

(11). A solution of 2 mg of **11** in 15 mL of absolute ethanol was irradiated in a quartz well suspended in a Srinivasan Rayonet photochemical reactor equipped with 16 2537-Å lamps for 30 min. The reaction was monitored by analytical GLC which showed little or no loss of starting material. No volatile products could be detected.

Photolysis of 4-Methyl-3-phenylcyclohex-2-en-1-one (12). A solution of 5.1 mg of **12** in 15 mL of absolute ethanol was irradiated in a quartz well in a Srinivasan Rayonet photochemical reactor equipped with 16 2537-Å lamps for 1 h. Analytical GLC showed a peak with retention time the same as one of the two unrecovered products of photolysis of **9**. The peak differed from that attributed to **14** (vide supra) and is tentatively attributed by us to compound **15**. There was insufficient quantity of material for further characterization.

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Differentiation of Excited-State and Biradical Processes. Photochemistry of Phenyl Alkyl Ketones in the Presence of Oxygen

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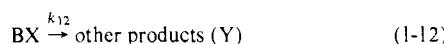
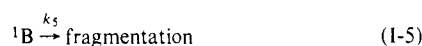
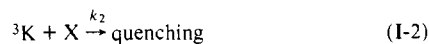
Abstract: The photochemistry of butyrophenone, valerophenone, γ -methylvalerophenone, and γ -phenylbutyrophenone has been examined in the presence of oxygen. The use of triplet quenchers to tune the triplet lifetime to a conveniently short value allows the differentiation of triplet state and biradical reactions. Typically oxygen quenches the triplet state with rate constants of $\sim 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and interacts with the biradicals with $k_8 \sim 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The interaction results in the formation of an intermediate which has as its main decay path the fragmentation to acetophenone, olefin and the regeneration of oxygen. About 75% of these intermediates decay giving type II products, while the other 25% yields a hydroperoxide. The ratio of products is probably controlled by spin statistical factors. Previous reports indicating that oxygen has no effect on the Norrish type II reaction are incorrect.

The behavior of the biradicals generated in the Norrish type II reaction has received considerable attention during the last few years. Several substrates have been shown to trap these biradicals in reactions involving hydrogen abstraction,^{2,3} addition to double bonds,⁴ and electron transfer.^{5,6} Far from

being unique, the examples which have been examined represent a few cases where the reactions of the biradical can be easily differentiated from those of the precursor excited states.

Photochemical processes involving the intermediacy of more

Scheme I



than one transient species are not uncommon. Singlet and triplet states, as well as free radicals are typical examples; for these, we have a number of general techniques which allow us to decide which is the reactive intermediate. Unfortunately, this is not the situation in the case of biradicals, probably reflecting our limited understanding of their chemistry.

The photochemistry of phenyl alkyl ketones in the presence of oxygen is an interesting example where one can test methods for the differentiation of triplet state and biradical processes. While it is known that oxygen quenches carbonyl triplets quite efficiently,^{7,8} the reports in the literature indicate not only quenching of the type II photofragmentation by oxygen,⁹ but also examples of an enhancement of the yields of fragmentation products^{10,11} and abundant examples where oxygen has no effect.¹² As if this did not provide sufficient variety, in the case of 2-methyl-1,5-diphenylpentane-1,5-dione¹³ oxygen has been reported to quench the formation of propiophenone but to have no effect on the other possible mode of photofragmentation which leads to the production of acetophenone.

In this paper we examine the photochemistry of butyrophenone, valerophenone, γ -methylvalerophenone, and γ -phenylbutyrophenone in polar and nonpolar solvents in the presence of oxygen. Some novel approaches have been used to differentiate the reactions of excited states from those of the intermediate biradical. The emphasis of this report is placed on these aspects and we evaluate the generality of these methods. Finally, we discuss reports in the literature indicating the absence of an oxygen effect and suggest a reinterpretation for these observations.

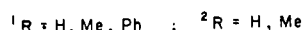
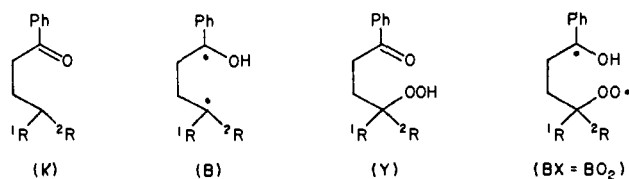
Results

When a solution of phenyl alkyl ketone is irradiated in the absence and presence of oxygen, the effect of the latter on the yields of photofragmentation can be extremely different depending on the ketone and solvent used. For example, in the case of butyrophenone, oxygen causes a decrease in the quantum yields suggesting that quenching is the *predominant*

effect. In contrast, in the case of γ -methylvalerophenone in benzene, oxygen causes an increase in the quantum yields of photofragmentation products. In preliminary reports we have shown that the enhancement of the yields has to be attributed to the interaction of the biradical with oxygen.¹⁰

Scheme I shows a general mechanism for the photochemistry of phenyl alkyl ketones bearing γ -hydrogen atoms in the presence of a molecule X. In the case of oxygen the occurrence of reaction I-8 has been conclusively established for γ -methylvalerophenone;¹⁰ therefore, the possibility of this type of interaction has to be considered in all cases, even if, as in the case of butyrophenone, it is not the predominant effect.

Reaction I-12 takes into account the formation of products other than those which are characteristic of the type II process. We have detected the formation of a hydroperoxide, which has been unequivocally identified in the case of γ -phenylbutyrophenone. K, B, Y, and BX are the structures of the molecules and intermediates involved in reactions of Scheme I in the case of oxygen.



The quantum yield of photofragmentation, Φ_{11} , equals the sum of the yields of reactions I-5 and I-9 and is given by

$$\Phi_{11} = \left(\frac{1}{1 + T[X]} \right) \left(\frac{1}{1 + B[X]} \right) (P_{11} + \beta B[X]) \quad (1)$$

where

$$P_{11} = \frac{k_5}{k_5 + k_6 + k_7} \quad (2)$$

$$\beta = \frac{k_9}{k_9 + k_{10} + k_{11} + k_{12}} \quad (3)$$

$$B = k_8 \tau_B = k_8/k_4 \quad (4)$$

$$T = k_2 \tau_T = k_2/k_3 \quad (5)$$

where τ_B and τ_T are the biradical and triplet lifetimes, respectively. For the four ketones considered in this work (note that this is not necessarily true for any ketone), the quantum yields of biradical production in the absence of oxygen or other quenchers are unity¹⁴ and therefore $P_{11} \equiv \Phi_{11}^0$, the quantum yield of photofragmentation under these conditions. Replacing in eq 1 we obtain

$$\frac{\Phi_{11}}{\Phi_{11}^0} = \left(\frac{1}{1 + T[X]} \right) \left(\frac{1}{1 + B[X]} \right) \left[1 + \left(\frac{\beta}{P_{11}} \right) B[X] \right] \quad (6)$$

This is an extremely useful equation and can be reduced to different forms depending on the experimental conditions, value of τ_T , etc. We have found it practical to define an "enhancement factor" for each system, as

$$\epsilon = \frac{\beta}{P_{11}} - 1 \quad (7)$$

ϵ is 0 when the reagent considered does not affect the fraction of the biradicals which give fragmentation; ϵ is positive when this fraction is increased, as is the case with alcohols,¹⁵ organophosphorus(V) compounds,¹⁶ and oxygen.¹⁰ For example $\epsilon = 0.5$ means that the fraction of biradicals which give fragmentation has been increased by 50%. ϵ can also have negative values when the fraction of biradicals leading to fragmentation is decreased. In particular $\epsilon = -1$ when trapping is a destruc-

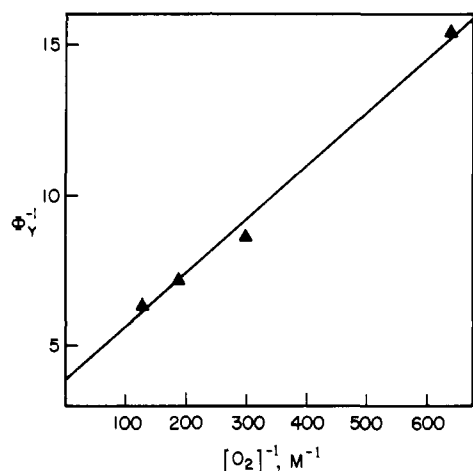


Figure 1. Plot of Φ_Y^{-1} vs. $[\text{O}_2]^{-1}$ γ -methylvalerophenone in benzene. See eq 9.

tive process, in the sense that when a biradical is trapped it cannot lead to fragmentation products; such is the case of thiols,² di-*tert*-butyl selenoketone,^{4b} and paraquat ions.^{5,6}

γ -Methylvalerophenone. The triplet lifetime of γ -methylvalerophenone in benzene is ~ 2 ns.¹⁷ This value of τ_T makes any interaction of oxygen with the triplet state insignificant for the range of oxygen concentrations used and for most practical purposes can be neglected. Under these conditions eq 8 can be obtained from either eq 1 or 6.

$$\frac{\Phi_{11}^\circ}{\Phi_{11} - \Phi_{11}^\circ} = \frac{1}{\epsilon} \left(1 + \frac{1}{B[\text{X}]} \right) \quad (8)$$

As we have already shown,^{10b} the plots of $\Phi_{11}^\circ/(\Phi_{11} - \Phi_{11}^\circ)$ vs. $[\text{O}_2]^{-1}$ are linear and lead to $B = 250 \text{ M}^{-1}$ and $\epsilon = 1.83$.

As mentioned above, the photolysis also results in the formation of a hydroperoxide. For example for $[\text{O}_2] = 0.0033 \text{ M}$, $\Phi_Y = 0.12$. This cannot be attributed to a reaction of the triplet state, since a simple calculation shows that it would require a rate of reaction of the triplet state with oxygen of at least $2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ which is over five times the rate observed (vide infra) and is rather high for any standards.⁷ Further, the same oxygen concentration leads to lower yields of peroxides in the case of valerophenone and butyrophenone which have longer lived triplets and therefore could be expected to undergo triplet state-oxygen interactions with higher yields.

If we neglect triplet quenching,

$$\frac{1}{\Phi_Y} = \left(1 + \frac{1}{B[\text{X}]} \right) \left(\frac{k_9 + k_{10} + k_{11} + k_{12}}{k_{12}} \right) \quad (9)$$

represents the behavior of the system, where Φ_Y is the quantum yield of peroxide formation. Figure 1 shows the results, which lead to $B = 220 \text{ M}^{-1}$ and $[k_{12}/(k_9 + k_{10} + k_{11} + k_{12})] = 0.26$; that is 26% of the biradicals which interact with oxygen yield a peroxide. The interaction of oxygen with the biradicals has also been established in laser photolysis experiments,^{6,18} from which rates in the $5\text{--}8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ range were obtained, depending on the solvent.

Analysis of the other two products of the Norrish type II reaction shows that the yields of olefin (methylpropene) remain within experimental error equal to those of acetophenone, while only minor changes were detected in the case of the cyclobutanols. Usually these increase slightly, but not enough to allow their use for reliable kinetic studies.

In polar solvents, e.g., methanol or wet acetonitrile, oxygen causes a small decrease of the yields of photoproducts and is discussed in some detail in the case of valerophenone (see below).

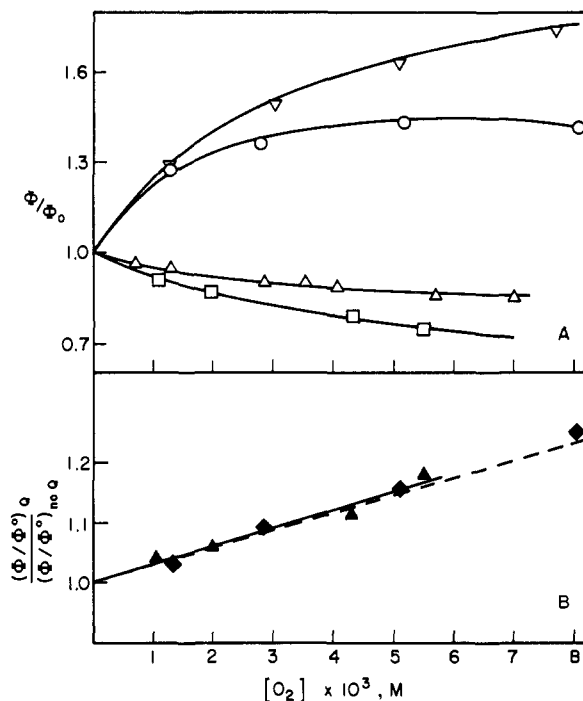


Figure 2. (Top) Fragmentation quantum yield data for valerophenone: ∇ , in benzene containing 0.1 M *cis*-1,3-pentadiene; \circ , in benzene; Δ , in wet acetonitrile containing 0.1 M *cis*-1,3-pentadiene; \square , in wet acetonitrile. (Bottom) Plots according to eq 11 in benzene (\diamond) and in wet acetonitrile (Δ).

For reasons that will become apparent in the sections to follow, it was important to establish whether conjugated dienes significantly trap type II biradicals and/or have an effect on their partition into products. Experiments in the presence of 0.1 M *cis*-1,3-pentadiene showed that the relative increase of the yields caused by oxygen is the same under these conditions as in the absence of diene. In other words, a 0.1 M concentration of diene does not significantly trap the biradicals and does not affect the fraction which yields fragmentation products.

Valerophenone. This is a particularly controversial example, the literature having many reports indicating that oxygen has no effect on the reaction. A closely related example is the case of poly(phenyl vinyl ketone), which has a triplet lifetime only slightly longer than that of valerophenone.¹²

We should perhaps begin this section by pointing out that laser photolysis studies have provided conclusive evidence showing that the intermediate biradical is scavenged by oxygen in the same way as that from γ -methylvalerophenone.^{6,10,18}

If a solution of valerophenone in benzene is irradiated in the presence of different concentrations of oxygen the yields of acetophenone production are increased as shown in Figure 2 (top).¹⁹

The triplet state of valerophenone is considerably longer lived than that of γ -methylvalerophenone (7 ns in benzene)¹⁷ and one would expect some triplet quenching. In fact, if one makes a plot using eq 8, the data does not behave linearly; further, careful chromatographic analysis of the samples shows that the maximum shown in Figure 2 (top) is real. This behavior is characteristic of many systems involving triplet quenching and biradical trapping as has also been observed in the photochemistry of 2-pentanone adsorbed in Vycor glass.¹¹

The problem is how to separate the interaction of oxygen with the triplet state and with the biradical, particularly when they tend to compensate. For this we have used what we call the "triplet-lifetime-tuning" technique. That is, examination of the case of γ -methylvalerophenone discussed above clearly

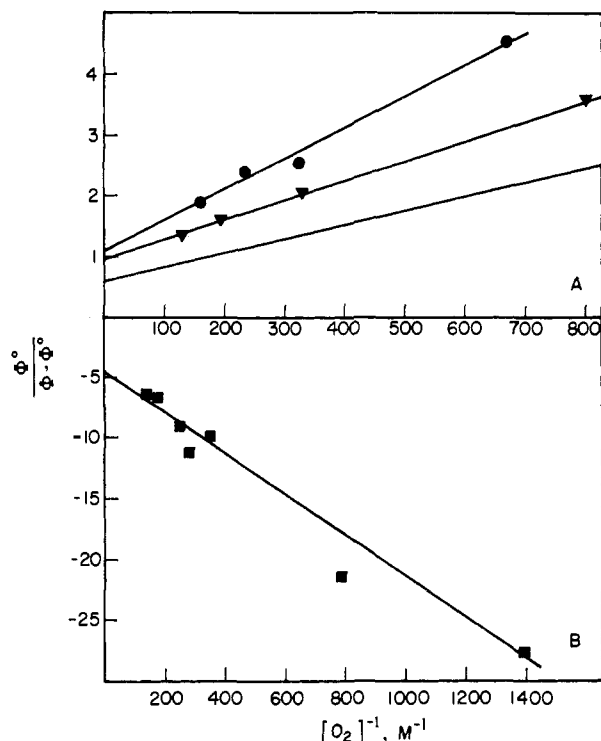


Figure 3. (Top) Plots according to eq 8 for butyrophenone (●) and valerophenone (▼) using the triplet-lifetime-tuning technique. The full line (with no experimental points) has been taken from ref 10 and corresponds to γ -methylvalerophenone. (Bottom) Same plot for valerophenone in wet acetonitrile using the triplet-lifetime-tuning technique. Note that the ordinate is negative.

shows that all that we need to be able to examine the biradical behavior independently of that of the triplet state is a short-lived triplet. This can be easily achieved by adding to the system a chemically inert triplet quencher, so that the new triplet lifetime is formally given by

$$\frac{1}{\tau_{T'}} = \frac{1}{\tau_T} + k_q[Q] \quad (10)$$

Equation 6 still holds where Φ_{II}° now refers to the yield in the absence of oxygen, but in the presence of a constant concentration of the quencher Q. The same is true for eq 8. Naturally, T has to be defined as a function of $\tau_{T'}$ rather than τ_T ; that is $T' = k_2\tau_{T'}$. The main consideration is to make $\tau_{T'}$ small enough that it will lead to $T'[X] \ll 1$ and therefore negligible. Figure 2 (top) shows the results for $\tau_{T'} = 1.6$ ns. Application of eq 8 to the data from Figure 2 (top) leads to the plot of Figure 3 (top) which gives $B = 270 \text{ M}^{-1}$ and $\epsilon = 1.10$. The quencher used in these experiments was 1,3-nonadiene. Dienes are almost ideal quenchers for the triplet-lifetime-tuning technique which requires nonreactive quenching even in oxygen saturated solutions.²⁰ A value of ϵ of 1.10 means 110% increase in the fraction of biradicals which proceed to fragmentation products. Taking into account the cyclobutanols and Φ_{II}° we estimate that 73% of the biradicals which interact with oxygen proceed to type II products.

The ratio of Φ/Φ_0 values in the presence and absence of the quencher Q provide the information to examine the effect of oxygen on the triplet state, that is,

$$\frac{[\Phi/\Phi_0]_Q}{[\Phi/\Phi_0]_{\text{no } Q}} = 1 + T[X] = 1 + k_2\tau_T[X] \quad (11)$$

where the subscripts Q and no Q refer to the additional quencher, 1,3-nonadiene in this case. Figure 2 (bottom) shows a plot of the data corresponding to eq 11 for benzene solvent

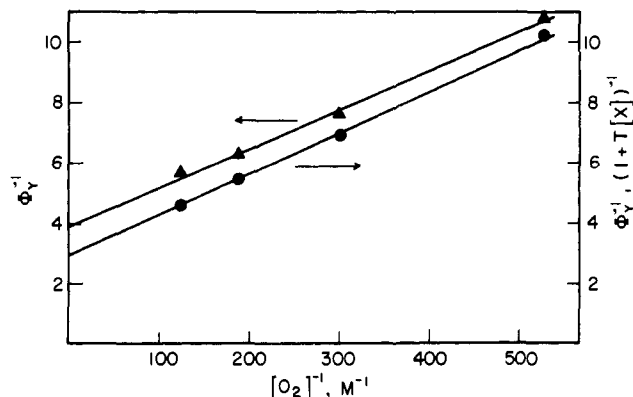


Figure 4. Plot of the peroxide yields for valerophenone in benzene corrected (●) and uncorrected (▲) for triplet quenching. See eq 9 and 12.

and should be interpreted as a normal Stern-Volmer plot and leads to $k_2\tau_T = 29 \text{ M}^{-1}$ from which we obtain $k_2 = 3.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

If the same type of experiments are carried out in wet acetonitrile (2% water), where reaction I-7 can be ignored, the resulting plots of $\Phi_{II}/\Phi_{II}^\circ$ which are also shown in Figure 2 (top) result in a decrease of the yields (*cis*-1,3-pentadiene was used in this case). Using the same approach as before we obtain $k_2\tau_T = 30 \text{ M}^{-1}$ (see Figure 2 (bottom)), which, using the triplet lifetime from the literature, gives $k_2 = 3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, a similar value to that given above.

It is interesting to note that eq 8 can also be used in the case where the reaction of the biradicals results in a reduction of the yields, only that in this case ϵ is negative. This type of behavior is usually observed in wet acetonitrile, where the probability of product formation (P_{II} plus cyclobutanols) is 1. This is shown in Figure 3 (bottom) and leads to $B = 260 \text{ M}^{-1}$ and $\epsilon = -0.23$; that is, if the fragmentation-to-cyclization ratio remains constant, 77% of the biradicals which interact with oxygen yield type II products. This value compares well with the value of 73% observed in benzene suggesting that the behavior of BO_2 is largely independent of the solvent.

The yields of peroxide formation are also affected by triplet quenching. To plot the data as in the case of eq 9 and Figure 1 it is necessary to correct the data to take into account triplet quenching, which leads to eq 12.

$$\left(\frac{1}{\Phi_Y}\right) \left(\frac{1}{1 + T[X]}\right) = \left(1 + \frac{1}{B[X]}\right) \left(\frac{k_9 + k_{10} + k_{11} + k_{12}}{k_{12}}\right) \quad (12)$$

Figure 4 shows corrected and uncorrected plots for the yields of peroxide; from the former we obtain $B = 220 \text{ M}^{-1}$ and $\sim 30\%$ of the biradicals which interact with oxygen give the peroxide.

Butyrophenone. Oxygen decreases the yield of photofragmentation of butyrophenone. Even in the low concentration region, in experiments using O_2/N_2 mixtures (see Experimental Section) we were unable to detect any enhancement of the yields. When the triplet-lifetime-tuning technique is used, for example using 0.1 M *cis*-1,3-pentadiene, which gives $\tau_{T'} = 1.9$ ns, the enhancement can be easily observed. The corresponding plot using eq 8 is shown in Figure 3 (top). Figure 5 (top) shows the effect of oxygen on Φ/Φ_0 in the absence and presence of 0.1 M *cis*-1,3-pentadiene. Figure 5 (bottom) shows a typical Stern-Volmer plot and one corrected for biradical behavior using eq 11. It is quite clear that ignoring the interaction with the biradical can introduce considerable error on the values of T .

The quantum yields of peroxide formation are shown in Figure 6. The curve is expected to give a maximum. The con-

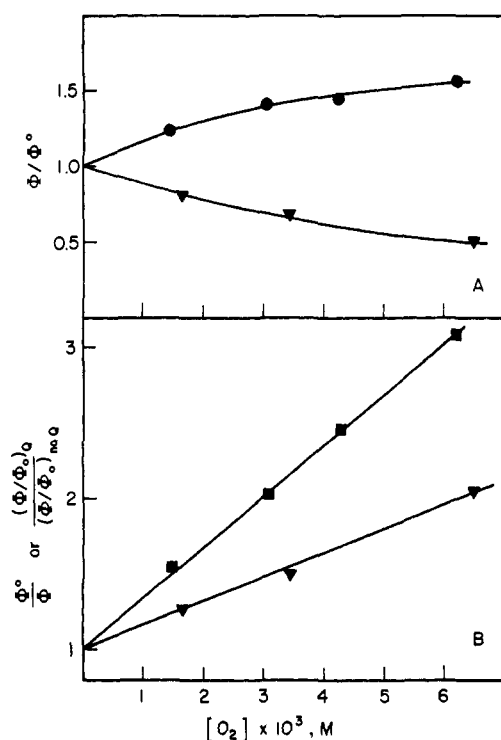


Figure 5. (Top) Quantum yield data for butyrophenone in benzene (▼) and in benzene containing 0.1 M *cis*-1,3-pentadiene (●). (Bottom) Stern-Volmer plots corrected (■) and uncorrected (▼) for biradical trapping; see text.

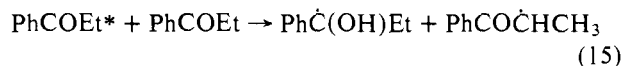
centration of oxygen at this point is determined by

$$[O_2]_{\max} = (BT)^{-1/2} \quad (13)$$

and

$$\Phi_{Y,\max} = \left(\frac{k_{12}}{k_9 + k_{10} + k_{11} + k_{12}} \right) \left(\frac{1}{1 + \sqrt{T/B}} \right)^2 \quad (14)$$

The agreement of the position at the maximum and the yield at that point is not very good. Figure 6 shows a plot of Φ_Y vs. $[O_2]$ and two calculated curves for values of $[k_{12}/(k_9 + k_{10} + k_{11} + k_{12})]$ of 0.25 and 0.31. To establish whether some peroxide was being formed in radical, rather than biradical, reactions, we carried out a series of experiments with propiophenone, which cannot give biradicals and found quantum yields for peroxide formation of the order of 0.02.²² The yields show a small inverse dependence with oxygen concentration suggesting that high oxygen concentrations tend to preclude, rather than assist, the process. This observation eliminates singlet oxygen as a possible candidate and strongly suggests that the production of free radicals, probably via reaction 15, provides the precursors for the generation of peroxide in the case of propiophenone.



There is a possibility that a chain process might be established, though we believe unlikely at the light intensities used and for the relatively strong C-H bonds in propiophenone.²³ We believe that the occurrence of a similar process in the case of butyrophenone is responsible for the lack of fully quantitative agreement between the concentration at the maximum and the quantum yield at that point (see Figure 6).²⁴

γ -Phenylbutyrophenone. The triplet state of γ -phenylbutyrophenone has a lifetime slightly longer than that of γ -methylvalerophenone.²⁵ The kinetic analysis in this case is very similar to that presented in the case of valerophenone, and the

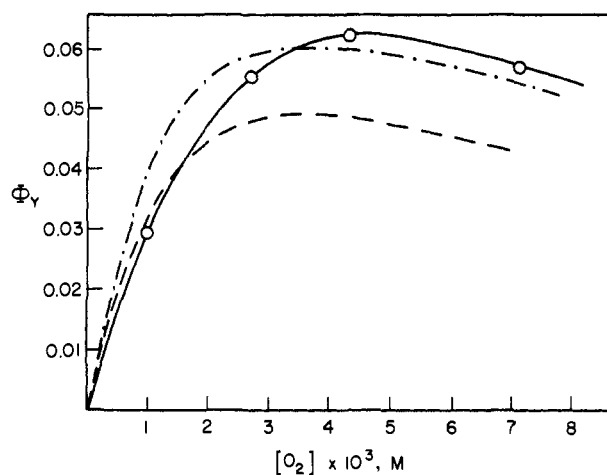


Figure 6. Quantum yield data for the hydroperoxide in the case of butyrophenone in benzene. The calculated curves correspond to $T = 340 \text{ M}^{-1}$ and $B = 21 \text{ M}^{-1}$ and a probability of peroxide generation of 0.25 (---) and 0.31 (-.-): see text.

results are consistent with a value of B of 200 M^{-1} and $\epsilon \sim 0.4$. Since ϕ_{11}° is 0.50,¹⁴ we estimate that 76% of the BO_2 complexes proceed to type II products, assuming that the quantum yield of cyclobutanols ($\phi_{\text{CB}}^\circ = 0.06$)¹⁴ remains constant. The smaller value of ϵ (compare, e.g., with γ -methylvalerophenone) leads to a correspondingly smaller increase in ϕ_{11} ; owing to this cause, the importance of triplet quenching by oxygen is larger than could be expected from the short triplet lifetime.

This ketone was examined largely for two reasons: (i) the olefin produced in this case, i.e., styrene, is not volatile and, we expected to be able to confirm whether the yield of olefin was identical with that of acetophenone under conditions where the analytical errors are minimized, and (ii) the hydroperoxide produced in this case, after reduction to the alcohol, yields 1,4-diphenyl-1-hydroxy-4-butanone which can be readily prepared from 1,4-diphenyl-3-butene-1,3-dione.²⁶ Both experiments yielded positive results and provided further confirmation of the mass balance as well as definite evidence for the structure of the hydroperoxide generated in the reaction.

Discussion

A rather common assumption, implicit in many papers where oxygen has been reported to have little or no effect on the Norrish type II reaction, is that the terms nondegassed and air saturated can be taken as equivalent. Naturally, this is not a bad assumption if quenching by energy transfer is the only process in which oxygen participates. However, as shown before, the interaction of oxygen with the biradicals results in oxygen consumption as a result of the production of a hydroperoxide, and special care is needed to ensure that the gas-liquid equilibrium is maintained at all times (see Experimental Section).

The analysis of eq 6 shows that, whenever there is an enhancement of the yields, one should expect a maximum and two points where $\Phi_{11}/\Phi_{11}^\circ = 1$, with the only condition that $k_2 \neq 0$. The concentrations at the two points mentioned above ($\Phi_{11}/\Phi_{11}^\circ = 1$) are

$$[X] = 0 \quad (16a)$$

$$[X] = \frac{\epsilon}{T} - \frac{1}{B} \quad (16b)$$

and the condition for an enhancement to be observable is given by

$$\epsilon > \left(\frac{T}{B} \right) \quad (17)$$

Table I

Property	Units	Butyrophenone	Valerophenone	γ -Methylvalerophenone
τ_T (benzene)	ns	120 ^a	7.6 ^a	1.9 ^a
τ_B (benzene)	ns	33 ^b	34 ^c	35 ^c
τ_B (wet acetone nitrile)	ns		70 ^c	76 ^c
B (benzene) ^d	M ⁻¹	210 ^e	270 ^e	250
B (wet acetone nitrile) ^d	M ⁻¹		260 ^e	
T (benzene) ^d	M ⁻¹	340 ^f	29	
k_2 (benzene)	M ⁻¹ s ⁻¹	2.9×10^9	3.8×10^9	
k_8 (benzene)	M ⁻¹ s ⁻¹	$(7.0 \times 10^9)^g$	8.4×10^9	7.1×10^9
ϵ (benzene)		0.94	1.09	1.83 ^h
ϵ (wet acetone nitrile)			-0.23	
Probability of peroxide	%	(25) ⁱ	30	26
[O ₂], eq 16b	M	Impossible	0.034	~0.19
Cyclization and fragmentation ^j		0.74	0.73	0.74

^a From ref 17. ^b Calculated assuming the value of k_8 as 7×10^9 M⁻¹ s⁻¹, the same as for γ -methylvalerophenone and in agreement with laser photolysis studies.^{10b,18} ^c From ref 6 and 18. ^d Typical errors are 20% or less and are also reflected in the values of k_2 and k_8 . ^e Obtained using the "triplet-lifetime-tuning" technique. ^f The value has not been extrapolated to zero butyrophenone concentration. A 10–20% increase in this value and in k_2 could be expected if this approach is used, since the relatively long triplet lifetime makes butyrophenone a good candidate for impurity quenching. ^g Assumed; see text and footnote b. ^h Corrected to take into account the small fraction of triplet quenching by oxygen. The uncorrected value is 1.72. This correction is not necessary for the other ketones because ϵ was obtained using the "triplet-lifetime-tuning" technique. ⁱ Estimated; see Figure 6. ^j Based on the fragmentation data and on the assumption that the fraction of biradicals which give cyclobutanols is the same for B and BO₂.

Analysis of the data presented above leads to the concentrations of oxygen at the point determined by eq 16b given in Table I. It seems clear that none of the ketones considered herein could possibly be at that point in the case of an air-saturated solution, where [O₂] $\sim 2 \times 10^{-3}$ M in most common organic solvents. Since B is usually of the order of 200–250 M⁻¹ in nonpolar media, the condition to observe no effect in an air-saturated solution of a simple ketone is $\epsilon/T \sim 0.006$ M.

A rather interesting example is that case of poly(phenyl vinyl ketone), for which numerous reports have indicated that oxygen has no effect on the photochemistry. We have carried out a series of laser photolysis experiments (which will be discussed in detail elsewhere²⁷) which show that $k_8 \approx 1 \times 10^9$ M⁻¹ s⁻¹; that is, while the rate is slower than in small molecules, it is still an extremely fast process. The question as to whether an air-saturated solution of poly(phenyl vinyl ketone) fulfills eq 16b cannot be answered from our data, and will require detailed studies of the yields of photodegradation. However, it is clear that, even if eq 16b is fulfilled, the conclusion that oxygen does not affect the photodegradation process is not warranted.

The importance of taking special care to maintain the gas-liquid equilibrium was also clear in a series of experiments with *nonstirred* samples of valerophenone in benzene, initially air saturated. When the radiation doses are small compared with the oxygen concentration, the observed value for ϕ_{11}/ϕ_{11}^0 is 1.29, the same as under equilibrium conditions. However, if the radiation dose is increased (always in nonstirred samples) the overall value of ϕ_{11}/ϕ_{11}^0 decreases to ~ 1.10 for doses of the order of 0.02 einstein L⁻¹.

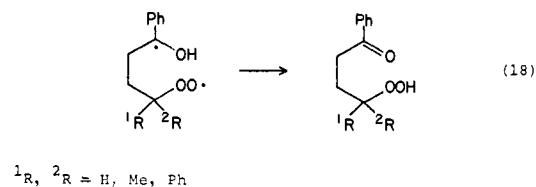
The question might be raised as to how general the methods used herein really are. In particular this question applies to the use of the triplet-lifetime-tuning technique, which allowed us to look independently at biradical processes, and, then, using, for example, the data from Figures 2 and 5 to be able to examine the behavior of the triplet state. In principle there is no limitation, provided that the quencher used does not trap the biradical and undergoes negligible chemical change (other than for example *cis-trans* isomerization) in the quenching process. In practice we observe that, when the use of the method requires quenching, >99.5% of the triplets the measurements become rather difficult. For example, when biradical trapping is of a destructive nature ($\epsilon = -1$), the method should be applicable when $500B \geq T$, though in limiting situations the results should be subjected to a critical scrutiny.

We believe at this point that the kinetics of the processes involved in the photochemistry of phenyl alkyl ketones in the presence of oxygen are fairly well understood. That is, Scheme I represents adequately these processes. Reaction I-4 has been included as an irreversible process, following our conclusion that the biradical lifetimes are determined by spin inversion.⁶ The rate of triplet quenching by oxygen of $\sim 4 \times 10^9$ M⁻¹ s⁻¹ is in agreement with previous observations that the process is somewhat slower than diffusion controlled and that quenching by oxygen is slower than by dienes.⁷

The rate of interaction of oxygen with the biradicals is $\sim 7 \times 10^9$ M⁻¹ s⁻¹ in benzene and the B values obtained in this study agree well with the values of k_8 and τ_B obtained in laser photolysis experiments.^{6,18}

The data for butyrophenone (see Figures 3 (top) and 5) provide a good measurement of B as 210 M⁻¹, which, assuming that the rate of biradical trapping is the same as in the other two examples, gives $\tau_B \approx 33$ ns. This value should resolve the controversy as to whether the biradical from butyrophenone is exceptionally long lived or not.¹⁶ Our results indicate that within experimental error the lifetimes of the biradicals from the three ketones in Table I are the same.

In a recent publication we suggested that the enhancement of the yields by oxygen (in other words $\beta > P_{11}$) was in a way similar to the effect of polar solvents, in the sense that one of the biradical ends would be protected by the oxygen molecule.⁹ We would expect the complex BO₂ (equivalent to BX in Scheme I) to have a peroxy-type structure. The lifetime of this complex has to be considerably shorter than that of B, otherwise we would probably be able to detect the ketyl chromophore in direct laser photolysis experiments or to observe electron transfer reactions. A reasonable limit is $\tau_{BO_2} < 10$ ns. The formation of the hydroperoxide of Scheme I from BO₂ can be expected to be ~ 55 kcal/mol exothermic.²⁸ From a mechanistic point of view it probably resembles the reaction of the biradicals with C=Se bonds, where the addition is followed by a hydrogen shift,^{4b} i.e., eq 18.



We were surprised to observe that within our experimental error the probability of peroxide formation from BO₂ was always close to 25%, while the probability of fragmentation plus cyclobutanols was always close to 75%. While the constancy of this 1:3 product ratio can conceivably be fortuitous, we tend to believe that it reflects spin statistical factors in a manner similar to that used to account for the probabilities of oxygen quenching of triplet states.^{29,30} Scheme II shows the basic set of reactions required to explain the behavior observed; that is,

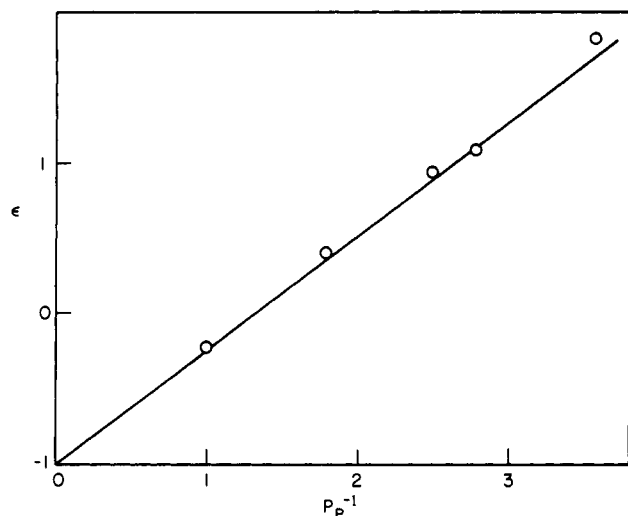
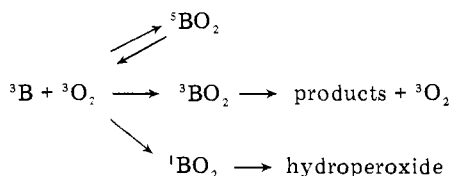


Figure 7. Correlation of the enhancement factor with the probability of product formation from B (see eq 19).

Scheme II



the quintet states (probability 5/9) would be dissociative in nature and are not expected to lead to any observable chemical change, the singlet state (probability 1/9) would yield the hydroperoxide in the ground state, while the triplet configuration (probability 3/9) would account for the formation of fragmentation and cyclization products accompanied by the regeneration of ground-state triplet oxygen. This last process is probably the most interesting one, since in the case of triplet quenching by oxygen the triplet configuration is dissociative.²⁹ A mechanism of this nature, which undoubtedly involves a considerable degree of speculation can explain the ratio of $\sim 1/3$ between the peroxide and other products and would require a rate of diffusion in benzene of at least $1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which does not seem unreasonable.

If our model based on spin statistical factors is correct and the probability of product formation from BO_2 is always 75%, then the values of ϵ and P_p (the probability of product formation from B) should correlate according to eq 19

$$\epsilon \sim \frac{0.75}{P_p} - 1 \quad (19)$$

where we have replaced β by 0.75 in eq 7 and P_{11} by P_p in order to refer to total type II products rather than just fragmentation. The approximation should be a good one for ketones with low cyclization yields as is the case for the examples considered herein.¹⁴ Figure 7 shows the corresponding plot using our values of ϵ and P_p values determined by Wagner.^{14,15} We were surprised to find that the correlation is far better than could be expected considering the errors involved in the measurements of both P_p and ϵ . It should be remembered that the line in Figure 7 is not based on the experimental data, that is, it has been calculated using eq 19. The quality of the correlation seems to support our conclusion that the constancy of the 3:1 product ratio is far from being fortuitous.

The discussion of spin statistical factors presented above involves the assumption that all of the biradicals which interact

with oxygen are in their triplet state. The agreement between Scheme II and our results support our earlier conclusion⁶ that the lifetime of type II biradicals is controlled by spin inversion, while the resulting singlet biradicals are extremely short lived.

An interesting example, which could be closely related to the one mentioned above is the interaction of triplet diphenylmethylene with ground-state molecular oxygen,³¹ which yields triplet benzophenone. The initial interaction can involve spin statistical factors leading to a reactive ${}^3\text{BO}_2$ (as in Scheme II).

Finally, we want to comment on the differences in intercepts in Figure 3 (top), which according to eq 8 reflect differences in ϵ . These differences seem to reflect largely the different probabilities of fragmentation *in the absence of oxygen*, rather than a different behavior of BO_2 .

Conclusion

Oxygen quenches the triplet state of carbonyl compounds with a rate constant of $\sim 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The interaction of oxygen with the biradicals occurs with a rate constant of $6\text{--}7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and results in the formation of an intermediate complex which has usually a $\sim 75\%$ probability of giving type II products and $\sim 25\%$ probability of producing a hydroperoxide. The results can be interpreted in terms of a mechanism (Scheme II) where the product ratios reflect spin statistical factors, and where all the elementary steps involved are spin allowed.

From the discussion above it is clear that the rather common conclusion that oxygen has no effect on the type II reaction is not warranted. We believe that all the results obtained in nondegassed solutions should be used with reserve and should be the subject of critical scrutiny before any valid conclusions can be drawn from them.

The reactions of biradicals can be differentiated from those of the precursor triplet states by studying the dependence of the quantum yields with substrate concentration under conditions where the triplet lifetime is adjusted by the use of suitable nonreactive quenchers.

Experimental Section

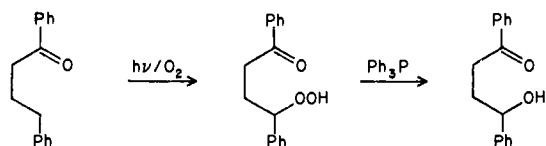
Materials. γ -Phenylbutyrophenone was prepared by reaction of γ -phenylbutyric acid (Aldrich) with phenyllithium. 1,4-Diphenyl-1-hydroxy-4-butanone was prepared by reduction of 1,4-diphenyl-3-butene-1,3-dione with lithium aluminum hydride.²⁶ All the other ketones were commercial products. Benzene (Spectrar, Mallinckrodt) and acetonitrile (Spectroquality, MCB) were used as received. Gases (oxygen, air, and a 3.8% oxygen in nitrogen mixture) were from Union Carbide. Undecane was used as an internal standard in benzene and benzonitrile in acetonitrile.

Irradiation. The samples were irradiated in a merry-go-round contained in a Rayonet reactor fitted with 16 RPR-3500 lamps. A combination of SP-200 high-pressure mercury lamp and a B&L high intensity monochromator were used for some of the preparative experiments.

Sample Preparation and Analysis. The samples were contained in matched tubes made of precision bore tubing (i.d. 0.2500 ± 0.0002 in., from Lab Crest Scientific, made of Corning 7740 glass). Between this tube and the grease-free stopcock there was a $\sim 30\text{-mL}$ bulb; this ensured that the pressure above the solution was constant during the irradiation.

The samples were degassed three times by freeze-pump-thaw cycles to a residual pressure of $<10^{-4}$ Torr. Then the vapor pressure was measured and, finally, oxygen, or a mixture of oxygen and nitrogen, was admitted and the total pressure measured using a high-performance gauge from Wallace and Tiernan (Model 62A-4D-0800X). The total pressure was corrected to take into account the vapor pressure of the solution. The gas, whether oxygen or a mixture with nitrogen, was chosen so that the total pressure measured to achieve a given concentration in solution was always at least twice the vapor pressure and usually three or four times this value. The oxygen con-

Scheme III



concentrations were then calculated using solubility data from the literature.³²

The samples were stirred periodically during the irradiation, with the intervals chosen so that the amount of peroxide formed (and oxygen consumed) between stirrings never exceeded 10% of the equilibrium oxygen concentration. A series of experiments was carried out to confirm that any further reduction of the irradiation time intervals did not affect the yields.

The samples were examined by gas chromatography using a 5-ft column of DC-11 silicone oil on Chromosorb W in a Beckman GC-5 chromatograph equipped with flame ionization detector.

Actinometry. The photolysis of valerophenone in benzene at 30 °C was used as an actinometer taking $\Phi_{ACP}^0 = 0.30$.¹⁵

Analysis for Hydroperoxide. These were carried out using the method of Banerjee and Budke,³³ as reported by Mair and Hall.³⁴ The measurements of iodine were carried out at 470 nm using a Cary 14 spectrophotometer.

The ratio ϕ_Y/ϕ_{I_2} was independent of the ketone concentration over the 0.01–0.1 M range.

Structure of the Hydroperoxide. While 25% of the BO_2 complexes formed yield a hydroperoxide, the actual quantum yields are frequently of the order of 0.1. This relatively low value reflects the facts that not all the biradicals are trapped by oxygen, and also that some of the triplets are quenched by oxygen. For example, in the case of valerophenone, eq 14 predicts a maximum value of ϕ_Y of 0.13 for an oxygen concentration of 0.013 M (corresponding to an oxygen pressure of ~ 1.4 atm).

For rather practical reasons, namely the availability of the expected product of reaction, the characterization of the hydroperoxide was carried out in the case of γ -phenylbutyrophenone (Scheme III).

The product of workup with triphenylphosphine, i.e., 1,4-diphenyl-1-hydroxy-4-butanone, was identified by comparison with an authentic sample using TLC. The chromatograms on alumina and silica plates and using several solvent mixtures provided evidence on the structure of the hydroperoxide as well as on the absence of any significant yields of other new products in low conversion experiments.

A series of experiments at rather high conversion (over 50%) were also carried out; these showed that the hydroperoxide is photosensitive, and TLC revealed the formation of two new products. NMR examination of a sample pretreated with triphenylphosphine from which acetophenone and styrene had been removed under high vacuum revealed the presence of 1,4-diphenyl-1-hydroxy-4-butanone as identified by its characteristic signal at δ 4.3 (t, 1 H, PhC—HOH). The expected signals in the δ 1–3 and aromatic regions were also observed, but these cannot be regarded as characteristic owing to the presence of other molecules of similar structure (e.g., parent ketone). Extraction by methanol of the material in the TLC spot assigned to 1,4-diphenyl-1-hydroxy-4-butanone followed by concentration, degassing, and UV irradiation ($\lambda > 330$ nm) gave acetophenone as the *only* product, providing further evidence confirming the characterization of the products.³⁵

In the case of γ -methylvalerophenone we have observed the formation of a new product by gas chromatography. This new product, which we presume is the hydroperoxide has a retention time similar to that of the cyclobutanols and is clearly photosensitive, since the hydroperoxide/cyclobutanols ratio decreases when the irradiation is continued to rather high conversions. The same product was among the products of the oxidation of γ -methylvalerophenone by oxygen initiated by azobisisobutyronitrile (24 h, 45 °C).

While the unequivocal characterization of the hydroperoxide was only carried out in the case of γ -phenylbutyrophenone, the observations mentioned above support our assumption that the hydroperoxide has the same structure in all cases. Further, also in the case of γ -methylvalerophenone, concentration of the product using liquid chromatography showed a well-defined singlet in the ¹H NMR

spectrum at δ 1.08, which compares well with the value of 1.12 for the methyl protons in *tert*-butyl hydroperoxide. Preparation of a similar sample, which by VPC was shown to be free of acetophenone, cyclobutanols, and parent ketone, showed in the IR a broad band at 3450 cm^{-1} which we attribute to the hydroperoxide group.

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