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# Photochemistry of aromatic ketones in sodium dodecyl sulphate micelles in the presence of unsaturated fatty acids

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*Abstract*: Laser-flash photolysis has been employed to characterize the behaviour of the free radicals created in the photochemical reaction of benzophenone (BZP), as well as of its lipoidal derivative, benzophenone-4-heptyl-4'-pentanoic acid (BHPA), with chosen unsaturated fatty acids in sodium dodecyl sulphate micelles. The calculated rate constants were used to study the "cage effect", *i.e.*, the recombination of the created radical-pairs (BZP, BHPA ketyl radical - lipid radical) inside the highly limited space of the SDS micelles. The "cage effect" appears to be the dominant event inside SDS micelles, dependent on the structure of both the reactants-precursors. The fractions of the initially created radical-pairs which escape the "cage effect" and exit into the surrounding aqueous phase do not exceed 16 %. This fact is of enormous importance for the self-control of the pathogenic process of lipid peroxidation.

*Keywords*: photosensitizers, benzophenone, free radicals, radical-pairs, micelles.

## INTRODUCTION

The lipid peroxidation phenomenon, implying the oxidative destruction of polyunsaturated moieties,[1] may be largely ascribed to the presence of double bonds in the hydrocarbon parts and to adjacent allylic and doubly allylic sites at which hydrogen abstraction (thus lipid radical formation) may be facilitated.[2,3] Once created, lipid radicals in the presence of oxygen undergo chain reactions leading finally to the formation of peroxide structures,[4] and causing a variety of pathological processes.[5]

While chain peroxidation effects have been studied extensively *via* autooxidation,[6] quantitative characterization of the degradation requires *controlled* initiation of H-abstraction from the allylic and doubly-allylic sites. Several radiation chemical studies carried out using $HO^{\bullet}$ radicals as the H-abstraction agent suffered from non-selectivity as to the site of attack in the complex environments.[4,7,8] Other oxygen-containing radicals, such as perhydroxyl ($HOO^{\bullet}$) or peroxyl ($ROO^{\bullet}$) (along with $HO^{\bullet}$) expressed different susceptibilities toward the site of the potential initiation.[9] On the other hand, the use of benzophenone (BZP), already well known as a very efficient initiator of polymerization processes,[10,11]

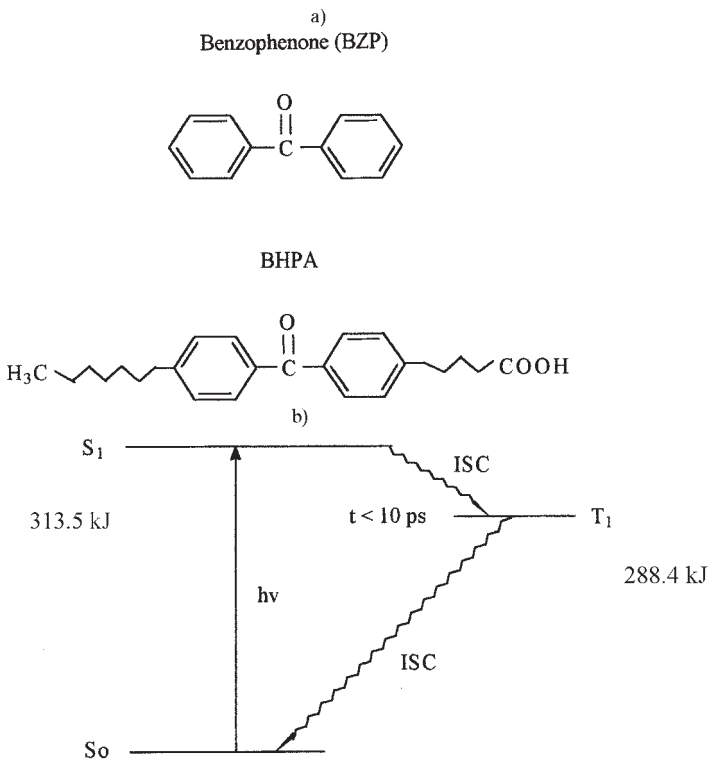



Fig. 1 (a) Structures of benzophenone (BZP) and its lipoidal derivative (BHPA): (b) Ground state ($S_0$) and two lowest excited states of benzophenone, singlet state $S_1$ and triplet state $T_1$ (created by intersystem crossing (isc) from the $S_1$ state). Like most carbonyl compounds, BZP participates in photochemical reactions *via* the longer-lived triplet state, $T_1$.

permits very selective abstraction from allylic and doubly-allylic sites by its triplet ($^3$BZP) and, hence, appeared to offer a promising approach for further quantitative chain peroxidation studies.[12] Benzophenone is a typical Type I photosensitizer, reacting directly with a lipid to generate reactive lipid free radicals.[13,14] H-abstraction by the longer-lived triplet states of aromatic ketones is a well known reaction in organic photochemistry.[15] Photosensitized oxidation of membrane lipids belongs to a variety of external stresses, enabling the production of peroxidation initiating agents.[16]

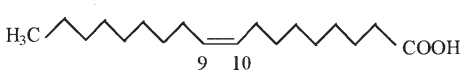
There are two possible approaches to the study of the mechanisms of photosensitized lipid peroxidation in biological membranes. The first one deals with experiments *in vivo*. The complexity of the involved processes appears to be a limiting factor for such an approach. The second one includes experiments on model membranes, with various degrees of molecular organization providing better control of the chain process inside: micelles,[17–19] liposomes,[9,20,21 and the references cited therein] artificial membranes,[22] even isolated natural membranes.[23] The latter approach was used in our previous work.[12,24,25] To obtain basic kinetic data, without the influence of any molecular organization, a series of

measurements in which the reactions of BZP with unsaturated lipid fatty acids were studied were performed in benzene solution.[12] The same reactions were also studied in micelles of sodium dodecyl sulphate[24] (SDS), and linoleic acid[25] (LA) to enable the effects of spatial, molecular organization to be estimated, by comparing the two sets of kinetic data from the two media. A step further concerning the study in SDS micelles involved the deployment of linoleic acid (18:2) as a lipid substrate.[24] Three other unsaturated fatty acids have been employed as the lipid substrates in this study: oleic acid, OA (18:1), linolenic acid, LNA (18:3), and arachidonic acid, AA (20:4). The structural differences of the employed lipids (caused by the different number of double bonds) should certainly bring more complexity into the investigated system. Simultaneously, this should contribute to a better understanding of the behaviour of the created lipid radicals in the highly restricted area of the SDS micelles, which should have significant biological relevance.

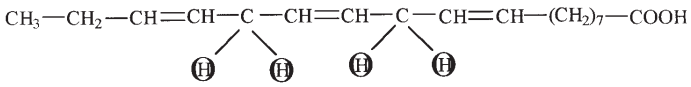
## MATERIALS AND METHODS

The samples of fatty acids were obtained from Nu-Chek Prep. Inc. (Elysian, MN) and were provided as 99 % pure in vials sealed under vacuum. Those used in this study were: oleic acid (18:1), linolenic acid (18:3) and arachidonic acid (20:4). Benzophenone was obtained from Sigma Chemical Co. (St. Louis, MO), and

OLEIC ACID, 18 : 1




LINOLENIC ACID, 18 : 3




ARACHIDONIC ACID, 20 : 4

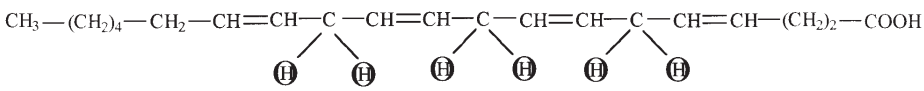



Fig. 2. Structures of oleic acid (OA, 18:1; up), linolenic acid (LNA, 18:3; middle), and arachidonic acid (AA, 20:4; bottom). The anti-conjugated structures permit the easy abstraction of allylic (OA) and doubly-allylic H-atoms (LNA, AA - circled) with the consequential production of lipid (fatty acid) radicals.

SDS was obtained from Eastman Kodak (Rochester, NY). Benzophenone-4-heptyl-4'-pentanoic acid (BHPA) was synthesized as previously described.[24]

A Quanta Ray Nd:Y AG nanosecond laser (third harmonic, 354 nm) was used to observe the kinetics of the radicals in the SDS micelles. The pulse duration was two nanoseconds, and the energy was 10 mJ/pulse. The reaction was followed at 540 nm (preferential absorption of BZP, BHPA-ketyl radical) and 620 nm (the triplets). The sensitizer concentration in the 0.2 mol $dm^{-3}$ SDS micellar system was $2.6 \times 10^{-3}$ mol $dm^{-3}$, ensuring a micelle to sensitizer ratio of about 100:1. This ratio eliminated possible triplet annihilation at the higher local concentrations, already seen in solution,[26] although $^3$BZP self-quenching in SDS micelles has been reported to be a minor event at SDS concentrations of 0.23 mol $dm^{-3}$ (very close to ours[27]). The fatty acid concentrations were 0.035–0.04 mol $dm^{-3}$.

Before the experiments, all the samples were depleted of oxygen using the freeze-thaw techniques, to avoid strong quenching of the triplets by oxygen; the reported value of the rate constant in benzene for $^3$BZP is $2.53 \times 10^9$ $dm^3$ $mol^{-1}$ $s^{-1}$.[28] The pH of all samples was adjusted to 7.

The structures of BZP and BHPA are shown in Fig. 1 (a), together with a schematic diagram of the ground state and the two lowest excited states (b). The structures of the fatty acids are shown in Fig. 2.

## RESULTS AND DISCUSSION

The decay of the triplets ($^3$BZP, $^3$BHPA) in reaction with lipids in homogeneous solution may be described by the following scheme[12]:

$$BZP + h\nu \rightarrow {}^1BZP \rightarrow {}^3BZP \quad (1)$$

$$^3BZP + RH \xrightarrow{k_H} R^{\bullet} + BZPH^{\bullet} \quad (2)$$

$$^3BZP + RH \xrightarrow{k_\pi} \text{Physical quenching by double bonds} \quad (3)$$

$$^3BZP \xrightarrow{k_i} \text{Products} \quad (4)$$

The overall decay is described by Eq. (5)

$$k_Q = k_i + k_r[RH] \quad (5)$$

where $k_r = k_H + k_\pi$, where $k_H$ is the rate constant for hydrogen abstraction and $k_\pi$ the rate constant for physical quenching; $BZPH^{\bullet}$ is a ketyl-radical, and [RH] denotes the lipids (fatty acids) concentration. Hence, the apparent rate constant ($k_Q$) is a linear function of the fatty acids concentration in homogeneous solution.[12] The same was found in SDS micelles with BZP and BHPA as the photosensitizers, and linoleic acid as the lipid substrate.[24]

However, some additional effects take place in the SDS limited area[29]:

$$^3BZP + RH \xrightarrow{k_H} {}^3(BZPH^{\bullet\bullet}R) \quad (6)$$

$$^3(BZPH^{\bullet\bullet}R) \xrightarrow{k_{isc}} {}^1(BZPH^{\bullet\bullet}R) \quad (7)$$

$$^1(BZPH^{\bullet\bullet}R) \rightarrow \text{Recombination, stable products} \quad (8)$$

$$^{1,3}(BZPH^{\bullet\bullet}R) \rightarrow BZPH^{\bullet} + R^{\bullet} \quad (9)$$

The new event (compared to solution) is shown by Eq. (6): the creation of a radical pair, BZP (BHPA) ketyl-radical – lipid radical, in its triplet state, $^3$(BZPH$^{\bullet\bullet}$R), which may be transformed to the singlet state – Eq. (7). The highly limited spatial area of the SDS micellar "cage" may then result in recombination of such radical pairs into stable products – Eq. (8). Eventually the radical pairs may separate before the recombination step; the radicals then escape the micelles – Eq. (9). The decay of the ketyl-radical absorption curve, shown in Fig. 3, has been used to calculate the fraction of such "escape events". The rapid decay reflects $k_{isc} + k_{ex.}$ ($= k_{app.}$, apparent rate constant that fits the curve), and the plateau behaviour of the free (ketyl) radical, expressed by the exit rate constant, $k_{ex}$.[30]

One of the major problems that should be considered concerning the photochemistry described by Eqs. (6–9) is the degree of BZP incorporation inside the SDS micelles. It was found that BZP is well incorporated, based on a relationship value between its "in" and "out" rate constants: 26000.[27]

Both BZP and BHPA are very reactive toward the chosen targets: the 4 allylic H-atoms in all three fatty acids, and especially the 4 doubly allylic H-atoms in linolenic acid, and the 6 doubly-allylic atoms in arachidonic acid. As has been shown, these H-atoms contribute dominantly to the overall H-abstraction rate constant, making the abstraction of other hydrogens almost negligible[12] (in this particular case this refers to H-abstraction from SDS molecules, having no allylic or doubly-allylic H-atoms).

Before measuring $^3$BZP and $^3$BHPA H-abstraction from the fatty acids in SDS micelles, it was necessary to determine the lifetimes of $^3$BZP and $^3$BHPA in SDS micelles in absence of the lipid substrates ($\tau_0$). The determination was performed according to procedure described by Encinas and Scaiano.[31] The $\tau_0$ value of $^3$BZP was 360 ns, which is in good agreement with the reported values of 320–380 ns.[32,33] The $\tau_0$ value for $^3$BHPA was 700 ns, which indicated a possible lower reactivity of $^3$BHPA, compared to $^3$BZP. This was already proved when the lipid substrate in the SDS micelles was linoleic acid.[24]

An important problem that has to be solved in this system is a clear separation of the absorption of the triplets and the corresponding ketyl-radicals, since they both have a strong absorption in the 400–600 nm region.[12] The absorption of the corresponding fatty acids radicals is of no interest here, since they absorb in the 275–285 nm region – *i.e.*, they are "invisible" at 540 nm.[12] By choosing the appropriate time scale of a couple of microseconds (Fig. 3), the overlapping was avoided. Fig. 3 fully represents the absorption of the ketyl-radical: it was found that $^3$BZP lives about 30 ns in 0.2 mol dm$^{-3}$ SDS micelles in the presence of linoleic acid, with the very same concentration of the fatty acids as used in this study: 0.04 mol dm$^{-3}$.[24] The decreasing part of the absorption curve represents the absorption of BHPA ketyl-radical in the SDS micelles, and out of them, according to Eq. (9), and the plateau the ketyl-radical absorption out of the micelles only, *i.e.,* in the surrounding aqueous phase.[24] These two absorptions (being proportional to the corresponding concentrations of the same species) are labeled as $A_0$ (the first one) and $A_\infty$ (the second one), re-

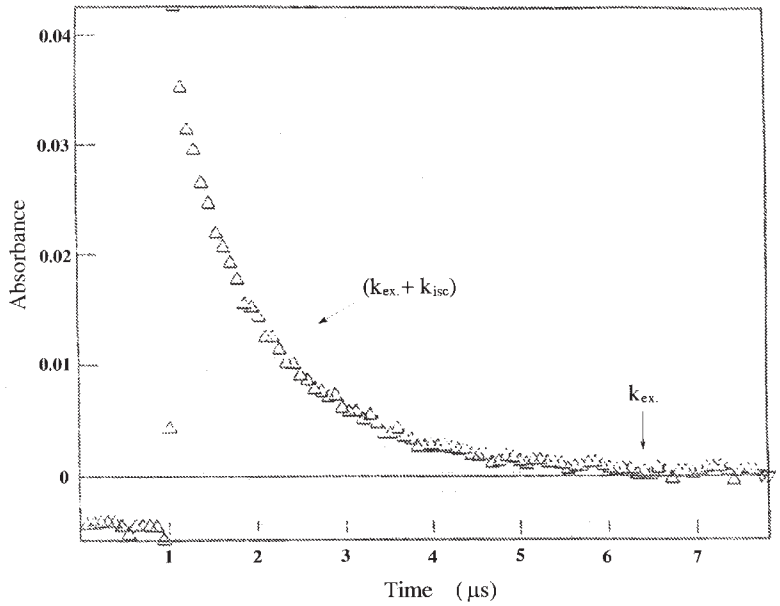



Fig. 3. Decay of the BHPA ketyl-radical in SDS-linolenate micelles, recorded at 540 nm. The faster decrease reflects the kinetics of $k_{ex.} + k_{isc}$, while plateau corresponds to behaviour of the free ketyl-radical. The concentrations involved: [SDS] = 0.2 mol dm$^{-3}$; [LNA] = 0.04 mol dm$^{-3}$; [BHPA] = 0.0026 mol dm$^{-3}$. Nd:Y AG laser, 354 nm. Absorption of the corresponding fatty acids radicals is negligible.

spectively. They were used to calculate the exit rate constants for the created radical-pairs (ketyl-radical – fatty acid radical), according to the formula[30]:

$$A_\infty / A_0 = k_{ex.} / (k_{ex.} + k_{isc}) \tag{10}$$

bearing in mind that

$$k_{ex.} + k_{isc} = k_{app.} \tag{11}$$

where $k_{app.}$ is the apparent rate constant, obtained by fitting the decreasing part of the absorption curve (Fig. 3). It is expressed in s$^{-1}$, since it is equal to $k_Q$ from Eq. (5), so describing pseudo-first order kinetics.[24] The relationship at the right side of Eq. (10) represents the fraction of the initially created radical-pairs that escape the micelles (*fr.*), according to Eq. (9).

The values of $k_{app.}$, $k_{ex.}$ and *fr*. are given in Table I.

The $k_{ex.}$ values obtained with $^3$BZP are about 2–3 times larger than the ones obtained with $^3$BHPA, when using OA and LNA as the lipid substrates; with AA the $k_{ex.}$ values are more similar. This is proof that the smaller BZP molecules enable an easier escape of the whole pair, when compared to the bigger BHPA molecule. Additional proof that the magnitude of the molecules play an important role in the escape event can be obtained by comparing the $k_{ex.}$ values obtained with $^3$BZP only for all three fatty acids: the order is OA > LNA > AA. the same order is valid for the fractions of the radical-pairs escaping the micelles (*fr.* – Table I). Simply, the smaller OA radicals escape the SDS micelles more easily than the

bigger LNA and AA radicals, of the same or similar concentrations. Intriguingly, the $k_{isc}$ values (= $k_{app} - k_{ex.}$) are also larger for OA ($1.53 \times 10^6$ $s^{-1}$) than for LNA or AA ($1.41 \times 10^6$ $s^{-1}$, for both), bearing in mind that recombination of the created radical pairs into stable products can arise from the singlet state only – Eq. (8), whereas the escape event can originate from the triplet as well as the singlet state of the radical-pairs – Eq. (9). Since it is not possible to estimate the subfraction of the escaped radical-pairs originating from the triplet state, it is also not possible to compare the recombination affinity of OA radicals with those of LNA and AA radicals (toward $BZPH^{\bullet}$). It may only be remarked that the OA radicals could have less steric hindrances for recombination, compared to $LNA^{\bullet}$ and $AA^{\bullet}$: one double bond causes less steric problems for recombination than 3 (LNA) or 4 (AA).

TABLE I. Kinetics of the radical-pairs created by $^3$BZP and $^3$BHPA H-abstraction from oleic acid (OA), linolenic acid (LNA) and arachidonic acid (AA), as the lipoidal substrates in SDS micelles. The concentration of the fatty acids was 0.040 mol $dm^{-3}$. The rate constants were obtained by fitting the absorption curve recorded at 540 nm (Fig. 3), where most of the absorption comes from ketyl-radicals. $k_{app.}$ – apparent rate constant, reflecting the behaviour of the radical-pairs inside, and the isolated radicals outside the micelles ($k_{app.} = k_{ex.} + k_{isc}$); $k_{ex.}$ – sum of the exit rate constants for the ketyl-radical and $OA^{\bullet}$ ($LNA^{\bullet}$, $AA^{\bullet}$) radicals, created by $^3$BZP ($^3$BHPA) H- abstraction from the investigated fatty acids; $k_{isc}$ – rate constant for inter-system crossing, to create radical-pairs in the singlet state, with possible recombination inside the micelles – Eq. (8); *fr.* – fraction of radical-pairs that escape recombination inside the SDS micellar "cage" - Eq. (9).

| Fatty acid | $k_{app.}/s^{-1}$ | $k_{ex.}/s^{-1}$ | *fr.*/% |
|---|---|---|---|
| | $^3$BZP H-abstraction | | |
| OA | $1.83 \times 10^6$ | $0.30 \times 10^6$ | 16.3 |
| LNA | $1.73 \times 10^6$ | $0.28 \times 10^6$ | 16.1 |
| AA | $1.64 \times 10^6$ | $0.21 \times 10^6$ | 12.9 |
| | $^3$BHPA H-abstraction | | |
| OA | $1.95 \times 10^6$ | $0.09 \times 10^6$ | 5.0 |
| LNA | $1.03 \times 10^6$ | $0.12 \times 10^6$ | 11.5 |
| AA | $1.17 \times 10^6$ | $0.14 \times 10^6$ | 11.5 |

The calculated *fr.* values with $^3$BZP for all three substrates do not exceed 16 % (Table I). This is a clear proof ot the "cage effect" in SDS micelles: the highly limited spatial area inside the micelles prevents a significant escape of the initially created radical-pairs and results in their recombination - Eq. (8). This was already reported in a previous paper.[24] This fact has very important biological relevance. Only those lipid radicals that escape the "micellar cage" can undergo the propagation step in the surrounding aqueous phase (reaction with oxygen, and the creation of $RO_2^{\bullet}$ radicals[9]) which finally leads to the creation of lipid peroxides structures at the end of the chain mechanism,[4] with a lot of pathological consequences. Bearing in mind that micelles represent rough biomembrane models, the very low *fr.* values - caused by the "cage effect" (Table I) represent a sort of self-defense against pathogenic lipid peroxidation processes.

The *fi*: values are generally lower with $^3$BHPA compared to the ones obtained with $^3$BZP (Table I) for all three fatty acids. This can be attributed to the more expressed surfactant character of BHPA (compared to BZP) leading to easier recombinations inside "the cage". This was already observed with BHPA and linoleic acid (as the lipid substrate) in SDS micelles.[24] However, the *fi*: value obtained with OA is about two times smaller than the ones obtained with LNA and AA. This may be linked to the fact that the $k_{app.}$ value for OA is about two times bigger than the ones for LNA and AA, while the $k_{ex.}$ values are much more similar - Table I. In other words, the $k_{isc}$ value for OA is about twice those of LNA and AA. Again, this can be explained by the higher affinity for recombination of the BHPA ketyl-radical with the OA radical, than to the LNA and AA radicals. The most probable reason lies in the structures of the fatty acids radicals. One double bond (OA) results in less steric problems for recombination than 3 (LNA) or 4 (AA). The $k_{ex.}$ values are less selective (when compared to the ones obtained with $^3$BZP), additionally proving that the "cage effect" is even more dominant with BHPA as the photosensitizer.

## CONCLUSION

Radical-pairs created through photochemical reaction of BZP and its derivative, BHPA, with unsaturated fatty acids (OA, LNA, AA) in SDS micelles undergo predominantly recombination inside the spatially restricted area of the "micellar cage" (Eq. 8); the escape of the radical-pairs into the surrounding aqueous phase (Eq. 9) appears to be a minor event. The "cage effect" is more pronounced with BHPA (compared to BZP) - due to the more surfactant character of BHPA - and with oleic acid as the counterpart (compared to LNA and AA), due to less steric hindrances for recombination.

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*Abbreviations*

| | |
|---|---|
| BZP | benzophenone |
| BHPA | benzophenone-4-heptyl-4'-pentanoic acid |
| SDS | sodium dodecyl sulphate |
| OA | oleic acid |
| LNA | linolenic acid |
| AA | arachidonic acid |

## ИЗВОД

### ФОТОХЕМИЈА АРОМАТИЧНИХ КЕТОНА У МИЦЕЛАМА НАТРИЈУМ-ДОДЕЦИЛ-СУЛФАТА У ПРИСУСТВУ НЕЗАСИЋЕНИХ МАСНИХ КИСЕЛИНА

ДЕЈАН З. МАРКОВИЋ

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Ласер-флеш-фотолиза је коришћена за карактерисање понашања слободних радикала створених фотохемијском реакцијом бензофенона (BZP), као и његовог липоидалног деривата, бензофенон-4-хептил-4'-пентанске киселине (BHPA), са изабраним несазићеним масним

киселинама у мицелама натријум-додецил-сулфата (SDS). Израчунате константе брзина искоришћене су за проучавање тзв. ефекта кавеза, тј. рекомбинације створених радикалских парова (BZP, BHPA кетил-радикал – липидни радикал) унутар лимитираног простора SDS мицела. Показано је да је ефекат кавеза доминантан унутар SDS мицела и да зависи од структура оба реактанта-прекурсора. Фракција иницијално створених радикалских парова која избегне ефекат кавеза и пређе у околну водену фазу не прелази 16 %. Ово је од изузетног значаја за самоконтролу патогеног процеса липидне пероксидације.

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