthetic mixture of the same composition as that of the unknown mixture as determined by this method. The results were thus found to be reliable to ±1·5—2%.

The remainder of the solvent was removed by fractional distillation, the column washed with ether, and the washings were added to the remaining high-boiling products. After evaporation of the ether, the high-boiling products were boiled under reflux with 2N-aqueous sodium hydroxide (100 ml.) for 18 hr. in order to hydrolyse esters. The warm mixture was extracted with benzene (3 × 30 ml.), and the combined extracts were washed with 2N-sodium hydroxide (2 × 30 ml.) and water (30 ml.), and dried ($MgSO_4$). After acidification by hydrochloric acid, the combined aqueous extracts were neutralised with solid sodium hydrogen carbonate. The resulting solution was boiled to coagulate the precipitate of gelatinous silicic acid, which resulted from attack by the alkali on the glass vessel during the hydrolysis of esters, and filtered through a hot funnel. The cold filtrate was extracted with ether (2 × 25 ml.) and the extracts, which contained phenols, were rejected. The aqueous layer, after acidification with hydrochloric acid was extracted with methylene chloride (4 × 30 ml.), and the extracts were dried ($MgSO_4$), filtered, and allowed to evaporate. The residue, after drying in a vacuum-desiccator, had m. p. ~114° (undepressed on admixture with benzoic acid).

The solvent was removed by fractional distillation from the benzene extracts obtained after ester-hydrolysis, and the column was washed with ether. The washings were added to the residue, which was transferred to a weighed semimicro-distillation flask packed with glass wool, with benzene as wash-liquid. The volatile solvents were removed at atmospheric pressure, and fractions, b. p. 20—50°/0·05 mm. (the forerun) and 50—120°/0·05 mm. (the binuclear fraction) were collected. The remaining involatile residue was weighed. Analysis of the forerun by gas–liquid chromatography showed it to consist of isopropylbenzene, together with very small amounts of α-methylstyrene and acetophenone, both of which may have been formed by autoxidation of isopropylbenzene.[10] The composition of the binuclear fractions was determined by precipitation of most of the 2,3-dimethyl-2,3-diphenylbutane (bicumyl) with cold nitromethane, and infrared spectrography of the nitromethane solutions, as described by Hey, Pengilly, and Williams.[11] This method was supplemented in some cases by analysis of the entire binuclear fraction by gas–liquid chromatography, through heated columns, with heated syringes for the injection of the solid samples or known mixtures thereof with biphenyl as diluent, in the fused state. Internal normalisation was used, and its reliability (±2%) checked by the analysis of synthetic mixtures of known composition. The results obtained by the two methods agreed well. The composition of the mixtures of isomeric isopropylbiphenyls (2-, 30 ± 2; 3-, 42 ± 2; 4-, 28 ± 2%) was, within experimental error, independent of the initial peroxide concentration, and agreed well with that obtained by Hey, Pengilly, and Williams.[11] These results are therefore not given in detail.

Attempts were made to estimate the composition of the mixtures of esters formed in these reactions. For these experiments, the hydrolysis stage was omitted from the procedure described above, and the esters were distilled with the binuclear fraction (b. p. 50—130°/0·05 mm.). However, it was impossible to separate the esters from the other components of this mixture by gas–liquid chromatography. A fraction containing most of the esters was, however, obtained by chromatography on alumina, and infrared spectrographic analysis of this fraction showed it to consist mainly of the isomeric isopropylphenyl benzoates.

The possible presence of α-cumyl benzoate among the reaction products was therefore investigated as follows. Benzoyl peroxide (10 g.) was allowed to decompose in isopropylbenzene (200 ml.) as previously described. Oxygen was rigorously excluded at all stages of the reaction and subsequent working-up, by carrying out all the operations under nitrogen. After removal of the excess of solvent and free benzoic acid, the residue was boiled under reflux for 18 hr. with 8% aqueous sodium hydroxide (100 ml.). After cooling and separation, the organic layer was washed with water (3 × 40 ml.) and boiled under reflux for 2 hr. with 10% hydrochloric acid (100 ml.). The aqueous layer was removed, and the organic layer washed with water and dried ($MgSO_4$). It was then fractionally distilled, and the fraction of b. p. 40—80°/20 mm. collected. Gas–liquid chromatography of this fraction showed it to be a mixture of isopropylbenzene and α-methylstyrene, the presence of which was confirmed by treatment with a solution of bromine in chloroform in the dark to give αβ-dibromo-α-methylstyrene, b. p. 138°/15 mm., having the correct infrared spectrum. The presence of α-methylstyrene at this stage is probably due to the dehydration of 1-methyl-1-phenylethanol resulting from the hydrolysis of α-cumyl benzoate, since its formation by autoxidation of isopropylbenzene is very unlikely under the conditions of this experiment.

For the reasonably accurate estimation of the free benzoic acid formed in these reactions, a series of runs, at varying initial peroxide concentrations, was carried out as previously described. Aliquot parts of the resulting mixtures were then added to ethanol (20 ml.) and titrated against a standard solution of sodium hydroxide in ethanol–water (1 : 1) with Thymol Blue as indicator. A blank titration was performed with each titration for benzoic acid. The sodium hydroxide solution was standardised against benzoic acid in isopropylbenzene, by the same procedure. The results showed that the molar yield of benzoic acid was almost independent of the initial peroxide concentration, except at very high and very low initial peroxide concentrations; however, especially at low concentrations, the reality of this effect is doubtful as, under these conditions, the analytical results are subject to rather large errors.

*Ethylbenzene.* These experiments were carried out, and the products isolated, as described for the reactions with isopropylbenzene. The binuclear fractions, which consisted of the isomeric ethylbiphenyls, *meso*- and (±)-2,3-diphenylbutane, were analysed by removal of the insoluble *meso*-2,3-diphenylbutane by treatment of the mixture with nitromethane, and infrared spectrographic analysis of the resulting mixture as described by Hey, Pengilly, and Williams.[11] The accuracy of the method was checked by the analysis of synthetic mixtures of known composition, the results being reliable to ±2%. The composition of the mixture of ethylbiphenyls was independent of the initial peroxide concentration, within experimental error, and the results (mean values: 2-, 51; 3-, 28; 4-, 21%) were in good agreement with those obtained by the previous workers.

A very small amount (~0·01 mole per mole of peroxide) of acetophenone was also obtained, as a forerun to the binuclear fraction. This may have been formed by autoxidation of ethylbenzene, but its yield was negligible.

Benzoic acid was estimated as previously described, but benzene was not estimated nor was the composition of the mixture of esters studied.

p-*Xylene.*—This solvent was chosen for detailed investigation since nuclear substitution gives a single product, and analysis is therefore simpler.

The reactions were conducted and the products worked up as described for the reactions with isopropylbenzene, except that the hydrolysis stage was omitted, and the esters were distilled with the binuclear fraction (b. p. 40—120°/0·05 mm.). This fraction was then shown by gas–liquid chromatography to contain only 4,4′-dimethylbibenzyl, 2,5-dimethylbiphenyl, 4-methylbenzyl benzoate, and 2,5-dimethylphenyl benzoate. A specimen of 4-methylbenzyl benzoate was isolated from the binuclear fraction obtained from the products of a reaction of benzoyl peroxide (6 g.) with *p*-xylene (200 ml.) by chromatography on alumina. The infrared spectrum of this specimen, and its retention time in a gas–liquid chromatogram, were identical with those of an authentic specimen.

In all the reactions with *p*-xylene, a very small amount (~0·01 mole per mole of peroxide) of *p*-methylbenzaldehyde was formed, probably by autoxidation of the solvent. It was obtained as a forerun to the binuclear fraction.

Benzene and benzoic acid were estimated as previously described. Their yields varied only slightly with the initial peroxide concentration, except at very low peroxide concentrations.

Yields of the various products per mole of benzoyl peroxide obtained at various concentrations of the peroxide in the three solvents are given in Tables 3—6. Since good agreement was obtained between the results of duplicate experiments, only one set of results for each concentration is given in Tables 3—5, which also contain values of the sums of the yields of some of the products, and of a quantity "*f*". The significance of these quantities is discussed in the following section.

*Purification of Materials.*—Isopropylbenzene, ethylbenzene, and *p*-xylene were shaken with successive portions of concentrated sulphuric acid until the washings were colourless, washed with saturated aqueous sodium hydrogen carbonate, then water, and dried ($MgSO_4$). They

TABLE 3.

Molar yields of products of decomposition of benzoyl peroxide in isopropylbenzene.

| $[P]_0$ (mole $l.^{-1}$) | Bicumyl | Isopropyl-biphenyls | Residue (as di-isopropyltetra-hydroquaterphenyl) | Esters | $(a + c)$ | $(a + \frac{1}{2}b + c + \frac{1}{2}d)$ | $f$ |
|---|---|---|---|---|---|---|---|
| | (*a*) | (*b*) | (*c*) | (*d*) | | | |
| 0·008 | 0·68 | 0·26 | 0·042 | — | 0·72 | 0·83 | 0·780 |
| 0·010 | 0·68 | 0·26 | 0·042 | — | 0·72 | 0·83 | 0·760 |
| 0·016 | 0·66 | 0·26 | 0·018 | — | 0·68 | 0·81 | 0·715 |
| 0·020 | 0·60 | 0·24 | 0·042 | — | 0·64 | 0·74 | 0·690 |
| 0·028 | 0·57 | 0·25 | 0·061 | — | 0·63 | 0·76 | 0·660 |
| 0·040 | 0·51 | 0·24 | 0·092 | 0·07 | 0·60 | 0·75 | 0·620 |
| 0·055 | 0·46 | 0·24 | 0·111 | 0·08 | 0·57 | 0·73 | 0·585 |
| 0·060 | 0·47 | 0·24 | 0·160 | 0·08 | 0·63 | 0·79 | 0·575 |
| 0·080 | 0·42 | 0·23 | 0·166 | 0·09 | 0·59 | 0·75 | 0·540 |
| 0·124 | 0·37 | 0·24 | 0·184 | 0·10 | 0·55 | 0·72 | 0·485 |
| 0·150 | 0·35 | 0·23 | 0·184 | 0·10 | 0·53 | 0·70 | 0·465 |
| 0·188 | 0·34 | 0·23 | 0·196 | 0·12 | 0·54 | 0·71 | 0·440 |
| 0·219 | 0·30 | 0·22 | 0·221 | 0·13 | 0·52 | 0·70 | 0·425 |
| 0·274 | 0·29 | 0·22 | 0·196 | 0·16 | 0·49 | 0·68 | 0·400 |
| 0·284 | 0·30 | 0·23 | 0·246 | 0·17 | 0·55 | 0·69 | 0·395 |
| 0·329 | 0·27 | 0·22 | 0·221 | 0·19 | 0·49 | 0·70 | 0·375 |
| 0·439 | 0·23 | 0·22 | 0·239 | 0·24 | 0·47 | 0·70 | 0·335 |

TABLE 4.

Molar yields of products of decomposition of benzoyl peroxide in ethylbenzene.

| | | |
|---|---|---|
| $[P_0]$ (mole $l.^{-1}$) | 0·021 | 0·124 |
| 2,3-Diphenylbutane (*a*) | 0·43 | 0·27 |
| Ethylbiphenyls (*b*) | 0·37 | 0·39 |
| Residue (as diethyltetrahydro-quaterphenyl) (*c*) | 0·09 | 0·16 |
| Esters (*d*) | 0·09 | 0·19 |
| $(a + c)$ | 0·52 | 0·43 |
| $(a + b/2 + c + d/2)$ | 0·75 | 0·72 |
| $f$ | 0·675 | 0·471 |

TABLE 5.

Molar yields of products of decomposition of benzoyl peroxide in *p*-xylene.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $[P_0]$ (mole $l.^{-1}$) | 0·010 | 0·015 | 0·025 | 0·033 | 0·050 | 0·074 | 0·099 |
| 4,4′-Dimethylbibenzyl (*a*) | 0·66 | 0·59 | 0·54 | 0·49 | 0·43 | 0·40 | 0·37 |
| 2,5-Dimethylbiphenyl (*b*) | 0·31 | 0·32 | 0·32 | 0·31 | 0·32 | 0·32 | 0·31 |
| Residue (as tetrahydrotetramethyl-quaterphenyl) (*c*) | 0·06 | 0·07 | 0·06 | 0·11 | 0·10 | 0·11 | 0·12 |
| 4-Methylbenzyl benzoate | 0·04 | 0·04 | 0·06 | 0·10 | 0·12 | 0·15 | 0·16 |
| 2,5-Dimethylphenyl benzoate (*d*) | 0·04 | 0·03 | 0·04 | 0·05 | 0·05 | 0·04 | 0·05 |
| $(a + c)$ | 0·72 | 0·66 | 0·60 | 0·60 | 0·53 | 0·51 | 0·49 |
| $(a + b/2 + c + d/2)$ | 0·89 | 0·84 | 0·78 | 0·78 | 0·71 | 0·69 | 0·67 |
| $f$ | 0·791 | 0·760 | 0·720 | 0·685 | 0·635 | 0·580 | 0·550 |

TABLE 6.

Molar yields of benzene and benzoic acid formed in reactions of benzoyl peroxide with alkylbenzenes.

| Alkylbenzene | Benzoic acid (mole/mole of peroxide) | Benzene (mole/mole of peroxide) |
|---|---|---|
| Isopropylbenzene | 0·52 | 0·51 |
| Ethylbenzene | 0·50 | Not measured |
| *p*-Xylene | 0·82 | 0·42 |

were then fractionally distilled over sodium at atmospheric pressure (b. p.s 153°, 135·5°, and 138°, respectively). Isopropylbenzene and ethylbenzene were redistilled over sodium, and *p*-xylene was further purified by fractional freezing. The solvents were stored in the dark over sodium, and their purities checked by gas–liquid chromatography before use.

Benzoyl peroxide was purified as described by Augood, Hey, and Williams,[14] and nitromethane as described by Augood, Cadogan, Hey, and Williams.[15]

*Reference Compounds.*—2,3-Dimethyl-2,3-diphenylbutane and *meso*- and (±)-2,3-diphenylbutane were prepared by Johnston and Williams's method.[16] 4,4′-Dimethylbibenzyl, prepared by the same method, had m. p. 83° (Found: C, 91·2; H, 8·7. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·57%).

2- and 3-Isopropenylbiphenyl were prepared from 2-iodo- and 3-bromo-biphenyl, respectively, by Mowry, Dazzi, Renoll, and Shortridge's method.[17] The products were hydrogenated in acetic acid with Adams platinum oxide, to give 2- and 3-isopropylbiphenyl. The 2-isomer had b. p. 82°/0·05 mm. and $n_D^{20}$ 1·5692 (Goodman and Wise [18] reported $n_D^{20}$ 1·5703) (Found: C, 91·35; H, 8·4. Calc. for $C_{15}H_{16}$: C, 91·8; H, 8·2%). The 3-isomer had b. p. 90°/0·15 mm., and $n_D^{20}$ 1·5800 (Hey, Pengilly, and Williams [11] reported b. p. 80°/0·1 mm. and $n_D^{20}$ 1·5807) (Found: C, 92·0; H, 8·0%).

4-Isopropylbiphenyl was prepared by Hey, Pengilly, and Williams's method.[11]

Specimens of 2-, 3- and 4-ethylbiphenyl, and 2,5-dimethylbiphenyl were kindly presented by Professor D. H. Hey.

4-Methylbenzyl benzoate, 2,5-dimethylphenyl benzoate, and 2- and 4-isopropylphenyl benzoate were prepared by standard methods.

## DISCUSSION

The kinetic results indicate that the decomposition of benzoyl peroxide in alkylbenzenes is similar to the reaction in a number of other solvents insofar as induced decomposition of the peroxide occurs, to an appreciable extent, by a mechanism which leads to 1·5-order kinetics. It is this induced decomposition which contributes the second term to equation (1). The first term of this equation, representing the first-order reaction, is generally considered to be contributed by the reaction of primary fission of benzoyl peroxide into two benzoyloxy-radicals, as in equation (2), although it is also possible for an induced decomposition to give rise to a first-order law, if chain-termination occurs by combination of two dissimilar radicals, *e.g.*,

$$R\cdot + S\cdot \longrightarrow \text{Products} \qquad (5)$$

The more usual termination reactions, namely those of the type

$$2R\cdot \longrightarrow \text{Products} \qquad (6)$$

give rise to 1·5-order kinetics. It is only in the absence of reactions of the type of (5) that the measured value of $k_1$ can truly be said to represent the rate of primary fission of the peroxide.

The comparative unimportance of reactions of this type in the decomposition in alkylbenzenes at the concentrations studied is inferred from the good agreement between the values of $k_1$ now reported and the rate-constants for the primary decomposition of benzoyl peroxide in benzene and toluene reported by Bawn and Mellish.[6] The latter values were obtained by the use, as a radical-trap, of *NN*-diphenylpicrylhydrazyl, which inhibits all radical-induced reactions, whatever their kinetic order. Admittedly, these results refer to different solvents, but, as Nozaki and Bartlett [2] pointed out, the rate of primary fission depends only to a small extent on the nature of the solvent, as would indeed be expected for homolysis. Comparison of these results is therefore permissible. Moreover, preliminary experiments on the reaction in *p*-xylene in the presence of inhibitors [19] indicate that the rate constant for the primary fission of benzoyl peroxide in this solvent is not lower than the value of $k_1$ reported in this paper.

[13] Overhoff and Tilman, *Rec. Trav. chim.*, 1929, **48**, 993.
[14] Augood, Hey, and Williams, *J.*, 1952, 2094.
[15] Augood, Cadogan, Hey, and Williams, *J.*, 1953, 3412.
[16] Johnston and Williams, *J.*, 1960, 1168.
[17] Mowry, Dazzi, Renoll, and Shortridge, *J. Amer. Chem. Soc.*, 1948, **70**, 1916.
[18] Goodman and Wise, *J. Amer. Chem. Soc.*, 1950, **72**, 3076.
[19] Gill and Williams, unpublished work.

It is therefore concluded that termination reactions of type (5) occur only to a small extent, if at all, in the reaction in alkylbenzenes. It would, however, be unwise to draw the same inference for all aromatic solvents and, indeed, there is evidence that reaction (5) makes an appreciable contribution to the total reaction in some such solvents.[19]

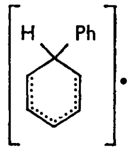
From the measured values of $k_1$ and $k_{3/2}$ for a given solvent, it is possible to calculate the proportion of the total amount of peroxide which decomposes by the primary and induced reactions [(2) and (3), respectively], at any initial peroxide concentration, since the fraction $f$ of the initial molar concentration of the peroxide which decomposes by primary fission is given by

$$f = 2\{K[P]_0^{1/2} - \ln(1 + K[P]_0^{1/2})\}/K^2[P]_0, \tag{7}$$

where $K = k_{3/2}/k_1$, and $[P]_0$ is the initial peroxide concentration.[20] Since, in the reaction of induced decomposition (3), one radical is consumed for each radical formed, the number of radicals consumed in termination reactions must equal the number formed by primary fission of the peroxide. The fission of each molecule of peroxide gives two radicals, and it follows that the molar yield of termination products is either equal to or double the fraction $f$, according as these products are formed by combination or by disproportionation of radicals.

The dimerisation of the benzyl-type radicals formed by α-hydrogen abstraction from the side-chains of alkylbenzenes is a termination of the first type, and the molar yield of its product (the dehydrogeno-dimer) may therefore be compared with $f$. This is done in Tables 3—5.

These Tables show that the dehydrogeno-dimers (*a*) form a substantial proportion of the total termination products, but that they are not the only termination products since their molar yield is consistently lower than the fraction $f$. It has been shown [21, 22] that the high-boiling residues obtained in reactions of benzoyl peroxide with aromatic solvents contain a substantial proportion of derivatives of quaterphenyl and tetrahydroquaterphenyl. The former compound is probably formed from the latter by oxidation, perhaps by air during the working-up. Tetrahydroquaterphenyl derivatives are thought to be formed by dimerisation of the primary radical adduct of a phenyl radical to the aromatic nucleus. These adducts, or " σ-complexes " have been shown [23, 24] to be intermediates in the phenylation of aromatic compounds and have been formulated as derivatives of the phenylcyclohexadienyl radical (I). This interpretation of the nature of the residues leads to the conclusion that, to the extent that they consist of quaterphenyl derivatives, they must be regarded as termination products. The exact composition of the residues is not known, and its determination presents great experimental difficulties. It has been assumed, therefore, in calculating this molar yield, that the residues consist entirely of the appropriate derivatives of tetrahydroquaterphenyl. This is certainly an overestimate, as similar residues obtained in reactions with other aromatic compounds are known to contain esters as well as terphenyl derivatives arising from further phenylation of the biaryls formed as primary products. [This is probably the reason why the sum of the molar yields of dehydrogeno-dimers (*a*) and residues (*c*) exceeds the fraction $f$ in some of the reactions with isopropylbenzene, namely, those in which benzoyl peroxide was present in very high concentration, when polyphenylation and other side-reactions would be expected to occur to the greatest extent.] This approximation does not, however, affect the validity



(I)

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[20] Godin, personal communication.

[21] Lynch and Pausacker, *Austral. J. Chem.*, 1957, **10**, 40, 165.

[22] De Tar and Long, *J. Amer. Chem. Soc.*, 1958, **80**, 4742; Hey, Perkins, and Williams, unpublished work.

[23] Milyutinskaya, Bagdasaryan, and Izraelevich, *J. Phys. Chem. S.S.S.R.*, 1957, **31**, 1019; Convery and Price, *J. Amer. Chem. Soc.*, 1958, **80**, 4101; Chang, Hey, and Williams, *J.*, 1959, 1871.

[24] Williams, " Homolytic Aromatic Substitution," Pergamon Press Ltd., London, 1960.

of the argument, as the same qualitative conclusions may be reached if the residues are disregarded. The nature of these residues is further considered later in this discussion.

Apart from the reactions in isopropylbenzene with high concentrations of benzoyl peroxide, it is clear from Tables 3—5 that the combined yields of dehydrogeno-dimers and residues are not sufficient to account for the total yield of termination products predicted from the rate-constants (the fraction *f*), although the discrepancy is fairly small.

It is also possible that the products of phenylation and benzoyloxylation of the solvents are formed in termination reactions, from the intermediate σ-complexes. Oxidation of these intermediates by benzoyloxy-radicals (8) obviously lead to the formation of biaryls,

$$[\mathrm{PhArH}]\cdot + \mathrm{Ph{\cdot}CO{\cdot}O}\cdot \longrightarrow \mathrm{PhAr} + \mathrm{Ph{\cdot}CO_2H} \qquad (8)$$

and this has been suggested [24] as a possible mode of formation of these compounds. Such a process is, however, a termination of type (5) and as such, as indicated above, can occur in the present reactions in alkylbenzenes only to a small extent. An alternative termination reaction which leads to the formation of biaryls is one of type (6), namely, reaction (9), and this process is consistent with the kinetics. In this reaction, dihydrobiaryls are formed, together with biaryls by disproportionation of the intermediate σ-complex.

$$2[\mathrm{PhArH}]\cdot \longrightarrow \mathrm{PhAr} + \mathrm{PhArH_2} \qquad (9)$$

Dihydrobiphenyl has been isolated from the products of the reaction of benzoyl peroxide with benzene, when this reaction was conducted under conditions of low concentration, and in the absence of air,[22] and reaction (9) is therefore an obvious possibility. Since no dihydrobiaryls were isolated from the products of the present reactions, it must be assumed that any such compounds formed are oxidised to biaryls, possibly by benzoyl peroxide, or by air during the working-up of the products. It is therefore suggested that (9) is the most important termination reaction which leads to the formation of biaryls in alkylbenzenes, although the possibility that (8) makes a small contribution cannot be entirely eliminated owing to the relative insensitivity of the kinetic test for its absence. Since (9) is a reaction of disproportionation, two molecules of the products are formed from each pair of radicals, and its molar yield (of biaryls) (*b*) must therefore be halved for comparison with the fraction *f*. However, some allowance must also be made for the phenolic esters formed by benzoyloxylation of the solvents, a process which is closely analogous to phenylation and, it is reasonable to assume, follows a similar mechanism. In the case of *p*-xylene, where only one ester is formed in this way, it was possible to determine the amount of this ester (2,5-dimethylphenyl benzoate) present in the ester fraction. Half of the molar yield of this ester (*d*) may therefore be included in the above sum. When this is done, in every case the resultant sum ($a + 1/2b + c + 1/2d$) exceeds *f* by a considerable margin (cf. Table 5). We conclude that, in this solvent, most of the biaryl and phenolic ester must be formed in a reaction other than one of chain-termination, that is, in a chain-transfer reaction in which a new radical is formed for each radical consumed. The most reasonable reaction of this type is (10), which represents the oxidation of the σ-complex by a benzoyl peroxide molecule. We conclude that this reaction is a major contributor to the induced decomposition of benzoyl peroxide in *p*-xylene.

$$[\mathrm{PhArH}]\cdot + (\mathrm{Ph{\cdot}CO{\cdot}O})_2 \longrightarrow \mathrm{PhAr} + \mathrm{Ph{\cdot}CO_2H} + \mathrm{Ph{\cdot}CO{\cdot}O}\cdot \qquad (10)$$

The same conclusion can be drawn from the results for isopropylbenzene and ethylbenzene. In the reactions in these solvents, however, it was not possible to determine the composition of the ester fraction, although the presence of an ester (α-cumyl benzoate) which cannot arise by nuclear benzoyloxylation was indicated qualitatively in the products of a reaction with isopropylbenzene. The total yield of esters was therefore used in computing the sums of the yields of possible termination products for comparison with the fraction *f* given in Tables 3 and 4, and indicates a conclusion analogous to that for the reaction with *p*-xylene. This approximation does not affect the validity of this conclusion, since the yield of esters is in most cases relatively small, and even if the esters are omitted from the calculation the above-mentioned sum still exceeds the fraction $f$ by a considerable margin.

The formation of $\alpha$-cumyl benzoate and 4-methylbenzyl benzoate in the reactions with isopropylbenzene and *p*-xylene, respectively, and the dependence of the yield of the latter ester on the initial concentration of the peroxide, are consistent with the formation of these esters in chain-transfer processes of type (11). This reaction therefore also contributes to the induced decomposition of the peroxide. Another ester-forming reaction which has been suggested as a contributor to the induced decomposition is (12), in which the radical which attacks the peroxide is the phenyl radical derived directly from it.[8,24]

$$\mathrm{Ar{\cdot}CR'_2{\cdot} + (Ph{\cdot}CO{\cdot}O)_2 \longrightarrow Ar{\cdot}CR'_2{\cdot}O{\cdot}CO{\cdot}Ph + Ph{\cdot}CO{\cdot}O{\cdot}} \tag{11}$$

$$\mathrm{Ph{\cdot} + (Ph{\cdot}CO{\cdot}O)_2 \longrightarrow Ph{\cdot}CO{\cdot}OPh + Ph{\cdot}CO{\cdot}O{\cdot}} \tag{12}$$

$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot} + (Ph{\cdot}CO{\cdot}O)_2 \longrightarrow Ph{\cdot}CO{\cdot}OPh + Ph{\cdot}CO{\cdot}O{\cdot} + CO_2} \tag{13}$$

A similar reaction (13) involving benzoyloxy-radicals has also been suggested.[2] One product of these reactions is phenyl benzoate, and Davies, Hey, and Williams[25] have recently shown that a little of this ester is formed in the reactions of benzoyl peroxide with chlorobenzene and with biphenyl. Reactions (12) and (13) are therefore possible in principle. However, very little phenyl benzoate is formed in the present reactions, and reactions (12) and (13) do not therefore contribute appreciably to the induced decomposition in alkylbenzenes. Moreover, it is not possible entirely to rule out other modes of formation of small amounts of phenyl benzoate, such as intramolecular decarboxylation of benzoyl peroxide, as suggested by Lynch and Pausacker,[21] or the combination of phenyl and benzoyloxy-radicals (14). This reaction probably also makes a small contribution, since very small amounts of biphenyl were detected among the products of some of the reactions, and biphenyl is almost certainly formed in a reaction analogous to (14), but involving two phenyl radicals. However, in the reactions in alkylbenzenes these products occur only to a very small extent, and the reactions leading to their formation are not considered further in this discussion.

$$\mathrm{Ph{\cdot} + Ph{\cdot}CO{\cdot}O{\cdot} \longrightarrow Ph{\cdot}CO{\cdot}OPh} \tag{14}$$

It is, however, noteworthy that the combined yields of all the esters other than those arising from nuclear benzoyloxylation [*i.e.*, the esters which could be formed by reactions (11)—(13)] is grossly insufficient to account for the observed extent of the induced decomposition [the fraction $(1 - f)$ of the initial peroxide concentration]. Thus induced decomposition caused by attack on the peroxide by some radical other than $\mathrm{Ar{\cdot}CR_2'{\cdot}}$, phenyl, or benzoyloxy must also occur to a considerable extent. This supports the earlier conclusion that the reaction of the $\sigma$-complex with the peroxide is a major contributor to the induced decomposition, since the $\sigma$-complex is the only other radical present which can react in this way.

It is now possible to formulate a scheme for the decomposition of benzoyl peroxide in alkylbenzenes, which is consistent with the product-distribution as well as the reaction kinetics, as follows:

$$\left.\begin{array}{l}
(a)\ \mathrm{P \longrightarrow 2R{\cdot}} \\
(b)\ \mathrm{R{\cdot} + Ar{\cdot}CR'_2H \longrightarrow Ar{\cdot}CR'_2{\cdot} + RH} \\
(c)\ \mathrm{R{\cdot} + Ar{\cdot}CR'_2H \longrightarrow \sigma{\cdot}} \\
(d)\ \mathrm{Ar{\cdot}CR'_2{\cdot} + P \longrightarrow Products + R{\cdot}} \\
(e)\ \mathrm{\sigma{\cdot} + P \longrightarrow Products + R{\cdot}} \\
(f)\ \mathrm{R{\cdot} + P \longrightarrow Products + R{\cdot}} \\
(g)\ \mathrm{2Ar{\cdot}CR'_2{\cdot} \longrightarrow Products} \\
(h)\ \mathrm{2\sigma{\cdot} \longrightarrow Products}
\end{array}\right\} \tag{15}$$

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[25] Davies, Hey, and Williams, *J.*, 1961, 562.

In this simplified scheme, σ• is the σ-complex formed by the addition of a phenyl or benzoyloxy-radical (R•) to the nucleus of the alkylbenzene $Ar{\cdot}CR'_2H$. The benzyl-type radical $Ar{\cdot}CR'_2{\cdot}$ is formed by α-hydrogen-abstraction from $Ar{\cdot}CR'_2H$ by the radicals R•. Reactions (15*d* and *e*) represent the induced decomposition of the peroxide by $Ar{\cdot}CR'_2{\cdot}$ and σ-complex, respectively. The products of (15*d*) are substituted benzyl benzoates, and of (15*e*) the biaryls and esters resulting from nuclear phenylation and benzoyloxylation. Reaction (15*f*) is the induced decomposition by phenyl and benzoyloxy-radicals (R•) which, as mentioned earlier, may occur to a small extent. Reactions (15*g* and *h*) are termination processes. The products of (15*g*) are dehydrogeno-dimers, and those of (15*h*) are the tetrahydroquaterphenyl derivatives occurring in the residues, and the biaryls and dihydrobiaryls formed by disproportionation. Biaryls are, however, also formed in reaction (15*e*). The termination reaction of coupling of the dissimilar radicals σ• and R• [reaction (8)] is omitted from this scheme, as the results provide no evidence for it in the reactions with alkylbenzenes. The possibility that it makes a small contribution cannot, however, be entirely overlooked.

It is a consequence of the kinetic laws governing the reaction that the molar yield of products of termination reactions should decrease, while the molar yield of products of reactions of chain-propagation should increase, with increasing initial peroxide concentration. Tables 3—5 reveal that these predictions are borne out with regard to the dehydrogeno-dimers, and to the 4-methylbenzyl benzoate (in the reaction with *p*-xylene). The yields of biaryls and of phenolic esters formed by nuclear benzoyloxylation, however, appear to be practically independent of the initial peroxide concentration. This is probably a consequence of the formation of these products in reactions of both types, in which the molar yields of the products vary in opposite senses, so that the resultant variation is small.

The molar yield of the residues, if they are considered to consist of tetrahydroquaterphenyl derivatives, however, increases with increasing initial peroxide concentration, that is, it varies in the sense opposite to that to be expected if these compounds are primary products of termination reactions. It is possible, therefore, that the residues formed in these reactions with alkylbenzenes do not consist mainly of derivatives of tetrahydroquaterphenyl, and are therefore not mainly termination products. It is clear that compounds other than tetrahydroquaterphenyls must occur in the residues, since further phenylation and benzoyloxylation of the primary products must occur. Moreover, α-hydrogen-abstraction from the biaryls and dehydrogeno-dimers can also take place, giving radicals which, by combination with other radicals of similar type, lead to high-boiling products. These processes, being subsequent reactions of primary products, should occur to a greater extent at higher initial peroxide concentrations, since the primary product : substrate ratio is then higher and the probability of reaction of radicals with the primary products is therefore increased. In the absence of detailed knowledge of the composition of the residues, it is impossible to assess the relative importance of reactions of termination and of chain-propagation in the formation of biaryls. The qualitative conclusions, namely, that reactions of both types makes contributions, and that reaction (15*e*) is the major contributor to the induced decomposition of the peroxide, are, however, inescapable.

One further conclusion may be drawn from the results. Hey, Pengilly, and Williams [11] identified benzene among the products of reactions of benzoyl peroxide with alkylbenzenes, and concluded that the radical R• responsible for α-hydrogen abstraction [reaction (15*b*)] was the phenyl radical. In the present experiments it was found that the molar yields of benzene and benzoic acid formed with all three substrates were almost independent of the initial peroxide concentration, except at very high and very low initial concentrations. These yields are given in Table 6. By a comparison of this Table with Tables 3 and 5, it may be seen that the molar yield of benzene is, in almost all cases, less than twice that of the dehydrogeno-dimer. Thus phenyl radicals cannot alone be responsible for the α-hydrogen-abstraction, since two moles of benzene should be formed for each mole of dehydrogeno-dimer formed in this way. It follows, therefore, that some α-hydrogen abstraction by benzoyloxy-radicals, leading to the formation of benzoic acid, also occurs.

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