

**646.** *Homolytic Aromatic Substitution. Part XXXI.\* The Reaction of Benzoyl Peroxide with Benzene.*

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The decomposition of benzoyl peroxide in benzene at 80° has been studied over a wide range of initial peroxide concentrations, and the yields of some of the products determined. The results accord with a simple scheme of primary reactions occurring at infinite dilution. At finite concentrations this scheme is complicated by a radical-induced decomposition of the peroxide, as well as by radical attack on the hydroaromatic products.

A previous communication<sup>1</sup> contained an account of investigations into the nature of the high-boiling (mol. wt. >200) products of the thermal decomposition of benzoyl peroxide in benzene at 80°, and their relevance to a mechanistic interpretation of the reaction. It was then thought that further understanding of the mechanism might be obtained by a re-examination of the lower-boiling products, with particular reference to variations in yields with changes in the initial concentration of the peroxide.

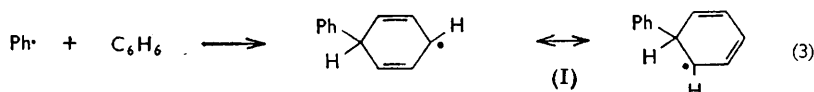
\* Part XXX, Hey, Saunders, and Williams, preceding Paper.

<sup>1</sup> Hey, Perkins, and Williams, *J.*, 1963, 5604.

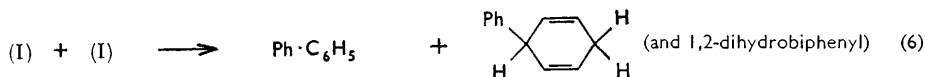
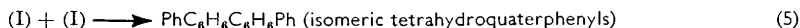
Earlier work has established that products of the reaction having molecular weights below 200 include carbon dioxide, benzoic acid, phenyl benzoate, biphenyl, and 1,4- and 1,2-dihydrobiphenyl.<sup>2,3</sup> Of these, only carbon dioxide and benzoic acid have previously been estimated quantitatively over a wide range of concentration of peroxide.<sup>4</sup> Furthermore, a comparison of various quantitative results in the literature reveals several marked inconsistencies. In the present work the yields of the above-named compounds, with the exception of carbon dioxide, have been estimated at initial peroxide concentrations in the range 0.01—0.33M, and an attempt has been made to correlate the results with published kinetic data.



Kinetic studies<sup>5</sup> of the decomposition of benzoyl peroxide, in a variety of solvents, including benzene, show that the spontaneous decomposition of the peroxide is almost invariably accompanied by a radical-induced decomposition. The spontaneous decomposition in carbon tetrachloride has been clearly shown<sup>6</sup> to involve cleavage of the peroxidic linkage (1), and comparison of kinetic data justifies the assumption that this is also true in benzene.



Spontaneous decarboxylation (2) of the resulting benzoyloxy-radicals then occurs. An aromatic solvent molecule is attacked by the resulting phenyl radical, in what has been shown to be a two-stage substitution reaction. The phenyl radical adds irreversibly to benzene (possibly by way of intermediate  $\pi$ -complex formation<sup>7</sup>) to give a phenylcyclohexadienyl radical (I) ( $\sigma$ -complex), which may subsequently be dehydrogenated [(3) and (4)]. These steps are supported by the absence of a hydrogen isotope effect in the unreacted solvent,<sup>8-10</sup> and by the isolation of products of the dimerisation and disproportionation of the intermediate (I) [(5) and (6)].<sup>3</sup> Such hydroaromatic products are more prominent at very low initial concentrations of peroxide where the extent of the induced decomposition is small and where the high dilution minimises the extent of radical attack on the reactive allylic centres of such products. The formation of identifiable hydroaromatic products in low yield has, however, also been demonstrated for reactions conducted at higher concentrations.<sup>10</sup>



A radical-destroying termination reaction which has been proposed<sup>11</sup> in addition to (5) and (6) is the interaction of a benzoyloxy-radical and the intermediate (I) (7).<sup>\*</sup> It has

\* Evidence has also been obtained recently for the limited occurrence of a coupling reaction between these two radicals.<sup>12</sup>

<sup>2</sup> Williams, "Homolytic Aromatic Substitution," Pergamon Press, London, 1960.

<sup>3</sup> DeTar and Long, *J. Amer. Chem. Soc.*, 1958, **80**, 4742.

<sup>4</sup> Barnett and Vaughan, *J. Phys. Chem.*, 1947, **51**, 936.

<sup>5</sup> Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686; 1947, **69**, 2299.

<sup>6</sup> Hammond and Soffer, *J. Amer. Chem. Soc.*, 1950, **72**, 4711.

<sup>7</sup> Petukhov, *Russian Chem. Rev.*, 1961, **30**, 630.

<sup>8</sup> Convery and Price, *J. Amer. Chem. Soc.*, 1958, **80**, 4101.

<sup>9</sup> Chang, Hey, and Williams, *J.*, 1959, 1871.

<sup>10</sup> Eliel, Meyerson, Welvert, and Wilen, *J. Amer. Chem. Soc.*, 1960, **82**, 2936.

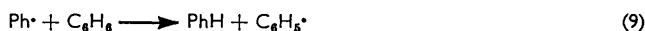
<sup>11</sup> Szwarc, *Discuss. Faraday Soc.*, 1953, **14**, 251.

<sup>12</sup> DeTar, Long, and Rendleman, unpublished results.

also been proposed<sup>13</sup> that the radical (I) is the species responsible for the induced decomposition of the peroxide (8).



A variety of other radical-radical\* or radical-substrate reactions may be written for the system, but, with two exceptions, no evidence has been adduced in favour of any of them. On the other hand, several radical-product reactions have been revealed at high peroxide concentrations, and some of these may also yield benzoic acid and biphenyl (see below). The two exceptions mentioned above are (a) the occurrence<sup>7,14</sup> to a very small extent of the identity reaction (9), and (b) the formation of phenyl benzoate. The latter process, which is also relatively unimportant, has been considered<sup>15</sup> to occur by benzoyloxylation of the benzene in steps analogous to (3) and (4), but with Ph· replaced by PhCO·O·. In this case, the first step (*i.e.*, addition of a benzoyloxy-radical to benzene) may be appreciably reversible (*cf.* ref. 16). Phenyl benzoate may also arise<sup>15</sup> from decomposition of the peroxide induced by a benzoyloxy-radical. Evidence for a duality of mechanism here comes from analogy with reactions of benzoyl peroxide with substituted benzenes, when unsubstituted phenyl benzoate accompanies the benzoyloxylation products.<sup>15</sup>



Preliminary experiments<sup>17</sup> confirmed previous reports of the labile nature of the tetrahydroquaterphenyls.<sup>3</sup> On mild pyrolysis these are converted into biphenyl and dihydrobiphenyls, presumably through the intermediate formation of resonance-stabilised phenylcyclohexadienyl radicals. This lack of stability of the tetrahydroquaterphenyls was also shown by their decomposition during gas chromatography and, in preparative experiments, by variation in the yield of the biphenyl fraction with the temperature of the work-up procedure. To eliminate the possibility of this pyrolytic reaction during the procedure for quantitative analysis of the low molecular weight products, a technique was developed in which the reactions, performed under reflux and in an atmosphere of oxygen-free nitrogen, were allowed to proceed to completion (>10 half-lives), after which the products were hydrogenated. This procedure greatly increased the thermal stability of the tetracyclic products, and the yields of biphenyl, dihydrobiphenyls (as phenylcyclohexane), and phenyl benzoate could readily be determined by gas chromatography. The hydrogen uptake in duplicate experiments was, however, not satisfactorily reproducible. It appeared to depend on the condition of the catalyst, and slight hydrogenation of the solvent benzene may have taken place. The measured yields of the products in question were, however, highly reproducible. In control experiments with authentic 1,4-dihydrobiphenyl, there was no evidence for disproportionation to give biphenyl during the hydrogenation. Yields of benzoic acid were determined volumetrically in a separate series of experiments.

The results of experiments carried out over a wide range of initial peroxide concentrations are shown in the Figure. The most striking feature is the marked variation in the yields of some products in the low concentration ranges. Extrapolation to infinite dilution, where no induced decomposition can occur, suggests that in such circumstances the yield of benzoic acid would be zero, and the yields of biphenyl and dihydrobiphenyl equal, at a value of

\* Several of the radical-radical reactions which may in principle be written involve the phenyl radical. These are, however, unimportant, since this species is so highly reactive that it is almost invariably removed by reaction with a solvent molecule before an opportunity occurs by collision for its reaction with any other radical species.

<sup>13</sup> Foster and Williams, *J.*, 1962, 2862.

<sup>14</sup> Barson and Bevington, *Trans. Faraday Soc.*, 1959, **55**, 1266.

<sup>15</sup> Davies, Hey, and Williams, *J.*, 1961, 562.

<sup>16</sup> Denney and Klemchuk, *J. Amer. Chem. Soc.*, 1958, **80**, 3289.

<sup>17</sup> Perkins, Ph.D. Thesis, London, 1962.

0.24 ± 0.04 mole/mole of peroxide. This accords with the hypothesis that under such conditions biphenyl and dihydrobiphenyl are formed almost exclusively by reaction (6).

Small quantities of some of these products may accompany the phenyl benzoate, whose extrapolated yield at zero peroxide concentration is about 0.03 mole/mole of peroxide. As mentioned above, the formation of phenyl benzoate probably occurs in several ways. The relative importance of these different pathways to phenyl benzoate may vary in different senses with peroxide concentration.

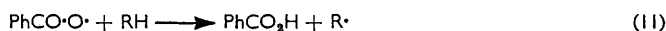
At infinite dilution the remainder of the peroxide may be accounted for as tetrahydro-*q*-quaterphenyls (reaction 5). Indeed, semiquantitative experiments have shown that the molar yield of *p*-quaterphenyl, obtainable by dehydrogenation of the reaction products with *o*-chloranil, is much higher at very low peroxide concentrations. Thus, at infinite dilution, the reaction is almost entirely accommodated by the processes (1), (2), (3), (5), and (6).

At finite concentrations, the variations in the yields of products, other than phenyl benzoate, must be considered in conjunction with the increasing incidence of induced decomposition of the peroxide. The most reliable published kinetic results appear to be those of Nozaki and Bartlett,<sup>5</sup> who concluded that benzoyl peroxide decomposes in benzene by two concurrent reactions of order 1 and 1.5 in peroxide, respectively (10). If P is the peroxide, and  $k_1$  and  $k_2$  are constants:

$$-d[P]/dt = k_1[P] + k_2[P]^{3/2} \quad (10)$$

The term in  $[P]^{3/2}$  arises from the induced decomposition. Such a rate relationship may be deduced<sup>18</sup> for a reaction scheme involving processes (1), (2), (3), (5), (6), and (8) only. Termination by process (7), instead of (5) and (6), leads to an induced reaction which is first-order in peroxide. Thus, if it be accepted that reaction (8) does represent the induced decomposition, and that secondary reactions, to be considered shortly, do not have a profound effect on the kinetics, the experimental evidence suggests that termination occurs largely by interaction of pairs of phenylcyclohexadienyl radicals [(5) and (6)].

Recent work has demonstrated that reaction (7), if it occurs at all, does not account for more than 5% of the products of the reaction in benzene.<sup>19</sup> Assuming a rate equation of the type of (10), it is possible<sup>20</sup> to calculate the proportion ( $f$ ) of the peroxide which decomposes by the induced mechanism as a function of the initial peroxide concentration  $[P]_0$ . There should be a correlation between  $f$  and the yield of benzoic acid, since, in the absence of reaction (7), the only source of acid so far considered is the induced decomposition of the peroxide (8). On making a comparison of this kind, using the values of  $k_1$  and  $k_2$



determined by Nozaki and Bartlett, it is found that the experimental yield of acid is actually some 20% greater than that calculated, over the whole range investigated. The calculated yields are very sensitive to the values of  $k_1$  and  $k_2$ , and it may be that this is the origin of

the difference. An alternative explanation, however, is that some benzoic acid is formed by hydrogen abstraction from the hydroaromatic products (II). Evidence for the formation of  $\text{R}\cdot$ , where  $\text{R}\cdot$  is the radical (II), has already been presented.<sup>1</sup> Transformation of the hydroaromatic products by addition of benzoyloxy-radicals to olefinic centres is also likely, as it has been claimed that there are non-phenolic hydroxyl groups in the high-boiling products of the reaction after alkaline hydrolysis.<sup>21</sup>

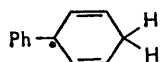
The yield of dihydrobiphenyl decreases as  $[P]_0$  is increased, partly because it is a product

<sup>18</sup> Godin, quoted in ref. 13.

<sup>19</sup> Gill, Ph.D. Thesis, London, 1963.

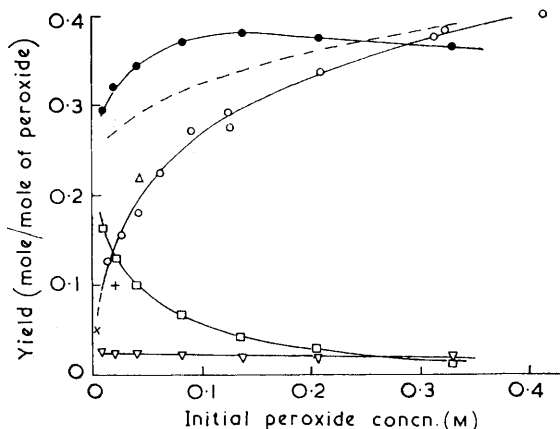
<sup>20</sup> Swain, Stockmeyer, and Clarke, *J. Amer. Chem. Soc.*, 1950, **72**, 5426.

<sup>21</sup> Lynch and Pausacker, *Austral. J. Chem.*, 1957, **10**, 40.



(II)

of the spontaneous reaction, and partly because of the subsequent transformations mentioned above. It is also possible that a little of the dihydrobiphenyl may ultimately be converted into biphenyl [for example, by way of (II), and then reaction analogous to (6)]. Similar considerations relate to the tetrahydroquaterphenyls, and, indeed, at high values



Yields of products from the reaction of benzoyl peroxide with benzene.

●, Biphenyl; □, dihydrobiphenyl (as phenylcyclohexane); ▽, phenyl benzoate. Benzoic acid: ○, this work; △, from Hartmann, Sellars, and Turnbull, *J. Amer. Chem. Soc.*, 1947 **69**, 2416; +, from ref. 3; ×, from Barson and Bevington, *Tetrahedron*, 1958, **4**, 147 (reaction at 60°).

The broken line refers to dihydrobiphenyl + benzoic acid. (Lynch and Pausacker<sup>21</sup> also report yields of benzoic acid for several values of the initial peroxide concentration. However, their yields, in common with those reported by other early investigators in the field, are appreciably higher than those presented here. A possible explanation of this difference may be that the benzene used in the early work was contaminated with saturated impurities such as cyclohexane. Gas chromatography of the benzene used in the present work did not reveal the presence of any impurities.)

of  $[P]_0$ , some *p*-quaterphenyl separates from the reaction mixture prior to any subsequent dehydrogenation.<sup>2,17,21</sup>

Biphenyl is formed in two primary steps, (6) and (8), and would be expected to be found in yields equal to the sum of those of the dihydrobiphenyls and benzoic acid. The deviation from this prediction is not large, and may probably be accounted for in terms of the side-reactions outlined above.

## EXPERIMENTAL

**Materials.**—Benzene and benzoyl peroxide were purified as described in Part II.<sup>22</sup> Biphenyl and bibenzyl were crystallised to constant m. p. (69 and 51°, respectively) from light petroleum (b. p. 40–60°), and phenyl benzoate crystallised to constant m. p. (70°) from ethanol. Phenylcyclohexane was dried (CaCl<sub>2</sub>) and fractionally distilled at atmospheric pressure. A middle fraction, b. p. 236–238°, was retained. 1,4-Dihydrobiphenyl was prepared by Hückel and Schwen's method.<sup>23</sup> The product was contaminated with biphenyl, for which a correction was applied in quantitative control experiments. Tetrachloro-*o*-benzoquinone (*o*-chloranil) was prepared by a modification<sup>1</sup> of Jackman's method.<sup>24</sup>

**Reaction of Benzoyl Peroxide with Benzene.**—(A). A number of experiments were carried out

<sup>22</sup> Augood, Hey, and Williams, *J.*, 1952, 2094.

<sup>23</sup> Hückel and Schwen, *Ber.*, 1956, **89**, 150.

<sup>24</sup> Jackman, *Adv. Org. Chem.*, 1960, **2**, 359.

by the following general procedure. The peroxide (2.000 g.) was added to a measured volume of boiling benzene, which had previously been dried by azeotropic distillation. The solution was refluxed under an atmosphere of oxygen-free nitrogen for 48 hr. and then cooled. Bibenzyl (0.750 g.) was added as an internal standard for analysis. The solution was transferred, using benzene as wash-liquid, to a hydrogenation flask containing 10% palladised charcoal (approx. 200 mg.) and the mixture was shaken with hydrogen at atmospheric pressure overnight. Hydrogen uptake was usually complete after about 4 hr. In order that the volume of solution hydrogenated should be 100—200 ml., it was in some instances necessary either to add benzene or to remove some by distillation between the addition of bibenzyl and the hydrogenation. The catalyst and any precipitated organic product were removed by filtration. The solvent was distilled through a 10-cm. vacuum-jacketed, helix-packed column until the volume of the residual liquid was about 15 ml. This was transferred quantitatively to a graduated flask and diluted to 20 ml. with dry benzene. The several solutions obtained in this way were then analysed by gas chromatography. The initial volume of benzene used in the experiments was varied within the range 25—800 ml., and the reactions at the two extreme concentrations were duplicated.

Quantitative gas chromatography was carried out with a Pye Argon Chromatograph fitted with a high-sensitivity argon beta-ray detector, which normally gives a linear response. The column used was of 10% Apiezon "L" on Celite (4 ft.  $\times$  4 mm. i.d.) at 150°, and with a flow of argon of *ca.* 75 ml./min. A number of synthetic mixtures each containing 0.750 g. of bibenzyl, as well as known weights of biphenyl, phenylcyclohexane, and phenyl benzoate were made up to 20 ml. with dry benzene. Analysis of these allowed calibration graphs to be constructed in which the peak heights of the compounds under consideration relative to the peak height of the internal standard (bibenzyl) were plotted against the weights of the compounds in the solutions. The unknown solutions were then analysed under identical conditions, and, from the peak height of any specific compound relative to that of bibenzyl, the weight of this compound could be obtained from the relevant calibration graph. The method of internal normalisation was employed because it was not practicable to reproduce accurately the size of sample injected. However, the use of solutions of a fixed concentration with respect to the internal standard ensured that closely similar charges were injected. Thus, any error due to slight non-linearity in the response of the detector was avoided. Chromatograms were rejected if the absolute height of the bibenzyl peak did not lie within 10% of a mean value. It was found that, for analytical purposes, the measurement of peak-heights was as satisfactory as measurement of areas.

A number of control experiments was necessary to test the accuracy of the method. (a) Subjection of a synthetic mixture of known composition, containing biphenyl, bibenzyl, phenylcyclohexane, phenyl benzoate, benzoic acid, and benzene to the procedures described above for hydrogenation and solvent removal did not affect its composition, as determined by gas chromatography, to more than 3%, which is of the same order as the accuracy of the analytical method. No complications, therefore, arose from these procedures, and, in particular, the aromatic nuclei were not appreciably reduced. (b) The lack of consistency of the hydrogen-uptake mentioned previously may have been due to some slight hydrogenation of the solvent benzene or biphenyl (to phenylcyclohexane). Phenylcyclohexane was just detectable ( $\sim\frac{1}{2}\%$  conversion) after hydrogenation of biphenyl in the presence of benzoic acid in a control experiment. (c) The inability to detect 1,4-dihydrobiphenyl on chromatography of a hydrogenated reaction mixture using polyethylene glycol adipate on Celite as the stationary phase indicated that the hydrogenation of the hydroaromatic products was complete, since the relevant compounds were known to be completely resolved under the conditions used. (d) The formation of biphenyl by irreversible hydrogen-transfer during hydrogenation, as has been reported with the 2,3-isomer under similar conditions,<sup>25</sup> was shown not to occur by gas-chromatographic analysis of a benzene solution of 1,4-dihydrobiphenyl after hydrogenation, when quantitative conversion into phenylcyclohexane was found to have occurred. It is assumed that 1,2-dihydrobiphenyl behaves in a manner similar to the 1,4-isomer. (e) The results of the analyses were unaffected by the addition of benzoic acid, which tends to "tail" badly under conditions used and hence might conceivably have interfered with some of the other peaks. Table 1 gives the results of the analyses of nine reaction mixtures.

<sup>25</sup> Woods, Bolgiano, and Duggan, *J. Amer. Chem. Soc.*, 1955, **77**, 1800.

(B). A simple volumetric procedure was developed for the estimation of benzoic acid in benzene, which gave results that were both self-consistent and in agreement with those obtained by extraction. A series of reactions at various initial peroxide concentrations was carried out in a thermostat at 80° for 72 hr. The solutions were diluted to convenient volumes in graduated flasks with AnalaR benzene, and aliquot portions (20 ml.) were added to ethanol (70 ml.). The benzoic acid was titrated with standard aqueous sodium hydroxide, using phenolphthalein as indicator, and the result corrected for the "blank" titre given by 70 ml. of ethanol. The sodium hydroxide was standardised against a standard solution of benzoic acid in benzene, and the result checked against standard hydrochloric acid. The value of the acid yield is subject to the greatest error at low values of  $[P]_0$ . The results are collected in Table 2. They compare

TABLE 1.

Yields (mole/mole of peroxide) from reaction of benzoyl peroxide with benzene.

| Expt. | Initial peroxide concn. (M) | Biphenyl | Phenylcyclohexane | Phenyl benzoate |
|-------|-----------------------------|----------|-------------------|-----------------|
| 1     | 0.330                       | 0.366    | 0.017             | 0.018           |
| 2     | 0.330                       | 0.367    | 0.015             | 0.019           |
| 3     | 0.206                       | 0.374    | 0.029             | 0.020           |
| 4     | 0.138                       | 0.382    | 0.043             | 0.021           |
| 5     | 0.083                       | 0.371    | 0.068             | 0.023           |
| 6     | 0.041                       | 0.346    | 0.100             | 0.025           |
| 7     | 0.0206                      | 0.320    | 0.131             | 0.026           |
| 8     | 0.0103                      | 0.299    | 0.165             | 0.026           |
| 9     | 0.0103                      | 0.294    | 0.159             | 0.028           |

favourably with values obtained by thorough extraction of the acid from the reaction mixtures with sodium hydrogen carbonate.

(C). A number of experiments was carried out in which a weighed quantity of benzoyl peroxide was allowed to decompose in a measured volume of benzene at 80° for 30 hr. An excess of *o*-chloranil was added, and the solution boiled for a further 15 hr., cooled, and the precipitated *p*-quaterphenyl filtered off and weighed. Some of the reaction mixtures were concentrated by distillation. A small correction was added to the yield of *p*-quaterphenyl to

TABLE 2.

Yields (mole/mole of peroxide) of benzoic acid, and initial peroxide concentrations.

|                           |       |       |                   |                   |        |       |                   |       |                   |                   |
|---------------------------|-------|-------|-------------------|-------------------|--------|-------|-------------------|-------|-------------------|-------------------|
| $[P]_0$ (M) .....         | 0.413 | 0.343 | 0.310             | 0.206             | 0.124  | 0.091 | 0.062             | 0.041 | 0.0258            | 0.0134            |
| PhCO <sub>2</sub> H ..... | 0.40  | 0.38  | 0.37 <sub>5</sub> | 0.33 <sub>5</sub> | 0.29 * | 0.27  | 0.22 <sub>5</sub> | 0.18  | 0.15 <sub>5</sub> | 0.12 <sub>5</sub> |

\* 0.27<sub>5</sub> and 0.28<sub>5</sub> by extraction.

make approximate allowance for its solubility in cold benzene. This correction, was, in all cases, less than 15% of the quantity isolated. It was found that the yield was independent of the presence of oxygen above the reaction mixture, and these experiments were not protected from oxygen. In any case, the results provide only a rough guide to the tetrahydro-*p*-quaterphenyl formed, as, by comparison of the biphenyl analyses above with the yield of biphenyl in dehydrogenation experiments,<sup>1</sup> it is evident that some cleavage of tetrahydroquaterphenyls to biphenyl occurs, even under the mild conditions of dehydrogenation with *o*-chloranil. The results of these experiments are shown in Table 3.

TABLE 3.

Corrected yields of *p*-quaterphenyl, and initial peroxide concentrations.

|  |        |        |                   |                   |                   |       |       |
|--|--------|--------|-------------------|-------------------|-------------------|-------|-------|
| $[P]_0$ (M) .....                              | 0.0052 | 0.0103 | 0.0206            | 0.041             | 0.083             | 0.186 | 0.372 |
| <i>p</i> -Quaterphenyl (mole/mole of peroxide) | 0.22   | 0.20   | 0.16 <sub>5</sub> | 0.12 <sub>5</sub> | 0.08 <sub>5</sub> | 0.04  | 0.03  |

We are indebted to the D.S.I.R. for a Research Studentship (to M. J. P.) during the tenure of which most of this work was carried out.