

THE PHOTOSENSITIZED DECOMPOSITION OF BENZOYL PEROXIDE IN BENZENE

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Abstract—The mechanism of the benzophenone and 2-acetonaphthone sensitized decomposition of benzoyl peroxide in benzene has been investigated. When benzophenone is the sensitizer, the yield of acid resulting from peroxide decomposition increases as the initial peroxide concentration decreases. We interpret this to mean that benzophenone ketyl radicals are formed by hydrogen abstraction from solvent benzene at low peroxide concentrations, and the ketyl radicals then induce the decomposition of peroxide. When 2-acetonaphthone is the sensitizer, the acid yield is unaffected by peroxide concentration, but does depend upon the 2-acetonaphthone concentration and the light intensity. At the same light intensity, the acid yield with 2-acetonaphthone as sensitizer is less than half the yield when benzophenone is the sensitizer in the region of peroxide concentrations where the latter sensitizer should not form ketyl radicals. This can be rationalized by assuming (i) induced decomposition of benzoyl peroxide by benzophenone, but not 2-acetonaphthone, triplets; (ii) vertical and nonvertical energy transfer, with multibond cleavage occurring preferentially from the non-spectroscopic peroxide triplet; or (iii) quenching of sensitizer triplets by benzoyloxy radicals. These may not be mutually exclusive, and additional data are needed to clarify these points.

THE mechanism of the photosensitized decomposition of benzoyl peroxide has been examined by three groups of workers.¹⁻³ Walling and Gibian¹ describe this reaction most completely. They concluded that benzophenone triplets transfer energy to benzoyl peroxide at a rate which in benzene was about three orders of magnitude below the diffusion-controlled rate. Scission of the O—O bond occurs either during or after the energy transfer step, and is presumably followed by the labyrinthine nightmare of reactions characteristic of benzoyl peroxide decomposition in benzene.⁴

Some aspects of the photosensitized reaction were puzzling, however. One of these was the apparent anomaly that, although anthracene ($E_T = 42$ kcal/mole⁵) and 2-acetonaphthone ($E_T = 59.3$ kcal/mole⁵) both sensitized peroxide decomposition, sensitizers whose lowest triplet levels fell between 42 and 59.3 kcal/mole did not sensitize the reaction. This problem now appears resolved by the report of Liu and Edman⁶ that energy transfer from the anthracene T_2 state ($E_T = 74.4$ kcal) may occur under suitable conditions.

Another surprising aspect of the reaction is the fit of the experimental data to a mechanism involving only triplet energy transfer. Bell and Linschitz⁷ have found from flash photolysis studies that benzophenone triplets ($E_T = 68.5$ kcal/mole⁵) abstract hydrogen from benzene with a rate constant of $9 \times 10^2 (\pm 50\%) \text{M}^{-1} \text{sec}^{-1}$. This means that in solvent benzene ketyl radicals will be formed at a rate of about $10^4 \times [\text{Ph}_2\text{CO}^{\cdot 1}] \text{sec}^{-1}$. If the rate constant for energy transfer from benzophenone triplets to benzoyl peroxide in benzene is $\sim 3.2 \times 10^6 \text{M}^{-1} \text{sec}^{-1}$,¹ then a significant (>10%) fraction of the benzophenone triplets should react with solvent at peroxide concentrations below $\sim 0.03\text{M}$. This would result in curvature of the reciprocal plot

of quantum yield for peroxide loss (ϕ_p) vs peroxide concentration at the low concentrations of peroxide, the direction of curvature depending upon the reactivity of ketyl radicals towards benzoyl peroxide. It is surprising therefore that Walling and Gibian obtained a straight line with a correlation coefficient of 0.998 out to $\sim 0.0065M$ peroxide in such a plot. This requires that the efficiency with which ketyl radicals attack peroxide be the same as the efficiency for sensitized decomposition ($\sim 25\%$), and that the former does not change with peroxide concentration!

If, in fact, some of the benzophenone triplets do react with benzene to give ketyl radicals, then one might detect this by measuring the quantum yield for acid formation (ϕ_A) as a function of peroxide concentration. Provided the yields of acid from the sensitized and ketyl radical induced reactions differ, ϕ_A/ϕ_p should vary with peroxide concentration. This communication reports the results of our measurements of ϕ_A and ϕ_p in benzene solution with both an n, π^* ketone (benzophenone) and a π, π^* ketone (2-acetonaphthone)⁸ as sensitizer. As will become apparent, our data provoke additional questions about the sensitized decomposition of benzoyl peroxide. Since we do not intend to pursue this work further, we present our results at this point since at least one conclusion clearly emerges, *viz.*, this reaction is more complex than heretofore assumed.

In Table 1 are given the quantum yields for peroxide loss and acid formation[†] as a function of peroxide concentration with the two ketones as sensitizers. The ketone

TABLE 1. EFFECT OF PEROXIDE CONCENTRATION ON THE PHOTOSENSITIZED DECOMPOSITION OF BENZOYL PEROXIDE^a

[Peroxide], M	Sens ^b	ϕ_p	ϕ_A
0.067	A	0.268	0.047
0.033	A	0.216	0.033
0.010	A	0.098	0.015
0.0067	A	0.082	0.024
0.0033	A	0.059	0.016
0.067	B	0.226	0.132
0.033	B	0.148	0.093
0.020	B	0.130	0.074
0.010	B	0.102	0.073
0.0067	B	0.095	0.073
0.0033	B	0.062	0.059

^a $I(3660 \text{ \AA}) = 8.5 \times 10^{-4} \text{ el}^{-1} \text{ min}^{-1} (\pm 15\%)$; solvent, C_6H_6 .

^b A = 0.075M 2-acetonaphthone; B = 0.020M benzophenone.

concentrations were adjusted to give optical densities of 1.5 at the irradiation wavelength (3660 Å). Reciprocal plots of ϕ_p vs [peroxide] give a slope and intercept for benzophenone of 0.037 ± 0.004 and 5.24 ± 0.55 , respectively, and for 2-acetonaphthone, 0.047 ± 0.006 and 4.00 ± 1.00 , respectively. Assuming simple energy transfer,

† The product acid, assumed to be benzoic, was determined by measuring the decrease in absorbance at 500 m μ of the *o*-nitrophenolate anion⁹ upon addition of an aliquot of the photolysis mixture to a standardized solution of the anion. Benzoyl peroxide was determined iodometrically¹⁰ by using freshly distilled acetic anhydride and measuring the iodine spectrophotometrically.

this corresponds to rate constants for energy transfer of $1.4 \times 10^6 \text{M}^{-1} \text{sec}^{-1}$ (benzophenone) and $8.5 \times 10^{-4} \text{M}^{-1} \text{sec}^{-1}$ (2-acetonaphthone), based upon triplet lifetimes of 10^{-5}sec for benzophenone⁷ and 10^{-3}sec for 2-acetonaphthone.¹¹ The intercepts indicate either that vibrational relaxation of excited peroxide molecules is competitive with O—O bond scission, or that geminate recombination of caged benzoyloxy radicals must occur to the extent of about 70%. These results are in qualitative agreement with those of Walling and Gibian.¹

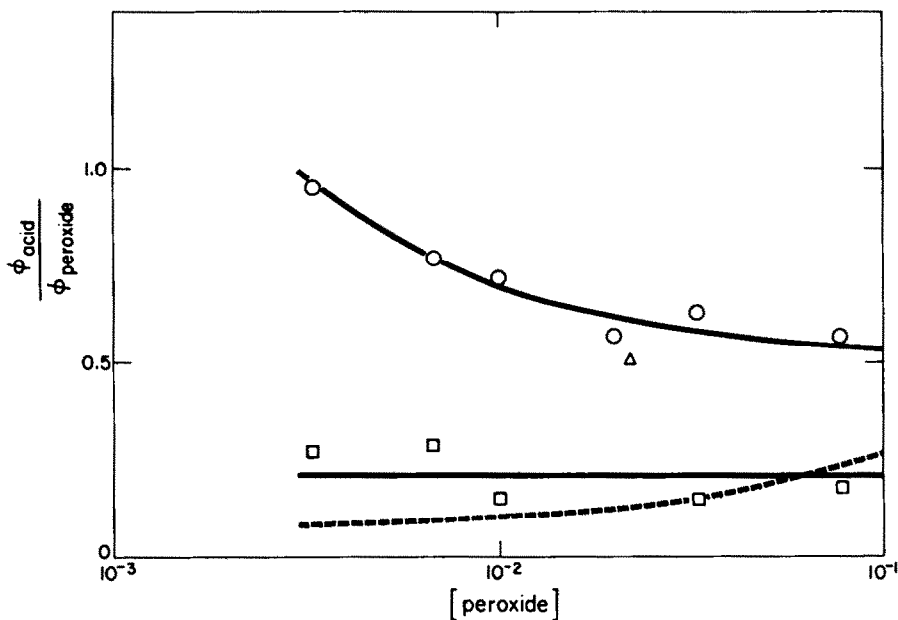


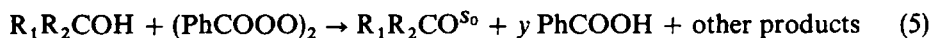
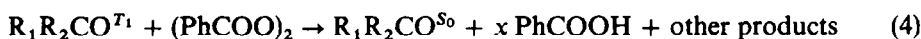
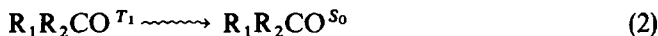
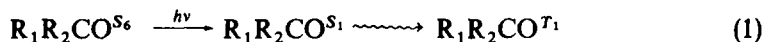
FIG. 1 Acid yield as a function of peroxide concentration: \circ ϕ_A/ϕ_P with benzophenone as sensitizer; \square ϕ_A/ϕ_P with 2-acetonaphthone as sensitizer; Δ data of ref. 3, benzophenone as sensitizer; - - - - acid yield in thermolysis (80°) in benzene from ref. 4.

That triplet energy transfer cannot be the *only* process occurring with benzophenone is shown by Fig. 1, where the ratio of quantum yields of acid to peroxide are plotted as a function of peroxide concentration for both ketones. In the case of 2-acetonaphthone, $\phi_A/\phi_P = 0.21 \pm 0.06$, whereas with benzophenone the ratio increases from 0.58 at 0.067M peroxide to 0.95 at 0.0033M peroxide. For the latter case, a reciprocal plot of ϕ_A/ϕ_P vs peroxide concentration indicates a limiting value of ~ 0.5 mole of acid per mole of peroxide decomposed. Clearly there are at least two phenomena which require rationalization: (i) ϕ_A/ϕ_P increases with dilution with benzophenone as the sensitizer, while with 2-acetonaphthone, ϕ_A/ϕ_P remains approximately constant. In the former case, the change in the ratio with peroxide concentration is in the *opposite* direction to the concentration effect observed in the thermolysis reaction in benzene (Fig. 1).^{4a} (ii) The limiting value for ϕ_A/ϕ_P (i.e. the value at high peroxide concentration) is about 2.5 times greater with benzophenone as sensitizer than with 2-acetonaphthone. The ratio in the latter case is nearer that observed in the thermolysis reaction (Fig. 1).^{4a}

The change in ϕ_A/ϕ_P with peroxide concentration obviously must arise from

different causes in the thermolysis and photolysis reactions. In thermolysis the increase in the acid yield with increasing peroxide concentration is believed to arise from the induced decomposition of peroxide by phenylcyclohexadienyl radicals.^{12a,13} Such an effect would be independent of the nature of the sensitizer if it were occurring in the photodecomposition reaction. We estimate by extrapolation of Nozaki and Bartlett's data^{12a} to 25° that less than 2% induced decomposition by phenylcyclohexadienyl radicals should be occurring at our photoinitiation rates and highest peroxide concentration (0.067M). Walling and Gibian¹ also concluded in their study that decomposition induced by phenylcyclohexadienyl radicals was negligible.

We believe that the increase in acid yield with lower initial peroxide concentration is a result of the reaction of ketyl radicals [formed by reaction of benzophenone triplets with solvent benzene (reaction 3)], with benzoyl peroxide (reaction 5). The phenyl radicals produced in step 3 would react with solvent benzene giving phenylcyclo-



hexadienyl radicals which, being less reactive than ketyl radicals, would be involved primarily in termination reactions. The yield of acid, then, would be a result of the relative rates of steps 3 vs 4 (where we temporarily ignore the details of reaction 4), of steps 5 vs 6, and of x vs y . Thus low peroxide concentration, while favoring ketyl radical formation, would disfavor induced decomposition (reaction 5) compared to termination (reaction 6).

According to this mechanism the quantum yields for peroxide loss and acid appearance will both be given by a summation of two terms:

$$\phi_P = \phi_P^S + \phi_P^K$$

$$\phi_A = \phi_A^S + \phi_A^K = x\phi_P^S + y\phi_P^K,$$

where superscript S refers to that part of the quantum yields arising by path 4 (assumed to involve energy transfer to some extent) and superscript K refers to that part of the quantum yields arising by path 5, i.e., the ketyl radical induced decomposition. Provided one knows both x and y , the observed quantum yields could be dissected into their components from which one could then determine k_4 by a reciprocal plot of ϕ_P^S vs [peroxide]. In the case of 2-acetonaphthone as sensitizer, if we assume $k_3 = 0$, then $x = 0.21 \pm 0.06$. However, this is not necessarily the value of x when benzophenone is the sensitizer. In one experiment in which 0.003M triphenylene ($E_T = 66.6 \text{ kcal}^5$) was substituted for benzophenone as sensitizer, we did obtain an acid yield of 0.25 mole per mole of peroxide decomposed, indicating that the amount of "primary" decarboxylation (i.e. that occurring in the cage or simultaneously with O—O bond scission) was about the same for 2-acetonaphthone and triphenylene. We hesitate to assume, however, that $x = 0.25$ for benzophenone also without a

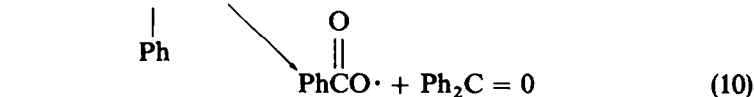
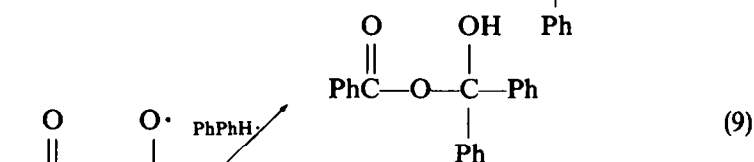
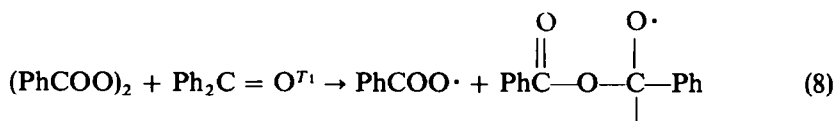
more extensive look at other hydrocarbon sensitizers. Moses¹⁴ has found, for instance, that the amount of "primary" decarboxylation occurring in the photosensitized decomposition of acetyl peroxide increases significantly with the triplet energy level of the sensitizer.

We have assumed arbitrary values of x and y to see what effect these have on k_4 , (determined by a reciprocal plot). The calculated values for k_4 lie in the range, 10^6 – $10^7 \text{ M}^{-1} \text{ sec}^{-1}$, i.e. k_4 is well below diffusion-controlled. This means that whatever chemistry is involved in reaction 4 when the ketone is benzophenone, it is only $\sim 10^2$ faster than (assumed) energy transfer from 2-acetonaphthone to peroxide.

The problem remains of determining the chemistry involved in step 4 for each sensitizer. The explanation must account for both a higher acid yield in the case of benzophenone and for the fact that the rate constants differ by only two orders of magnitude despite a difference in triplet energy levels of 9.2 kcal/mole. Several possibilities may be considered.

(i) n, π^* -Triplets are notorious for doing things other than transfer energy, and one suspects that the difference in behavior between benzophenone and 2-acetonaphthone at the higher peroxide concentrations may be connected with this fact. With benzoyl peroxide, induced decomposition is a common occurrence under a variety of conditions. It would not be surprising to find, therefore, that benzophenone triplets could induce the decomposition of benzoyl peroxide.

The literature abounds in examples of nucleophilic¹⁵ and radical^{15b, 16} displacements on oxygen in peroxides. Induced decompositions of benzoyl peroxide involving initial electron transfer *from* peroxide are also known.¹⁷ The transition state in radical induced decomposition is, however, stabilized by charge delocalization involving electron transfer *to* peroxide.¹⁸ If one were to postulate induced decomposition of benzoyl peroxide by benzophenone triplets, the most reasonable course would appear to be nucleophilic attack by the excited ketone on the peroxide. Nucleophilic attack of benzophenone triplets on benzoyl peroxide should proceed according to reaction 8. The resulting hemiacylal radical would be partitioned between the



hydrogen-abstraction reaction 9, yielding a hemiacylal, and fragmentation by reaction 10. The high yield of acid could result from reactions 8 + 9, the hemiacylal breaking down to acid and benzophenone.

(ii) The relationship between the rate constant for energy transfer between spectroscopic triplets of a sensitizer and acceptor in the region where this transfer is less than diffusion-controlled is given by the equation

$$\frac{\Delta \log k}{\Delta E_T} = - \frac{1}{2.303 RT}$$

where k is the true (second order) quenching rate constant.^{11,19} For non-vertical excitation, this slope diminishes. The difference in triplet energy levels between 2-acetonaphthone and benzophenone is 9.2 kcal/mole. If k_4 for benzophenone is interpreted as a second order rate constant for triplet energy transfer from the ketone to a spectroscopic triplet of benzoyl peroxide, then the rate constant for the same process for 2-acetonaphthone must be near zero. Since the observed rate constant is far from zero, this could be considered as indicative of non-vertical energy transfer from 2-acetonaphthone, and possibly benzophenone, to peroxide.

If non-vertical excitation is used to explain the small value for $\Delta \log k/\Delta E_T$, then multibond cleavage must occur more readily from the lower-energy, nonspectroscopic triplet than from the spectroscopic triplet. This is the opposite from what occurred in the photosensitized decomposition of acetyl peroxide,¹⁴ where increasing triplet energy of the sensitizer in the non-vertical energy transfer region resulted in increasing "primary" decarboxylation. Szwarc²⁰ has pointed out, however, that the process of breaking two bonds does not necessarily require more energy than the rupture of one bond. Such is the case when a bond in the intermediate radical resulting from single bond cleavage is thermodynamically unstable. Thermochemical calculations show²¹ that a negative dissociation energy occurs in R—COO radicals when R = CH₃, C₂H₅, or n-C₃H₇. In the case of benzoyl peroxide, D(Ph—COO) was estimated to be 0 ± 3 kcal/mole, and therefore decarboxylation is approximately a thermally neutral process. Delivery of triplet energy non-vertically to benzoyl peroxide would presumably result in rotational distortion of the peroxide, and multibond cleavage may be the preferred path for energy dissipation. In the case of the spectroscopic triplet, on the other hand, movement of atoms does not occur during the energy transfer step. The energy may be partitioned such that less rotational energy is delivered to the C—C bond, and O—O bond scission is preferred.

(iii) That the rate constants for energy transfer from benzophenone and 2-acetonaphthone to peroxide are well below diffusion-controlled admits the possibility of reversible energy transfer. On the other hand, a nonspectroscopic peroxide triplet may not survive long enough to transfer energy back to ground state sensitizer. In any case, it was believed important to determine if reversible energy transfer was occurring with either sensitizer.

Accordingly, the concentration of each sensitizer was increased by 6.7-fold (Table 2). With benzophenone as sensitizer, there was no detectable effect, within experimental error, on ϕ_A or ϕ_P when the ketone concentration was increased. It is clear from Table 2, however, that with the π, π^* ketone, 2-acetonaphthone, the reaction stoichiometry depends not only on sensitizer concentration, but also on light intensity. An increase in either results in a diminution of the acid yield. At a given light intensity, an increase in 2-acetonaphthone concentration diminishes ϕ_A and ϕ_P by almost the same amount. Thus, 2-acetonaphthone is quenching a reaction in which one mole

TABLE 2. EFFECT OF SENSITIZER CONCENTRATION AND LIGHT INTENSITY ON QUANTUM YIELDS FOR PEROXIDE AND ACID^a

[PhCOPh] M	[C ₁₀ H ₇ COCH ₃] M	10 ⁴ × I el ⁻¹ m ⁻¹	10 ⁶ × Rate, Mm ⁻¹ ,		φ _A	φ _P	φ _A /φ _P
			acid	peroxide			
0.020	—	9.3	68.2	95.4	0.073	0.102	0.72
0.133	—	8.6	58.1	91.0	0.068	0.106	0.64
—	0.075	8.0	11.8	78.5	0.015	0.098	0.15
—	0.50	8.2	2.1	69.1	0.002	0.084	0.02
—	0.075	1.6	8.2	20.0	0.051	0.125	0.41
—	0.50	1.6	2.0	14.3	0.013	0.089	0.15

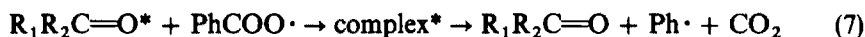
^a [Peroxide] = 0.01M.

of acid is formed for each mole of peroxide decomposed, and leaves unquenched a reaction in which very little acid is formed from the decomposition of the peroxide. The unquenched reaction may be decomposition via the non-spectroscopic triplet, since, as mentioned previously, reversible energy transfer from this triplet may not be efficient and a large amount of "primary" decarboxylation is reasonable. If the quenched reaction is that occurring from the spectroscopic triplet, then one must postulate an energy barrier between this triplet and the non-spectroscopic one in order that the former survive long enough to be quenched. This means that benzophenone at sufficiently high concentrations should also quench the spectroscopic triplet.

At constant ketone concentration, both φ_A and φ_P diminish with increasing light intensity, the former between 1.3 and 2.2 times as much as the latter. In the absence of induced decomposition, one ordinarily thinks of benzoic acid as arising from the reaction of benzoyloxy with phenylcyclohexadienyl radicals. This being a radical-radical reaction, it should increase in importance with increasing light intensity, whereas the acid yield decreases as the intensity is raised. Induced decomposition of benzoyl peroxide by a radical capable of delivering a hydrogen atom to the peroxide (e.g. ketyl, phenylcyclohexadienyl) would increase with decreasing light intensity, but then φ_A/φ_P values should increase with peroxide concentration. Over the range of peroxide concentrations investigated, however, this ratio is approximately constant (Fig. 1). The abstraction by benzoyloxy of a hydrogen atom from the methyl group of 2-acetonaphthone would also increase with decreasing light intensity, but this should result in a *higher* acid yield with increasing 2-acetonaphthone. Also, this would not explain the effect of light intensity on φ_P.

An explanation for the effect of light intensity which would fit the data available is that 2-acetonaphthone triplets are quenched by benzoyloxy radicals under the conditions of our experiments. Yang and Murov²² have proposed that the decrease in the quantum yield of photoreduction of benzophenone in 2-propanol with increasing light intensity results from triplet quenching by the ketyl radicals in solution. This conclusion is substantiated by the absence of racemization of *d*-2-octanol when benzophenone is irradiated in this alcohol.²³ The lowest light intensity used by Yang and Murov was $\sim 9 \times 10^{-4}$ el⁻¹ m⁻¹,²⁴ and they examined an approximately seventyfold variation in intensity. Our highest light intensity is almost exactly equal to Yang and Murov's lowest, but 2-acetonaphthone has a triplet lifetime which

is approximately one hundredfold longer than benzophenone.¹¹ Thus, quenching of 2-acetonaphthone triplets by benzoyloxy is very reasonable. If, in the thermalization of the triplet-radical complex, all or part of the excitation energy is



localized in the radical, then decarboxylation should result. The diminution in ϕ_p then results from the competition of the quenching reaction (7) with the energy transfer step (5). Since peroxide triplets do not decompose with unit efficiency, the effect on ϕ_p may be less than on ϕ_A , as observed.

This result could explain the higher acid yield when benzophenone is the sensitizer. Since the triplet lifetime of benzophenone is shorter than that of 2-acetonaphthone by about two orders of magnitude, benzoyloxy radicals would survive in the former case and the acid yield would be higher. Decomposition of peroxide could then proceed from the same, and only one, triplet state with both sensitizers. The concentration effect of 2-acetonaphthone (Table 2) could also be a result of the reversibility of the single energy transfer step. Thus, peroxide triplets, which ordinarily would undergo O—O bond scission, would be replaced by 2-acetonaphthone triplets, which would then be available for quenching by benzoyloxy radicals. Since the triplet lifetime of triphenylene is about two orders of magnitude longer than that of benzophenone,¹¹ this may also explain the near equivalence of the acid yields when triphenylene and 2-acetonaphthone are sensitizers.†

The above rationalizations of the data are not intended to be mutually exclusive. It is obvious that additional experiments are necessary to elucidate further the details of energy transfer to benzoyl peroxide.

EXPERIMENTAL

The experimental procedures were similar to those previously reported.²⁵

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† Triplet quenching by benzoyloxy radicals should be of decreasing importance with increasing peroxide concentration. In the limit of high peroxide concentration, all sensitizer triplets would transfer energy to peroxide, and thus none would be available for reaction (7). This implies that the acid yield (ϕ_A/ϕ_p) may slightly increase at high peroxide concentration. A referee has noted, however, that ϕ_A/ϕ_p may be slightly decreasing with increasing peroxide concentration when 2-acetonaphthone is the sensitizer (Fig. 1). Clearly further work is desirable using π,π^* sensitizers with triplet lifetimes at least as long as that of 2-acetonaphthone in order to determine the dependence (if any) of ϕ_A/ϕ_p on peroxide concentration.

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