Tetrahedron Vol. 25, pp. 2059 to 2070. Pergamon Press 1969. Printed in Great Britain

INDUCED DECOMPOSITION OF BENZOYL PEROXIDE BY THE BENZOPHENONE KETYL RADICAL

W. F. SMITH, JR. and B. W. ROSSITER

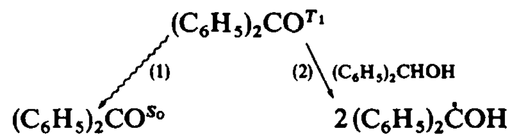
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

(*Received in USA* 14 *August* 1968; *Received in the UK for publication* 12 *November* 1968)

Abstract—Benzophenone ketyl radicals [$(C_6H_5)_2\dot{C}OH$] induce the decomposition of benzoyl peroxide in benzene at 25°. In the presence of benzhydrol, the resulting benzoyloxy radicals ($C_6H_5COO\cdot$) abstract hydrogen from the alcohol, resulting in the formation of benzoic acid and more benzophenone ketyl radicals. Chain lengths are short. Termination is principally between phenylcyclohexadienyl radicals (or possibly between phenylcyclohexadienyl and benzoyloxy radicals), indicating that the rate determining step is the hydrogen abstraction from alcohol. This result is contrasted with the results of thermolysis of benzoyl peroxide in alcohols at higher temperatures. By comparing the reactivity of the benzophenone ketyl radical with its O-Me analog, it is concluded that the transition state for the induced decomposition probably involves a partial hydrogen transfer from the ketyl radical to one of the peroxide O atoms.

INTRODUCTION

ABSORPTION of light by benzophenone is known to result in conversion with high efficiency of the benzophenone to its triplet state.[1] If benzophenone is excited in benzene solution containing benzhydrol, the resulting triplets are partitioned between reactions (1) and (2). The rate constants at 25° in benzene for (1) and (2) are known,[1,2]



$$\begin{tikzcd} & (C_6H_5)_2CO^{T_1} \arrow[dl, dashed, "(1)"] \arrow[dr, "(2)"', "(C_6H_5)_2CHOH"] & \\ (C_6H_5)_2CO^{S_0} & & 2\,(C_6H_5)_2\dot{C}OH \end{tikzcd}$$

and therefore the yield of ketyl radicals can be calculated for any concentration of benzhydrol. If a third substance, X, is introduced which is capable of quenching benzophenone triplets (3), the yield of ketyl radicals can still be calculated, provided k_3 is

$$(C_6H_5)_2CO^{T_1} + X^{S_0} \xrightarrow{k_3} (C_6H_5)_2CO^{S_0} + X^{T_1} \tag{3}$$

known. Then, by proper adjustment of [$(C_6H_5)_2CHOH$] and [X], reaction (2) can be made to predominate over reaction (3). A means is thereby provided for studying the reaction of ketyl radicals with ground state X, albeit in the presence of a large amount of alcohol.* We have previously used this method to investigate the reaction of benzophenone ketyl radicals with an azomethine dye.[5]

Our interest in benzoyl peroxide as X stems from the following considerations. The

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* It is not always appreciated that the quenching by X of benzpinacol formation is not a diagnostic test for triplet energy transfer by reaction (3), since X may "quench" by reacting with ketyl radicals.[3] Likewise, a decrease in the quantum yield for ketone disappearance cannot be taken as unambiguous evidence of triplet energy transfer since hydrogen transfer from a ketyl radical to X would result in the return of benzophenone to its ground state.[4]

thermolysis (80°) of benzoyl peroxide is known to be accelerated by alcohols, an effect which has been attributed[6] to the chain sequence,

$$R_1R_2\dot{C}OH + (C_6H_5COO)_2 \rightarrow R_1R_2CO + C_6H_5COOH + C_6H_5COO\cdot \quad (4)$$

$$C_6H_5COO\cdot + R_1R_2CHOH \rightarrow C_6H_5COOH + R_1R_2\dot{C}OH. \quad (5)$$

Kinetic chain lengths in these systems are ~5–50, depending upon the alcohol. At 25°, the uncatalyzed first-order rate constant for benzoyl peroxide decomposition is only $1{\cdot}8 \times 10^{-5}$ hr^{-1} ($t_{\frac{1}{2}} \cong 4$ yrs).[5] Thus, a more rapid means of initiation is necessary to study reactions such as (4) and (5) at lower temperatures. The method described in the first paragraph can be used for this purpose, and has at least two advantages: (1) Depending upon the light intensity and concentrations of alcohol and peroxide, initiation by reaction (2) is 10^4–10^5 times more rapid than thermolysis of benzoyl peroxide at 25°. (2) Because of anticipated short chain lengths, kinetic complications are minimized by initiating the reaction with a radical which is already involved in one of the propagation steps.

In choosing benzene as solvent to study the reaction of ketyl radicals with benzoyl peroxide, we were aware of a possible complication. Thermolysis of benzoyl peroxide in benzene (no alcohol present) results in both a unimolecular and an induced reaction, the activation energy for the former being the greater.[6] As a result, more chain decomposition, presumably by phenylcyclohexadienyl radicals,[7] occurs at lower temperatures.

The fraction, f, of phenylcyclohexadienyl radicals which will induce the decomposition of peroxide with rate constant k_p is[6]

$$f = \frac{[(C_6H_5COO)_2]}{[(C_6H_5COO)_2] + R_i^{\frac{1}{2}}\dfrac{\sqrt{2k_t}}{k_p}},$$

where k_t is the termination rate constant, and R_i is the rate of formation of radicals. An estimate of f under our conditions was obtained by substituting into this equation appropriate values for $[(C_6H_5COO)_2]$, R_i, and $(\sqrt{2k_t})/k_p$. These are, respectively, 5×10^{-4}M, $2{\cdot}15 \times 10^{-6}$ el^{-1} min^{-1}, and $1{\cdot}9 \times 10^3$M$^{\frac{1}{2}}$ sec$^{\frac{1}{2}}$, the last value resulting from extrapolation of Nozaki and Bartlett's data for benzene solution to 25°. Thus, photoinitiation by the method described in the first paragraph should lead to <1 per cent induced decomposition at our lowest light intensity ($2{\cdot}15 \times 10^{-6}$ el^{-1} min^{-1}). We therefore assume phenylcyclohexadienyl radicals are not involved in any propagation steps under our conditions.

RESULTS AND DISCUSSION

Dependence of chain length upon benzhydrol concentration. In Table 1 are presented some data for the ketyl radical induced decomposition of benzoyl peroxide in benzene at 25° as a function of benzhydrol concentration. The quantum yields for ketyl radical formation (ϕ_K) were calculated assuming that $k_1 = 10^5$ sec^{-1},[2] $k_2 = 2{\cdot}0 = 10^6$M^{-1} sec^{-1},[2] and $k_3 = 3{\cdot}2 \times 10^6$M^{-1} sec^{-1}.[8] Since k_3 is ~3 orders of magnitude less than diffusion-controlled, relatively low concentrations of benzhydrol could be used without introducing complications from reaction (3). At the lowest benzhydrol concentration

(0·029M) only ~3% of the benzophenone triplets which do not return to their ground state would transfer triplet energy to peroxide.

TABLE 1. EFFECT OF BENZHYDROL CONCENTRATION ON THE BENZOPHENONE KETYL RADICAL INDUCED DECOMPOSITION OF BENZOYL PEROXIDE[a]

$[(C_6H_5)_2CHOH]$, M	ϕ_P	ϕ_K[c]	ϕ_P/ϕ_K
0·029	0·85	0·73	1·17
0·050	1·03	0·99	1·04
0·066	1·37	1·13	1·21
0·124	1·79	1·42	1·26
0·200	2·41	1·60	1·51
0·500	3·80	1·81	2·10
0·500[b]	0·72	0·75	0·96

[a] Solvent = degassed C_6H_6; $t = 25°$; I (3660 Å) = $1·77 \times 10^{-5}$ el^{-1} min^{-1} ± 6%; $[(C_6H_5COO)_2]_0 = 5·0 \times 10^{-4}$M; $[(C_6H_5)_2CO] = 2·0 \times 10^{-2}$M.

[b] 0·500M $(C_6H_5)_2CHOCH_3$ in place of $(C_6H_5)_2CHOH$; $[(C_6H_5COO)_2]_0 = 6·2 \times 10^{-4}$M.

[c] Calculated on the assumption that $k_r = 2·0 \times 10^6 M^{-1}$ sec^{-1} for benzhydrol, and $k_r = 0·6 \times 10^6 M^{-1}$ sec^{-1} for benzhydryl methyl ether.

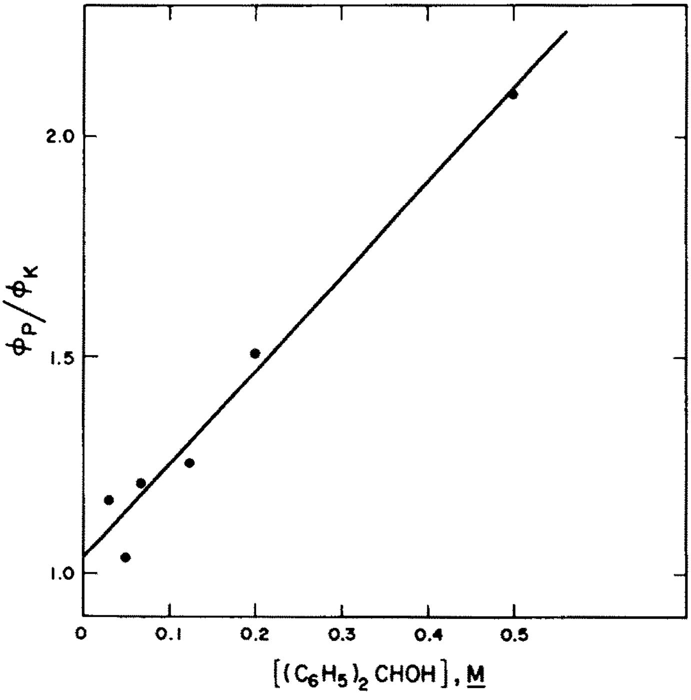

FIG. 1 Dependence of chain length on benzhydrol concentration for the induced decomposition of benzoyl peroxide by a ketyl radical.

The ratios of quantum yields for peroxide disappearance to ketyl radical formation (ϕ_P/ϕ_K) indicate that, above ~0·05M benzhydrol, a chain is involved, presumably reactions (4a) and (5a). Fig. 1 shows a plot of ϕ_P/ϕ_K (which is equivalent to

$$(C_6H_5)_2\dot{C}OH + (C_6H_5COO)_2 \rightarrow (C_6H_5)_2CO + C_6H_5COOH + C_6H_5COO\cdot \quad (4a)$$

$$C_6H_5COO\cdot + (C_6H_5)_2CHOH \rightarrow C_6H_5COOH + (C_6H_5)_2\dot{C}OH \quad (5a)$$

the chain length) versus benzhydrol concentration. The plot is reasonably linear with a least squares slope and intercept of 2·14 ± 0·16 and 1·04 ± 0·04.

Dependence of chain length on light intensity. The effect of a 37-fold variation in light intensity (3660 Å) on the rate of peroxide decomposition is shown in Fig. 2. The linear dependence of *rate* on I means that the *chain length* is independent of I.

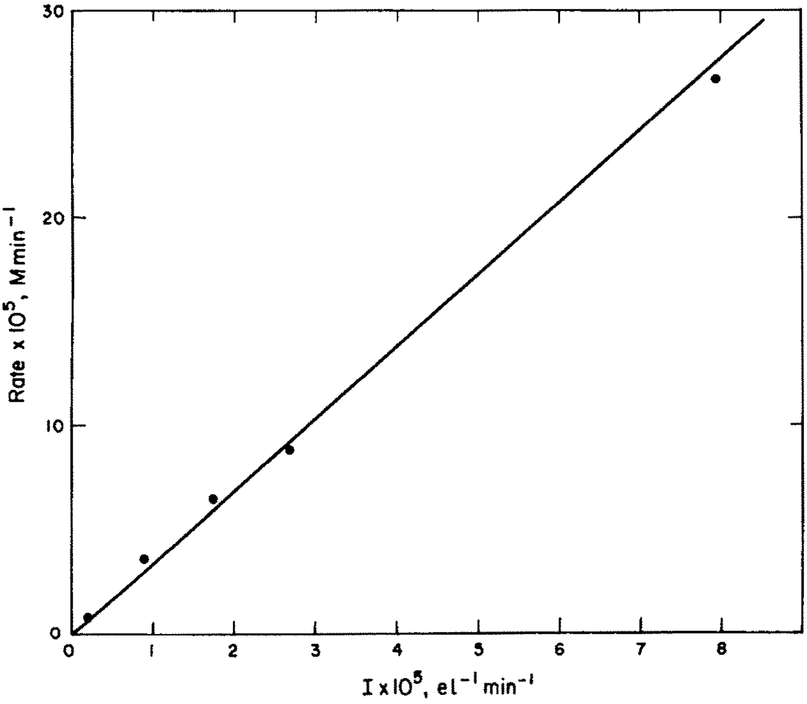

FIG. 2 Dependence of intial rate of benzoyl peroxide decomposition on light intensity (3660 Å). $[(C_6H_5COO)_2]_0 = 5{\cdot}0 \times 10^{-4}$M; $[(C_6H_5)_2CO] = 2{\cdot}0 \times 10^{-2}$M; $[(C_6H_5)_2CHOH] =$ 0·50M.

Nature of the termination step(s). Benzoyloxy radicals are known[7] to readily decarboxylate with formation in benzene solvent of phenylcyclohexadienyl radicals [reactions (6) and (6a)]. Consequently, there are six possible termination steps

$$C_6H_5COO\cdot \rightarrow C_6H_5\cdot + CO_2 \quad (6)$$

$$C_6H_5\cdot + C_6H_6 \rightarrow C_6H_5{-}C_6H_6\cdot \quad (6a)$$

(kinetically) between three different radicals, i.e. ketyl radicals (symbolized below as "K·"), benzoyloxy radicals ("X·"), and phenylcyclohexadienyl radicals ("σ·"). These reactions are:

$$\mathrm{K\cdot} + \mathrm{K\cdot} \rightarrow \ldots. \tag{7}$$

$$\mathrm{K\cdot} + \mathrm{X\cdot} \rightarrow \ldots. \tag{8}$$

$$\mathrm{X\cdot} + \mathrm{X\cdot} \rightarrow \ldots. \tag{9}$$

$$\mathrm{K\cdot} + \sigma\cdot \rightarrow \ldots. \tag{10}$$

$$\mathrm{X\cdot} + \sigma\cdot \rightarrow \ldots. \tag{11}$$

$$\sigma\cdot + \sigma\cdot \rightarrow \ldots. \tag{12}$$

The dependence of chain length upon benzhydrol concentration and light intensity will depend upon which terminations step (or steps) is operative. These kinetic orders are tabulated in Table 2 and derived in the Appendix. It may be seen that the possible termination reactions may be divided into two sets: (1) Those which result in chain lengths with a non-zero dependence on I. These reactions do not involve phenylcyclohexadienyl radicals. (2) Those which result in chain lengths which are independent of I. These always involve phenylcyclohexadienyl radicals. Since we observe experimentally that the latter is the case in this system, termination must involve phenylcyclohexadienyl radicals.

TABLE 2. CALCULATED DEPENDENCE OF ϕ_P/ϕ_K ON BENZHYDROL CONCENTRATION AND LIGHT INTENSITY FOR TERMINATION BY REACTIONS (7)–(12)

Termination reaction	Order in:	
	$[(C_6H_5)_2CHOH]$	I
7	0	−0·5
8	0·5	−0·5
9	1·0	−0·5
10	1·0	0
11	1·0	0
12	1·0	0

In order to distinguish between termination reactions (10), (11), and (12), all of which involve phenylcyclohexadienyl radicals, we consider now the dependence of chain length upon benzhydrol concentration. This is given by the following equation (cf. Appendix for derivation):

$$\frac{\phi_P}{\phi_K} = \left(1 - \frac{f_{10}}{2}\right) + \left(\frac{1 + f_{12}}{2}\right)\frac{k_{5a}}{k_6}[(C_6H_5)_2CHOH],$$

where f_{10} and f_{12} are the fractions of phenylcyclohexadienyl radicals which terminate by reactions (10) and (12), respectively, and $(f_{10} + f_{11} + f_{12}) = 1$. Since the intercept in Fig. 1 is nearly unity, $f_{10} \cong 0$ and termination must be by steps (11) and/or (12).

TABLE 3. PRODUCT ANALYSIS. REACTION OF BENZOYL PEROXIDE WITH BENZOPHENONE KETYL RADICAL[a]

Irradiation time, hr.	$[(C_6H_5COO)_2] \times 10^2$, M	$[(C_6H_5COOH)] \times 10^3$, M	$[C_6H_5—C_6H_5] \times 10^4$, M	Phenyl balance[b]			Chain length (ϕ_P/ϕ_K)
				C_6H_5COOH	$C_6H_5—C_6H_5$	Unaccounted	
0	1·87	—	—	—	—	—	—
1	1·56	4·53	4·3	0·73	0·07	0·20	1·8
2	1·37	8·14	5·6	0·81	0·06	0·13	1·5
3	1·19	11·37	6·0	0·84	0·04	0·12	1·4

[a] Solvent = degassed C_6H_6; $t = 25°$; I (3660 Å) = $1·75 \times 10^{-5}$ el^{-1} min^{-1}; $[(C_6H_5)_2CO] = 2·0 \times 10^{-2}$ M; $[(C_6H_5)_2CHOH] = 0·50$ M.

[b] Defined as $\dfrac{[C_6H_5COOH \text{ or } C_6H_5 - C_6H_5]}{2\{[(C_6H_5COO)_2]_0 - [(C_6H_5COO)_2]_t\}}$

Although we cannot rule out one of these steps to the exclusion of the other (nor is there any reason *a priori* why both may not be occurring), we favor reaction (12) as the predominant termination mechanism for the following reasons: (1) The results of a product analysis (Table 3*) show that the loss in benzoyl peroxide is not completely accounted for by the formation of benzoic acid and biphenyl, as it should be if reaction (11) were the only termination step; (2) For short chains, the acid yield is significantly different for termination by (11) versus (12). The calculated fraction of phenyls which would be accounted for as benzoic acid is plotted as a function of chain length in Fig. 3, on the assumption that termination is by reactions (11) or (12). At our lowest conversion of peroxide (16·5% cf. Table 3), where side reactions should be minimal, a chain length of 1·8 and an acid yield (expressed as phenyl) of 73% was obtained. This corresponds almost exactly to that expected from Fig. 3 for termination by reaction (12). (3) Chromatography (silica gel) of the sample irradiated for 2 hr (Table 3) resulted in the separation of a luminescent fraction. The mass spectrum† of this material showed the main component to be biphenyl, but there were also peaks at *m/e* 156 (phenylcyclohexadiene), 230 (terphenyl), 232 (dihydroterphenyl), 306 (quaterphenyl), 308 (dihydroquaterphenyl), and 310 (tetrahydroquaterphenyl).

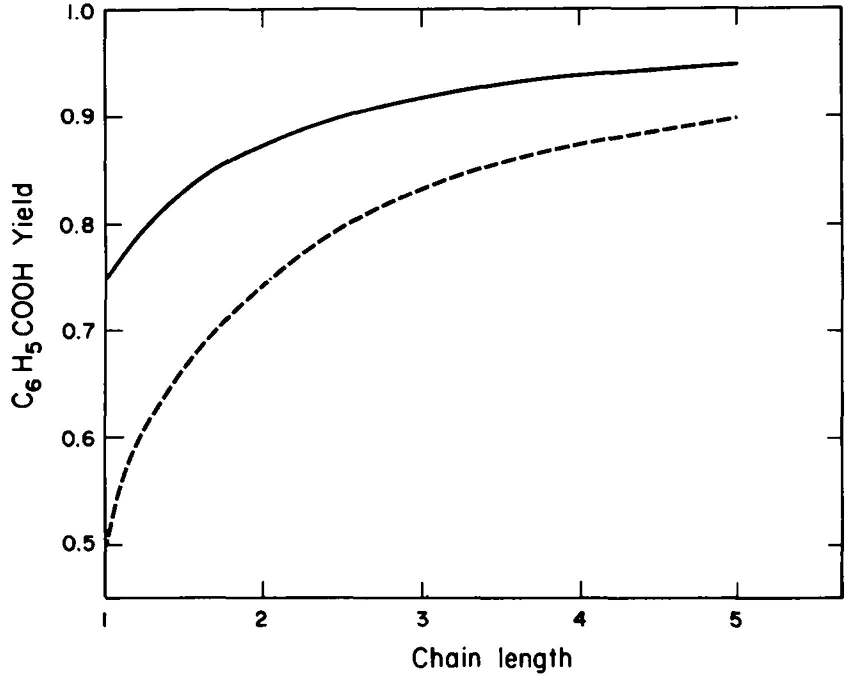

FIG. 3 Calculated benzoic acid yield (expressed as phenyl balance, footnote, Table 3) for termination by (———) reaction (11) and (– – – –) reaction (12).

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* Under the conditions in Table 3, ~94 per cent of the benzophenone triplets which do not return to the ground state should react with benzhydrol to give ketyl radicals.

† We are indebted to Mr. D. P. Maier for the mass spectrometric determination.

Comparison with peroxide thermolyses in neat alcohols. The thermolyses of di-*t*-butyl alcohol[9] at 125° and benzoyl peroxide[6] at 60° in neat alcohols are terminated by reactions analogous to the cross termination reaction (8). Although phenylcyclohexadienyl radicals would not be present in these systems, the presence of phenyl radicals in the latter case was shown by the isolation of benzene (0·24 mole/mole peroxide) from the decomposition of benzoyl peroxide in isobutyl alcohol.[10] Nonetheless, termination reactions between benzoyloxy radicals and phenyl radicals, or between phenyl radicals, apparently do not occur. This result, in combination with the observed kinetics,[6,9] indicates that at these temperatures both reactions (4) and (5) are rate controlling. Our results indicate that at 25°, the hydrogen abstraction reaction is the rate determining step.

These differences are at least partly understandable on thermo-chemical grounds. The heats of reaction for (4a) and (5a) may be estimated from the following cycles:

$$(C_6H_5COO)_2 \rightarrow 2C_6H_5COO\cdot + 33\ \text{kcal/mole}^{6}$$

$$(C_6H_5)_2\dot{C}OH \rightarrow (C_6H_5)_2\dot{C}{-}\dot{O} + H\cdot + 104\ \text{kcal/mole}^{11}$$

$$(C_6H_5)_2\dot{C}{-}\dot{O} \rightarrow (C_6H_5)_2C{=}O - 69\ \text{kcal/mole}^{11}$$

$$C_6H_5COO\cdot + H\cdot \rightarrow C_6H_5COOH - 102\ \text{kcal/mole}^{12}$$

$$(C_6H_5)_2\dot{C}OH + (C_6H_5COO)_2 \rightarrow (C_6H_5)_2CO + C_6H_5COOH + C_6H_5COO\cdot \quad - 34\ \text{kcal/mole}$$

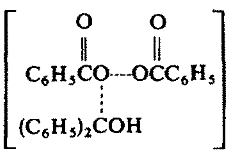
$$(C_6H_5)_2CHOH \rightarrow (C_6H_5)_2\dot{C}OH + H + 78\ \text{kcal/mole}^{11}$$

$$C_6H_5COO\cdot + H\cdot \rightarrow C_6H_5COOH - 102\ \text{kcal/mole}^{12}$$

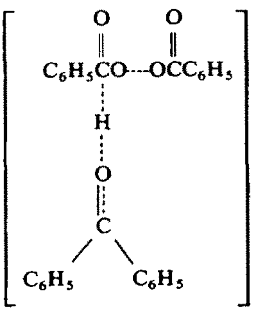
$$C_6H_5COO\cdot + (C_6H_5)_2CHOH \rightarrow C_6H_5COOH + (C_6H_5)_2\dot{C}OH - 24\ \text{kcal/mole}$$

Reaction (5a) is thus ~10 kcal/mole less exothermic than reaction (4a). If activation energies are in the same order, then the rate of reaction (5a) relative to reaction (4a) should increase with increasing temperature.

Structure of the transition state in the induced decomposition (*reaction* 4a). Either of two transition states, I or II, would be reasonable for reaction 4a, as both have precedents. The induced decomposition of benzoyl peroxide in ethers results from attack of α-alkoxyalkyl radicals at the peroxide linkage, analogous to I.[13–15] On the other



I



II

hand, the induced decomposition of di-*t*-butyl peroxide in primary and secondary alcohols[9] and amines[16] proceeds by hydrogen transfer.

Substitution of benzhydryl methyl ether for benzhydrol in our system would affect not only reaction (4a), but also reactions (2), (5a) and possibly the termination step. The effect on (2), however, was determined independently by measuring the rate of photoreduction of benzophenone by benzhydryl methyl ether by a procedure analogous to that of Moore, *et al.*[1] Results are given in Table 4. A plot of rate^{-1} versus [ether]$^{-1}$ is linear with a least-squares slope and intercept of 1·90 × 10^3 and 1·15 × 10^4, respectively. Thus, k_d/k_r = 0·16$_5$, where $1/k_d$ is the lifetime of benzophenone triplets in fluid benzene at 25°, and k_r is the rate constant for hydrogen abstraction from the ether by triplet benzophenone. For benzhydrol, k_d/k_r = 0·033[17]–0·05[1], and therefore hydrogen abstraction is 3·3–5 times more rapid from the alcohol than from the ether. This is in accord with the known sensitivity of benzophenone triplets towards substrate polarity.[11] Assuming $k_r^{(C_6H_5)_2CHOH} = 2 \times 10^6 M^{-1} sec^{-1}$,[2] then $k_r^{(C_6H_5)_2CHOCH_3}$ = 0·4–0·6 × $10^6 M^{-1} sec^{-1}$.

TABLE 4. RATE OF PHOTOREDUCTION OF BENZOPHENONE BY BENZHYDRYL METHYL ETHER[a]

$[(C_6H_5)_2CHOCH_3]$	Rate × 10^4 M min^{-1}
1·0	0·721
0·10	0·342
0·050	0·197
0·030	0·134

[a] Solvent = degassed C_6H_6; t = 25°; $[(C_6H_5)_2CO]_0$ = 0·10M.

If k_r is known for the ether, the yield of ketyl radicals can be calculated in the presence of peroxide. The results of such an experiment are shown in the last row of Table 1. Here, ϕ_K refers only to ketyl, not to ketyl + $(C_6H_5)_2COCH_3$, radicals. The ratio ϕ_P/ϕ_K is, within the limits of experimental error, unity. Since every ketyl radical should react with peroxide, we conclude that *under these conditions* (a) methoxydiphenylmethyl radicals are not inducing the decomposition of benzoyl peroxide, and (b) benzoyloxy radicals decarboxylate much more rapidly than they abstract hydrogen from benzhydryl methyl ether. Thus, transition state II is favored for the decomposition of peroxide induced by the ketyl radical.

EXPERIMENTAL

Materials. Benzene was Baker and Adamson Reagent A.C.S. Grade. The solvent was used as supplied, except in the photoreduction studies, in which it was stirred with conc H_2SO_4, washed, dried, and distilled from P_2O_5. Benzoyl peroxide (Wallace and Tiernan, Inc.) was precipitated 5 times from $CHCl_3$ with MeOH and dried on a vacuum line. Benzhydrol (Eastman Kodak Co., Eastman Grade) was recrystallized 3 times from ligroin (b.p. 63–75°), with charcoal decolorization on the first recrystallization. Benzophenone (Eastman Kodak Co., Eastman Grade) was twice recrystallized from EtOH. Benzhydryl methyl ether was prepared by the method of Bergman and Fujise,[18] b.p. 137–140°/6 mm. (Found: C, 84·8, 84·6; H, 7·2, 7·1. Calc. for $C_{14}H_{14}O$: C, 84·9; H, 7·1%).

Irradiations were performed with 3 different lamps, although in all cases the emission near 3660 Å was isolated: (1) A Hanovia Utility Model Lamp (Cat. No. 30600) in conjunction with a Corning CS7-37 Glass Filter and a $\frac{1}{8}$ in thickness of plate glass. The lamp is a 100-W, medium-pressure quartz-Hg-vapor arc lamp. This light source was used for experiments in which the benzhydrol concentration was varied and in the product studies. (2) An Osram HBO 200-W w/2 super-pressure Hg lamp, powered by a George W. Gates and Co. Model P-210D power supply. The lamp was mounted at the focal point of a 60-mm spherical mirror. The resulting beam was collimated with a quartz lens and passed through a 3660 Å interference filter (Bausch and Lomb, Inc.). This arrangement, in conjunction with suitable wire gauze filters, was used to study the effect of light intensity on the induced decomposition of the peroxide. (3) A 450-W, Hanovia Type L high-pressure Hg arc contained in a water-cooled quarta immersion well. Concentric about the arc was a merry-go-round, constructed by W. G. Herkstroeter, which accommodated 12 tubes and rotated at 1 rpm. Between the samples and the lamp were placed four sets of three filters each (Corning CSO-52, CS1-69, and CS7-37) at 90° intervals. The photoreduction of benzophenone by benzhydryl methyl ether was carried out with this arrangement.

Actinometry was carried out by the method of Hatchard and Parker.[19]

Samples were prepared for kinetic studies by degassing 3-ml. aliquots in 18 × 156 mm Pyrex-glass culture tubes and sealing them. Actinometry was performed in identical tubes, but the degassing step was omitted. For product studies, 25-ml. samples were degassed in 32 × 200 mm Pyrex tubes and sealed.

Analyses. Benzoyl peroxide was determined iodometrically with freshly distilled Ac_2O as solvent,[20] and measuring the I_2 spectrophotometrically. An average of more than 100 determinations gave $[(C_6H_5COO)_2] = 3{\cdot}75 \times 10^{-5}\ D_{362\,m\mu}$, where $D_{362\,m\mu}$ is the observed density at 362 mμ of the liberated iodine, and the peroxide concentration is expressed as molarity. Benzoic acid was determined by measuring the decrease in absorbance at 500 mμ of the *o*-nitrophenolate anion[21] upon addition of an aliquot of the unknown. Biphenyl was determined by vapor-phase chromatography with a Carbowax 20M column and an SE-30 column. Results from each column were averaged. The photoreduction of benzophenone by benzhydryl methyl ether was followed by measuring the decrease in absorbance at 350, 355, 360, 365, and 375 mμ.[1]

Acknowledgements—The authors are grateful to Mr. K. L. Eddy, for extensive assistance in the laboratory, and to Professor Henry Linschitz, for helpful discussions.

REFERENCES

[1] W. M. Moore, G. S. Hammond and R. P. Foss, *J. Am. Chem. Soc.* **83**, 2789 (1961).

[2] J. A. Bell and H. Linschitz, *Ibid.* **85**, 528 (1963).

[3] [a] H. E. Zimmerman and G. E. Samuelson, *Ibid.* **89**, 5971 (1967);
[b] H. E. Zimmerman, P. Hackett, D. F. Juers and B. Schroder, *Ibid.* **89**, 5973 (1967).

[4] [a] P. J. Wagner, *Ibid.* **89**, 2503 (1967);
[b] *Ibid.* **89**, 2820 (1967).

[5] W. F. Smith, Jr., and B. W. Rossiter, *Ibid.* **89**, 717 (1967).

[6] [a] K. Nozaki and P. D. Bartlett, *Ibid.* **68**, 1686 (1946);
[b] P. D. Bartlett and K. Nozaki, *Ibid.* **69**, 2299 (1947).

[7] [a] D. H. Hey, M. J. Perkin and G. H. Williams, *J. Chem. Soc.* 3412 (1964);
[b] G. B. Gill and G. H. Williams, *Ibid.* 995 (1965).

[8] C. Walling and M. J. Gibian, *J. Am. Chem. Soc.* **87**, 3413 (1965).

[9] E. S. Huyser and C. J. Bredeweg, *Ibid.* **86**, 2401 (1964).

[10] H. Gelissen and P. H. Hermans, *Ber. Dtsch. Chem. Ges.* **58B**, 765 (1925).

[11] C. Walling and M. J. Gibian, *J. Am. Chem. Soc.* **87**, 3361 (1965).

[12] L. Jaffe, E. J. Prosen and M. J. Szwarc, *J. Chem. Phys.* **27**, 416 (1957).

[13] W. E. Cass, *J. Am. Chem. Soc.* **69**, 500 (1947).

[14] D. B. Denney and G. Feig, *Ibid.* **81**, 5322 (1959).

[15] E. H. Drew and J. C. Martin, *Chem. & Ind.* 925 (1959).

[16] E. S. Huyser, C. J. Bredeweg and R. H. VanScoy, *J. Am. Chem. Soc.* **86**, 4148 (1964).

[17] G. S. Hammond and R. P. Foss, *J. Phys. Chem.* **68**, 3739 (1964).

[18] E. Bergman and S. Fujise, *Liebig's Ann.* **483**, 65 (1930).

[19] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* **A235**, 518 (1956).
[20] K. Nozaki, *Ind. Eng. Chem.* (Anal. Ed.) **18**, 583 (1946).
[21] L. Kesner and E. Muntwyler, *Analyt. Chem.* **38**, 1164 (1966).
[22] C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, N.Y., 1957, pp. 243–244.
[23] C. Walling and V. Kurkov, *J. Am. Chem. Soc.* **88**, 4727 (1966).

APPENDIX

In addition to the symbols for radicals given in the text, let B = benzophenone, BH_2 = benzhydrol, and P = benzoyl peroxide. We assume the following equations are sufficient to describe the observed reactions:

(I) Initiation

$$B^* + BH_2 \rightarrow 2K\cdot \qquad r_i = \phi_K \cdot I$$

(II) Propagation

$$K\cdot + P \rightarrow R + X\cdot \qquad r_{p1}K$$

$$X\cdot + BH_2 \rightarrow XH + K\cdot \qquad r_{p2}X$$

$$X\cdot \rightarrow \sigma\cdot \qquad r_{p3}X$$

(III) Termination

$$K + K \rightarrow \text{inert products} \qquad r_{t11}K^2$$

$$K + X \rightarrow \ldots. \qquad r_{t12}KX$$

$$K + \sigma \rightarrow \ldots. \qquad r_{t13}K\sigma$$

$$X + X \rightarrow \ldots. \qquad r_{t22}X^2$$

$$X + \sigma \rightarrow \ldots. \qquad r_{t23}X\sigma$$

$$\sigma + \sigma \rightarrow \ldots. \qquad r_{t33}\sigma^2$$

r_i is the rate of formation of ketyl radicals, and is equal to the quantum yield for ketyl radical formation, ϕ_K, times the light intensity, I. The r_p and r_t include rate constants and all concentration terms other than radical concentrations for the propagation and termination steps, respectively.

For convenience, we consider rate expressions for (A) termination involving phenylcyclohexadienyl radicals ($\sigma\cdot$), and (B) termination *not* involving phenylcyclohexadienyl radicals separately.

(A) Termination involving $\sigma\cdot$.

$$\text{Let } f_{t13} = \frac{r_{t13}K}{r_{t13}K + r_{t23}X + r_{t33}\sigma} = \frac{r_{t13}K}{\sum_{i=1}^{3} r_{ti3}R_i}$$

$$= \text{fraction of } \sigma\cdot \text{ terminating by path } t13$$

Similarly,

$$f_{t23} = \frac{r_{t23}X}{\sum_{i=1}^{3} r_{ti3}R_i}$$

$$f_{t33} = \frac{r_{t33}\sigma}{\sum_{i=1}^{3} r_{ti3}R_i}$$

$$\sum_{i=1}^{3} f_{ti3} = 1$$

The steady state conditions for K·, X·, and σ· are, respectively:

$$r_i - r_{p1}\mathrm{K} + r_{p2}\mathrm{X} - f_{t13}\sigma \sum_{i=1}^{3} r_{ti3}R_i = 0,$$

$$r_{p1}\mathrm{K} - r_{p2}\mathrm{X} - r_{p3}\mathrm{X} - f_{t23}\sigma \sum_{i=1}^{3} r_{ti3}R_i = 0,$$

$$r_{p3}\mathrm{X} - (1 + f_{t33})\sigma \sum_{i=1}^{3} r_{ti3}R_i = 0,$$

and the steady state condition for radicals is:

$$r_i = 2\sigma \sum_{i=1}^{3} r_{ti3}R_i.$$

Solution of the steady state equation for σ· for the concentration of X gives:

$$\begin{aligned}\mathrm{X}\cdot &= \frac{1 + f_{t33}}{r_{p3}}\sigma \sum_{i=1}^{3} r_{ti3}R_i \\ &= \left(\frac{1 + f_{t33}}{2}\right)\frac{r_i}{r_{p3}}\end{aligned}$$

The rate of loss of peroxide, $r_{p1}\mathrm{K}$, is obtained from the steady state equation for K· as:

$$-\frac{\mathrm{d}P}{\mathrm{d}t} = (r_i - f_{t13}\sigma \sum_{i=1}^{3} r_{ti3}R_i) + r_{p2}\mathrm{X}.$$

Substituting for $\sigma \sum_{i=1}^{3} r_{ti3}R_i$ from the steady state equation in radicals, and for X·, we have:

$$-\frac{\mathrm{d}P}{\mathrm{d}t} = r_i\left\{\left(1 - \frac{f_{t13}}{2}\right) + \left(\frac{1 + f_{t33}}{2}\right)\frac{r_{p2}}{r_{p3}}\right\}$$

$$-\frac{\mathrm{d}P/\mathrm{d}t}{r_i} = \frac{\phi_{\mathrm{P}}}{\phi_{\mathrm{K}}} = \left(1 - \frac{f_{t13}}{2}\right) + \left(\frac{1 + f_{t33}}{2}\right)\frac{r_{p2}}{r_{p3}}$$

(B) Termination not involving σ·.

This set of equations has already been solved for other systems[22, 23] using conventional steady state approximations. The result, as applied to the present system, is:

$$-\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{r_{p1}r_{p2}r_i^{\frac{1}{2}}}{(2r_{t11}r_{p2}^2 + 2r_{t12}r_{p1}r_{p2} + 2r_{t22}r_{p1}^2)^{\frac{1}{2}}}.$$

The chain length is therefore given by:

$$\frac{-\mathrm{d}P/\mathrm{d}t}{r_i} = \frac{\phi_{\mathrm{P}}}{\phi_{\mathrm{K}}} = -\frac{r_{p1}r_{p2}r_i^{-\frac{1}{2}}}{(2r_{t11}r_{p2}^2 + 2r_{t12}r_{p1}r_{p2} + 2r_{t22}r_{p1}^2)^{\frac{1}{2}}}$$

Limiting expressions are obtained by letting r_{t11}, r_{t12} and r_{t22} become zero.