

# Photolysis of ketones in oxygen-saturated micellar solution: oxygen scavenging of C-centered radicals in microheterogeneous media

Eugene N. Step\*\*, Nicholas J. Turro\*

Department of Chemistry, Columbia University, New York, NY 10027 (USA)

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## Abstract

The oxygen scavenging of C-centered radicals in microheterogeneous media was studied by investigation of the photolysis of several ketones (dibenzyl ketone (DBK), *o*- and *p*-methyl-dibenzyl ketone (*o*-MeDBK and *p*-MeDBK) and *a*,1-2,4-diphenylpentan-3-one (*a*,1-DPP)) in oxygen-saturated sodium dodecylsulfate (SDS) micellar solution. The acyl- and benzyl-type radicals initially formed during the photolysis of these ketones can undergo geminate micellar and random bulk aqueous recombination or can react with oxygen in the bulk or micellar phases to yield peroxy radicals. The efficiency of radical scavenging by oxygen was calculated on the basis of three experimental parameters, i.e. the recombination probability  $P_r$  of a primary acyl-benzyl radical pair (RP), the secondary cage effect for benzyl-benzyl RP recombination and the chemical yield of dibenzyls. Under a partial pressure of 1 atm, oxygen was found to scavenge only those radicals which enter the bulk aqueous phase if the lifetime of the geminate radicals inside the micelles is relatively short (about 20 ns). However, for micellized geminate radicals with a longer lifetime (about 70–80 ns), scavenging by oxygen inside the micelles successfully competes with geminate radical recombination. These results are compared with other investigations involving the dynamics and partitioning of oxygen in SDS micelles.

## 1. Introduction

Oxygen reacts extremely rapidly with C-centered free radicals in both the aqueous and organic phases [1, 2]. The rate constants of the reactions of various radicals with oxygen are generally not very sensitive to either the structure of the radicals or the solvents, although they may be somewhat decreased by extensive resonance stabilization of the radicals. For example, for the moderately resonance-stabilized benzyl radical, the rate constants for reaction with oxygen are only slightly smaller than those of non-stabilized radicals ( $k_q = (1.6\text{--}4.9) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [1]). Even for the diphenylmethyl radical, the rate constant for reaction with oxygen is quite high,  $k_q = 6.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  [3]. However, for the extensively resonance-stabilized triphenylmethyl radicals, reaction with oxygen is slower and may be reversible at room temperature [4, 5].

Reaction of lipid alkyl radicals, formed by hydrogen abstraction or electron transfer, with oxygen in aerobic cells yields peroxy radicals and is one

of the pathways of lipid peroxidation (termed a type I reaction). The rates, as well as other characteristics of this major biological reaction, are obviously very important in understanding the oxidative degradation of biological systems. For example, the rate constants of oxygen scavenging of diphenylmethyl radicals generated photochemically in phospholipid vesicles were measured recently and were found to depend on the size of the vesicles [6].

Micellar systems are considered to be one of the simplest working models for the structure of cell membranes and are widely used for mechanistic investigations of radical processes of biological importance [7]. For micellar solutions, as well as for other microheterogeneous phases, oxygen represents a relatively unique case for which an efficient radical scavenger can penetrate inside a micelle without changing significantly the micellar size, shape, polarity, etc. The partition coefficient  $K$  of oxygen between (SDS) micelles and water has been measured directly [8] and by kinetic treatment of singlet oxygen decay data [9] giving similar results ( $K = 2.9$ ). A limited amount of data is available on the dynamics of molecular or singlet oxygen in micellar systems obtained in fluorescence

\*Corresponding author.

\*\*Present address: The Dexter Corporation, East Water Street, Waukegan, IL 60085-5652, USA.

quenching experiments [9–11]. These data lead to the following working model of the sites and dynamics of oxygen in SDS micellar systems. Because of the high bulk concentration of water (approximately 50 M) and the low concentrations of micelles (under typical conditions, about 1–10 mM), the probability of finding an oxygen molecule in a given micelle is of the order of a few per cent or less. Furthermore, because of the rapid rate of exit of an oxygen molecule from a micelle, the residence time of an oxygen molecule in a micelle is very short (of the order of tens of ns or less). Thus, in spite of its high scavenging efficiency for C-centered radicals in homogeneous solution, the scavenging efficiency for geminate radical pairs in micelles by oxygen may be low because of the low occupancy number of oxygen in micelles and the competition between the fast exit rate and scavenging even when the oxygen is located in a micelle containing a radical pair.

The objective of this report is to investigate the efficiency of oxygen scavenging of C-centered radicals generated during the photolysis of several ketones (derivatives of dibenzyl ketone) in SDS micelles and to determine the site or sites (aqueous or micellar phases) at which the scavenging by oxygen molecules occurs. We shall demonstrate that, although oxygen can scavenge free radicals in both aqueous and micellar phases, the efficiency of scavenging of radicals in the micellar phase depends on several factors, including the occupancy number of oxygen in the micelles and the rate of exit of the radicals from the micelles. As a result of these factors, the scavenging reaction of oxygen in micellar systems contrasts with that observed in homogeneous solutions, for which the efficiency of scavenging is generally high and is typically independent of the structure and lifetime of the radical being scavenged. In particular, we show that the efficiency of scavenging of radicals by oxygen in micellar solution depends both on the structure of the radicals and their lifetime inside a micelle.

Radicals of different structure were generated by the photolysis of several ketones (Fig. 1) in oxygen-saturated (partial pressure, 1 atm) SDS micellar solution. Only a limited number of studies are available on the photochemistry of ketones in the presence of oxygen [12, 13]. Recently, we have found that the photolysis of some ketones, which have triplet lifetimes too short to be quenched by oxygen, provides a clean method of production of peroxy radicals in oxygen-saturated hexane solution [14]. In non-viscous homogeneous solutions, all C-centered radicals formed during these photolyses

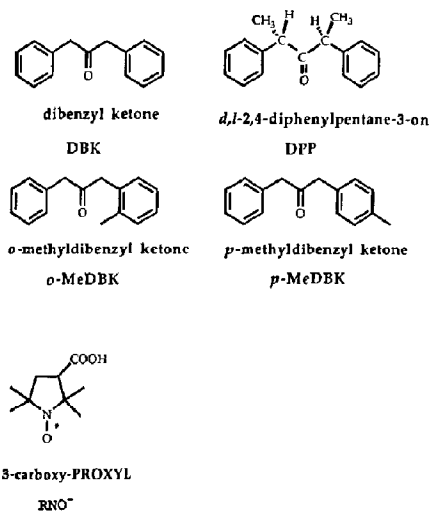


Fig. 1. Structures of compounds used in this study.

are efficiently scavenged by oxygen to form peroxy radicals, and radical–radical combination reactions are completely inhibited. For example, during the photolysis of a diastereoisomeric mixture of 2,4-diphenylpentan-3-ones (DPP) in oxygen-saturated hexane, no diphenylbutanes (DPB), products of alkyl radical combination reactions) are formed, whereas in a deoxygenated solution the yield of DPB is about 75% [14]. For the photolysis of a ketone, solubilized in a micellar solution, the yield of peroxy radicals will depend on several factors: (a) the reaction rate of a radical with oxygen, and the probability of finding an oxygen molecule within a micelle (occupation number); (b) the exit rate of a radical from a micelle into the aqueous phase where it is likely to be scavenged efficiently by oxygen molecules present in the bulk aqueous phase; (c) the competing exit rate of an oxygen molecule which happens to be located in a micelle and which also contains a radical or radical pair; (d) the combination rate of micellized radical pairs. The objective of this report is to sort out these factors both qualitatively and quantitatively.

## 2. Experimental details

Dibenzyl ketone (DBK) (Aldrich) was recrystallized from ethanol prior to use. *o*-Methyldibenzyl ketone (*o*-MeDBK) and *p*-methyldibenzyl ketone (*p*-MeDBK) were synthesized according to a published procedure [15]. 2,4-Diphenylpentan-3-one (DPP) was synthesized by methylating DBK [16], and *d,l*-DPP was isolated by reverse phase high performance liquid chromatography (HPLC) on

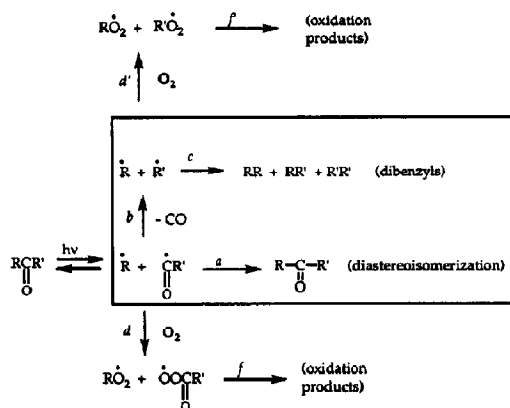
a C-18 column (eluent, 85:15 MeOH-H<sub>2</sub>O). 3-Carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (3-carboxy-PROXYL, RNO<sup>-</sup>) was purchased from Aldrich and used as received.

The photolysis of ketones (2–3 mM) in an aqueous SDS solution (0.1 M) was carried out in a quartz cell positioned in a Rayonet photochemical reactor equipped with a set of lamps emitting at 300 nm. The solutions were thoroughly purged with either Ar or O<sub>2</sub> before (approximately 1 h) and during photolysis. After photolysis aliquots of the reaction mixture were extracted with EtOAc-CH<sub>2</sub>Cl<sub>2</sub> (4:1). DBK (benzophenone for the photolysis of DBK) was added as an internal standard for gas chromatography (GC) analysis, which was performed on a Hewlett Packard 5890 gas chromatograph with a 25 m Carbowax 20M capillary column.

### 3. Results and discussion

The general mechanistic photochemistry of all four ketones under investigation (DBK, *p*- and *o*-MeDBK and *a*,1-DPP, see Fig. 1 for structures) is well established [15–17]. In deoxygenated organic solvents and micellar solutions, rapid (typically 1 ns or less)  $\alpha$  cleavage of triplet ketones occurs as the dominant primary photochemical process. Subsequent decarbonylation of acyl radicals occurs, followed by coupling of benzyl radicals, to yield symmetrical and non-symmetrical dibenzyls as the main photolysis products in the absence of scavengers. In the case of *a*,1-DPP in micellar solution, a significant amount of diastereoisomerization also occurs as the result of recombination of the primary geminate pair, and this reaction provides a simple chemical method to monitor the primary geminate pair. Photolysis of ketones in the presence of oxygen yields a set of oxidation products (Scheme 1) resulting from oxygen scavenging of the primary or secondary radical pairs produced by  $\alpha$  cleavage. For example, photolysis of *p*-MeDBK in SDS solution saturated with oxygen, as monitored by GC, in addition to dibenzyls, yields benzaldehyde, tolylaldehyde, benzyl and tolyl alcohols, benzoic and tolylic acids together with a trace of phenylacetic acid. All these products are expected from the termination reactions of peroxy radicals, which are formed from reactions of parent benzyl radicals with oxygen.

The experimental parameters measured in this work, which represent the efficiency of radical scavenging by oxygen during the photolysis of ketones (see Fig. 1) in SDS micelles, are: (a) the



Scheme 1.

chemical yield of dibenzyls resulting from geminate and random recombination of benzyl radicals; (b) cage and scavenging (see below) effects of secondary radical pairs (for *o*- and *p*-MeDBK); (c) the probability *P* of photostereoisomerization (for *a*,1-DPP).

The steps expected to be involved in the oxygen scavenging of the primary and secondary pairs are listed in Scheme 1. The decrease in the chemical yield of dibenzyls (due to step c in Scheme 1) during the photolysis of ketones in the presence of oxygen represents the fraction of benzyl radicals scavenged by oxygen in both micellar and aqueous phases. The primary cage effect is defined as the fraction of primary geminate pairs that undergo recombination relative to the converted ketone, and the secondary cage effect is defined as the fraction of secondary geminate pairs that undergo combination reactions relative to the converted ketone [15]. The value of the cage effect may be different in the presence of oxygen if oxygen molecules can react with geminate radical pairs. This process is generally inefficient in homogeneous solutions but, as demonstrated below, can be significant in micellar solution. The “scavenging effect” of oxygen may be decomposed into two experimentally measurable parameters: the total fraction of the converted ketone that results in scavenged products (bulk plus cage scavenging) and the fraction of geminate pair scavenging (cage scavenging only). For example, in a micellar system, a significant amount of geminate combination reactions occur within a micelle. The cage effect is the parameter which expresses the fraction of geminate reaction. In the presence of oxygen, it is expected that all of the radicals which escape from the micelle will be efficiently scavenged by oxygen in the bulk aqueous phase (step d' in

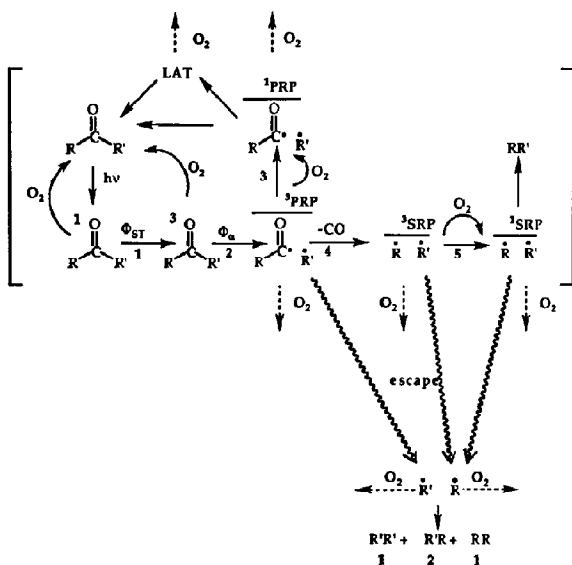
Scheme 1). The photostereoisomerization reaction (step a in Scheme 1) of *a*,1-DPP provides a means to determine directly the probability of recombination ( $P_r$ ) of the primary geminate *sec*-phenethylacetyl-*sec*-phenethyl micellized radical pair [16, 18]. The influence of oxygen on  $P_r$  is determined by the ability of oxygen to scavenge a primary micellar geminate pair (step d in Scheme 1). The lifetime of the latter is determined by rapid decarbonylation of phenacyl radicals (step b in Scheme 1).

The experimental data given in Tables 1 and 2 (see later) were analyzed in terms of the mechanism depicted in Scheme 2 (Scheme 1 depicts the results of oxygen scavenging implied in Scheme 2). Almost all the physical and chemical processes after primary excitation of the ketones to the  $S_1$  state may be influenced by interaction with oxygen. For example, oxygen quenches the excited singlet states of different compounds with rate constants which are close to the diffusion rate limit [19]. The rate constants for triplet quenching by oxygen are commonly about an order lower, due to a spin-statistical factor of  $\frac{1}{9}$  [19]. Fluorescence (singlet) quenching by oxygen in micelles has generally been found to require a complex kinetic scheme, which includes specific micellar diffusion (including entrance and exit from a micelle) of both the fluorescing molecule and the quencher [20, 21]. The kinetic treatment of fluorescence quenching by  $O_2$  in micellar solutions has been reviewed recently [11]. For example, an SDS micellar solution saturated with oxygen at 1 atm (experimental

conditions employed in this paper) was measured to have an average occupancy number of oxygen molecules in a micelle of  $\langle O_2 \rangle = 0.06-0.10$  [11]. This means that, although the entrance rate of oxygen into micelles is considered to be extremely high (approximately  $(1-3) \times 10^{10} M^{-1} s^{-1}$ ) [10, 11], only about 6%–10% of the micelles contain an oxygen molecule at any particular instant because of the rapid escape rate.

We now analyze the possible influence of oxygen on the singlet and triplet states of the ketones in micellar solution. For the ketone molecules examined in this report, the efficiency of  $S_1$  quenching by  $O_2$  can be estimated by simple kinetic considerations. For a calibration system, the fluorescence quenching of different pyrene derivatives by oxygen in SDS micelles has been found to proceed with a first-order rate constant,  $k = (1.1-1.4) \times 10^7 s^{-1}$  [11a]. Since quenching of an excited pyrene monomer in homogeneous medium is a near-diffusion-controlled process [19], the lifetimes of excited pyrene derivatives in SDS micelles are about 70–90 ns and are probably determined by an intramicellar diffusional encounter with oxygen. The lifetime of the  $S_1$  excited DBK molecule is rate determined by intersystem crossing and has been measured to be about 2 ns [22]; therefore, even assuming a diffusion coefficient of oxygen in micelles that is somewhat larger than that for pyrene, we can overlook any significant  $O_2$  quenching of  $S_1$  of the ketones investigated in micelles (see Scheme 2, stage 1). Similar arguments may be applied to the  $T_1$  quenching by oxygen (Scheme 2, stage 2), since for DBKs the lifetime of an excited triplet state is about 100 ps or less [23], a value even shorter than the singlet lifetime, and is rate determined by  $\alpha$  cleavage to produce a primary acyl-benzyl radical pair. Thus, from kinetic analysis, we conclude that neither the  $S_1$  nor the  $T_1$  states of the ketones investigated in this report will be significantly influenced by oxygen under the conditions employed.

The following experiments provide support for the validity of the conclusions made in the above kinetic analysis. If oxygen quenches (physically) the  $S_1$  and/or  $T_1$  states of DBKs, the quantum yield of disappearance and the conversion of the ketones must be smaller for photolysis in the presence of oxygen than in its absence. However, under comparable conditions of photolysis and low conversion of DBK and *o*-MeDBK, the rate of photolysis of the starting ketones in the presence of oxygen is actually slightly larger than the rate of photolysis in the absence of oxygen. This result confirms the absence of  $S_1$  and  $T_1$  physical quench-

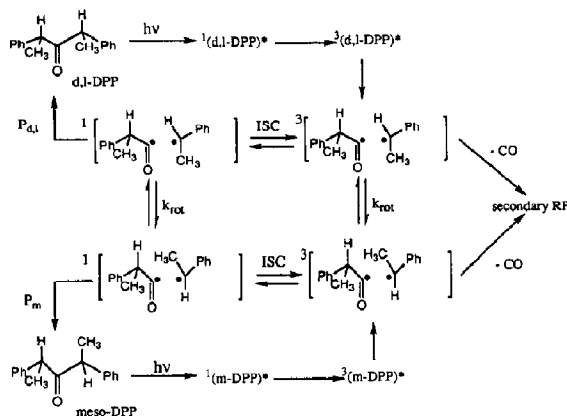


Scheme 2.

ing by oxygen, so that it is assumed that the rates of radical pair generation from the DBKs investigated in the presence of oxygen are similar to those in the absence of oxygen. We speculate that the slightly larger rate of photolysis of the starting ketone in the presence of oxygen is caused by an oxygen-induced decomposition of light-absorbing transients, which are typical unstable products of reversible head-to-tail recombination of primary radical pairs during the photolysis of DBK in micelles [24]. The build up of such transients during photolysis produces species that possess a strong absorption and which can compete with DBK, even at very low concentration, for the exciting photons.

The next question to be addressed is whether oxygen changes the value of  $P_r$ , the probability of primary acyl-benzyl radical pair recombination, during the photolysis of ketones. Two mechanisms may induce this change. Since oxygen is a paramagnetic species, it may induce intersystem crossing of triplet radical pairs to singlet radical pairs, which would increase  $P_r$ . On the other hand, oxygen can scavenge one of the radicals of the primary radical pair, which would consequently decrease  $P_r$  by providing an irreversible competing scavenging reaction (stage 3 in Scheme 2).

Of the ketones investigated, only *d,l*-DPP possesses a structure which allows for the direct determination of  $P_r$ . This determination is made as follows. For the photolysis of *d,l*-DPP, the influence of oxygen on  $P_r$  is determined directly through the loss of the diastereoisomeric purity of the ketone during photolysis (Scheme 3) [16, 18]. The extent of stereoisomerization was measured during *d,l*-DPP photolysis in SDS solution in the presence (1 atm) and absence of oxygen. The experimental data were plotted according to



Scheme 3.

the following equation [18]

$$\log(Z/Z_0) = \beta \log(1-f) \quad (1)$$

where  $Z$  and  $Z_0$  are the stereoisomeric purity of the ketone after and before photolysis,  $f$  is the fraction of conversion (disappearance of starting ketone) and  $\beta$  is the efficiency of stereoisomerization. The parameter  $P_r$  may be found directly from the experimental value of  $\beta$  [18]

$$P_r = \beta/(\beta + 1) \quad (2)$$

The values of  $\beta$  and, consequently,  $P_r$  for the triplet primary radical pair ( $^3$ PRP) from *d,l*-DPP (Fig. 2) were found to be the same with and without oxygen ( $\beta = 0.169$ ;  $P_r = 0.145$ ). The absence of an oxygen effect on the value of  $P_r$  for  $^3$ PRP formed during photolysis of *d,l*-DPP in micelles demonstrates that no oxygen scavenging of either primary geminate *sec*-phenethylacyl or *sec*-phenethyl radicals occurs during the lifetime of the geminate primary radical pair (stage 3 in Scheme 2 is not important for *d,l*-DPP). Due to the fast decarbonylation of the *sec*-phenethylacyl primary radical pair from *d,l*-DPP, it has a lifetime of only about 20 ns [25]; therefore the lack of an effect of oxygen on  $P_r$  of  $^3$ PRP is attributed to the short chemical lifetime of the primary geminate pair. This result allows an estimation of 20 ns to be made as a lower limit for radicals to be scavenged within an SDS micelle by oxygen at a partial pressure of 1 atm, i.e. only radicals surviving longer than 20 ns can be scavenged by oxygen under these conditions.

Let us now estimate the lifetime of  $^3$ PRP formed during the photolysis of DBKs in SDS micellar solution. Because of a slower rate of decarbonylation, these radical pairs are relatively long lived compared with  $^3$ PRP from *d,l*-DPP, and we need

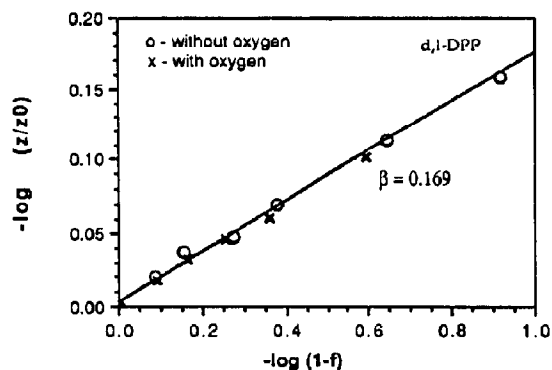
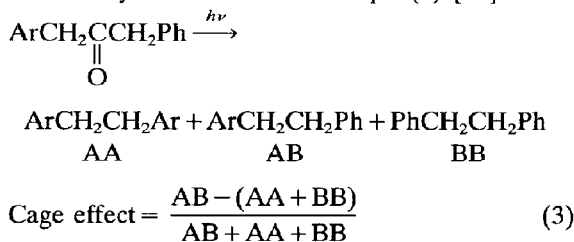


Fig. 2. Photodiastereoisomerism of *d,l*-DPP in 0.1 M SDS micellar solution in the presence (1 atm) (×) and absence (○) of oxygen. The experimental data are plotted according to Eqn. (1).

to take into account processes other than decarbonylation of phenacyl radicals. For  $^3\text{PRP}$  generated during DBK photolysis in SDS micelles, the most recently measured rate constants of pertinent processes are [26]: geminate recombination,  $k_{\text{gem}} = 1.2 \times 10^7 \text{ s}^{-1}$ ; decarbonylation of phenacyl radical,  $k_{-\text{CO}} = 3.5 \times 10^6 \text{ s}^{-1}$ ; exit rate constants for phenacyl radical, approximately  $6.6 \times 10^6 \text{ s}^{-1}$  (compared with  $1.4 \times 10^6 \text{ s}^{-1}$  reported for the benzyl radical [27]). From these data, the effective lifetime of the benzyl-phenacyl  $^3\text{PRP}$  is about 50 ns. Similar lifetimes also apply for radical pairs from *o*- and *p*-MeDBK, but are probably slightly higher due to the smaller rates of escape of substituted benzyl radicals from micelles.

After decarbonylation, the primary radical pairs produced from DBKs are converted to secondary benzyl-benzyl (or substituted benzyl) radical pairs. The secondary radical pair (lacking a facile chemical reaction such as decarbonylation) is presumably more long lived than the primary radical pair and its lifetime is limited by micellar recombination and escape from the micelle. Thus there is competition between the processes of radical escape from the micelle into the aqueous phase with the formation of a statistical mixture of dibenzyls and geminate intramicellar recombination resulting in the formation of an unsymmetrical dibenzyl product. We can estimate the lifetime of the secondary radical pair to be the inverse of the sum of geminate recombination and micellar escape rate constants of benzyl radicals [26, 27], which gives a lifetime of about 75 ns.

In the absence of scavenging reactions, the competition between geminate recombination and micellar escape processes for the secondary radical pair is expressed through the secondary cage effect which may be evaluated via Eqn. (3) [15]



The secondary cage effects according to Eqn. (3) are 0.34 and 0.40 for *p*- and *o*-MeDBK respectively in deoxygenated micellar solution. Thus a substantial amount of secondary cage recombination occurs. In the presence of 1 atm of oxygen, none of the symmetrical coupling products (AA or BB) are produced. Thus we can conclude that all of the escaping secondary radicals are efficiently scav-

enged by oxygen in the bulk phase, i.e. the "scavenging bulk effect" for the bulk phase is completely efficient. However, these experiments do not yield the efficiency of the "scavenging cage effect" of oxygen scavenging of micellized geminate benzyl radicals.

To estimate the scavenging cage effect, a new experiment was devised which allows differentiation to be made between oxygen scavenging of geminate pairs in the micellar phase and oxygen scavenging of escaped free radicals in the bulk phase. The fundamental idea was to employ a negatively charged scavenger that is only capable of reacting with radicals in the bulk phase. In competition with oxygen for radicals produced by photolysis, this selective aqueous scavenger will only influence the fraction of oxygen scavenging that occurs in the bulk phase, but cannot interfere with oxygen scavenging that occurs in the micellar phase. The negatively charged aqueous scavenger 3-carboxy-PROXYL nitroxide radical ( $\text{RNO}^-$ ) was used [28, 29] (see Fig. 1 for the structure of this scavenger). Nitroxide radicals are very efficient scavengers of C-centered radicals [30]. Under slightly basic conditions at  $\text{pH} > 7$ ,  $\text{RNO}^-$  is completely ionized, is dissolved only in the aqueous phase and is unable to penetrate the SDS micelles [29].

The scavenging of benzyl radicals during the photolysis of *p*-MeDBK in SDS-phosphate buffer solution ( $\text{pH} 7.8$ ) was performed with  $\text{RNO}^-$  only and with  $\text{RNO}^-$  together with oxygen as scavenger. At a concentration of 18 mM nitroxide, essentially all of the benzyl radicals entering the aqueous phase are expected to be scavenged on the basis of the following kinetic considerations. The lifetime of free benzyl radicals in the aqueous phase during DBK photolysis in SDS micelles has been determined to be about 20  $\mu\text{s}$  [26] and the scavenging rate constant for benzyl radicals by nitroxides is about  $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  ( $1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for  $\text{H}_2\text{O}$ -MeOH (2:1) mixture [30b]). In the case of scavenging of benzyl radicals by Fremy's salt (a double negatively charged nitroxide salt) in SDS solution, the rate of decay of benzyl radicals vs. the scavenger concentration reached a plateau at about 15 mM of Fremy's salt [27a]. Experiments under both scavenging conditions showed that all benzyl radicals which escape into the aqueous phase were scavenged and all recombinations of benzyl radicals were geminate (Table 1). The total chemical yield of dibenzyls is decreased from 0.70 without scavenging to 0.31 in the presence of  $\text{NO}^-$  but in the absence of oxygen and to 0.12 in the presence of  $\text{NO}^-$  and oxygen. Since oxygen can

TABLE 1. Chemical yield of dibenzyls (DBs) in *p*-MeDBK photolysis in SDS-phosphate buffer (pH 7.8) (solution I) with 3-carboxy-PROXYL (RNO<sup>-</sup>) and oxygen

|                   | Solution |                                 |  |
|-------------------|----------|---------------------------------|--|
|                   | I        | I + RNO <sup>-</sup><br>(18 mM) | I + RNO <sup>-</sup><br>(18 mM) + O <sub>2</sub> |
| Cage (scavenging) | 0.42     | 1                               | 1  |
| Yield of DBs      | 0.70     | 0.31                            | 0.12   |

TABLE 2. Chemical yields of dibenzyls (DBs) during the photolysis of ketones in SDS aqueous solution

|                        | Total yield of DBs |                 |                 |                          |
|------------------------|--------------------|-----------------|-----------------|--------------------------|
|                        | DBK                | <i>p</i> -MeDBK | <i>o</i> -MeDBK | <i>d</i> , <i>l</i> -DPP |
| Without O <sub>2</sub> | 0.590              | 0.658           | 0.560           | 0.527                    |
| With O <sub>2</sub>    | 0.073              | 0.089           | 0.072           | 0.300                    |

penetrate the micellar boundary and can scavenge radicals inside the micelles, this result means that a fraction (0.19 or about 33%) of all benzyl radicals scavenged by oxygen are scavenged within micelles. Furthermore, of all geminate micellized benzyl radicals, about 60% are scavenged by oxygen and about 40% recombine to form dibenzyls (under 1 atm of oxygen).

When the total yields of dibenzyls formed during photolysis of the ketones in SDS in the absence and presence of oxygen are compared, the data for *d*,*l*-DPP are very different from those of the other ketones (Table 2). For the photolysis of DBKs in the presence of oxygen, the yield of dibenzyls is about 12% of that in the absence of oxygen; however, for *d*,*l*-DPP the yield is 57% of that in the absence of oxygen. The secondary radical pair cage recombination of benzyl radicals competes with radical escape from the micelles and, in the presence of oxygen, with oxygen scavenging. The probable reason for the smaller influence of oxygen on the yield of DPBs on recombination of *sec*-phenethyl radicals is the larger hydrophobicity of these radicals. The lower rate of escape from the micelles causes the cage effect of this radical pair in SDS micelles to be larger (up to 0.6–0.8 [27b]). Therefore, even if all the radicals in the aqueous phase are scavenged, the decrease in the yield of DPB will not be as large as that of DBKs, because the inherent secondary cage effect is larger. It is also possible that the rate constant of the *sec*-phenethyl radical reaction with oxygen may be smaller than that of benzyl radicals due to the additional resonance stabili-

zation of *sec*-phenethyl radicals. This may result in a less effective competition of oxygen scavenging inside micelles with geminate radical recombination, although this factor is expected to be less important.

Our results are in qualitative agreement with those on the oxygen quenching of fluorescence in micelles. For example, the fluorescence quenching of pyrene derivatives by oxygen in SDS micelles, which is believed to be a diffusion-controlled process, has been found to be first order with a rate constant  $k_q = (1.1\text{--}1.4) \times 10^7 \text{ s}^{-1}$  [11a]. This rate constant indicates that the lifetime of the excited species in the presence of oxygen is about 70–90 ns (assuming that nearly all encounters with oxygen are reactive [19]), which is in excellent correlation with our data. In contrast with the fluorescence quenching experiments, the interpretation of the results in the present work does not require postulation of a specific kinetic model, and the lifetime of the micellar radical pair, which can be measured independently, provides an internal clock for monitoring the time scale of radical scavenging by oxygen within a micelle.

#### 4. Conclusion

Although oxygen is known to be one of the most efficient scavengers of C-centered radicals, the scavenging of radicals by oxygen in microheterogeneous medium, such as micelles, depends on both the residence lifetime of the radicals and the solubility of oxygen in the various phases of the system. On the basis of our experiments, in SDS micellar solution, due to the low oxygen occupancy inside the micelles, oxygen may be used as selective scavenger of free radicals in the aqueous phase for micellized geminate radical pairs with lifetimes up to about 20 ns (e.g. *d*,*l*-DPP). If the residence lifetime of the radicals inside the micelles is larger (about 70–80 ns) e.g. the secondary radical pairs from DBKs, oxygen acts as a scavenger of radicals in both the aqueous and micellar phases. In both cases, the aqueous phase scavenging of radicals is complete, while in the micellar phase, scavenging competes with radical recombination.

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