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Micellar Free Radical Initiators

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Abstract—The effect of the nature of the surfactant, peroxide (ROOH), and medium on the rate of radical initiation in a surfactant–ROOH mixed micellar system has been studied. Cationic surfactants, as distinct from anionic and nonionic ones, have been found to catalyze ROOH decomposition to form radicals. Cationic surfactants in an organic medium exhibit higher catalytic effect than in an aqueous solution. The catalytic activity of the surfactants is strongly dependent on the counterion nature. The highest catalytic activity is shown by cetyltrimethylammonium chloride.

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Many industrially significant processes, such as radical polymerization, oxidation of organic compounds, radical chain chlorination, sulfochlorination, telomerization, polymer structuring, are carried out in the presence of free radical initiators [1]. The most widely used initiators are peroxides, azo compounds, and organometallic compounds that provide necessary initiation rates at elevated temperatures (50–100°C). At low temperatures, photoinitiation and redox systems are applied. Thus, the H_2O_2–$FeSO_4$ system, well known as Fenton's reagent, produces radicals according to the scheme [1, 2]:

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + HO^* + HO^-,$$

$$H_2O_2 + Fe^{3+} \longrightarrow Fe^{2+} + H^+ + HO_2^*.$$

Redox radical initiation occurs in the similar reactions of organic hydroperoxides with compounds of other transition metals [2]. It was shown in [3–9] that the cationic surfactant cetyltrimethylammonium bromide (CTABr), like transition metal compounds, exerts a catalytic effect on the processes of radical chain oxidation of hydrocarbons and lipids by molecular oxygen. The key reaction that determines the catalytic effect of CTABr is the accelerated decomposition of hydroperoxide into free radicals:

$$n\mathrm{ROOH} + m\mathrm{surfactant} \longleftrightarrow \{n\mathrm{ROOH}\cdots m\mathrm{surfactant}\}$$

$$\longrightarrow \mathrm{RO}_2^* + \mathrm{products}(*).$$

As distinct from CTABr, the anionic surfactants sodium dodecyl sulfate (SDS) and aerosol OT (AOT) either have no effect on the oxidation rate or decrease it [4, 8, 11].

In the present work, we studied the effect of the nature of the surfactant, peroxide, and medium on the radical initiation rate in a surfactant–ROOH mixed micellar system with the aim to reveal the most active combinations to generate radicals under mild conditions.

EXPERIMENTAL

Cationic surfactants from Fluka—cetyltrimethylammonium chloride (CTACl), bromide (CTABr), and hydrogen sulfate ($CTAHSO_4$); dicetyldimethylammonium bromide (DCDMABr); and cetylpyridinium bromide (CPBr)—were additionally dried in a vacuum prior to use.

2-Phenylisopropyl hydroperoxide (cumyl hydroperoxide) (CHP) (Aldrich) was thoroughly purified by the procedure described in detail in [10]. Limonene hydroperoxide (LHP) was obtained by the autooxidation of R(+)-limonene with molecular oxygen at 70°C. Hydrogen peroxide (H_2O_2) (Reakhim, Russia) of pure for analysis grade (a 30% solution) was used without additional purification, and chlorobenzene and water were distilled twice.

The hydroperoxide concentration in experiments was determined by the iodometric method. The radical formation rate was determined by the inhibitor method with the use of quercetin (3,3',4',5,7-pentahydroxyflavone) (Q) (Fluka) and the stable nitroxyl radical 4-(spirotetrahydrofuryl-2')-2-spirocyclohexyl-1,2,3,4-tetrahydroquinoline-1-oxyl ($>NO^\bullet$) as a free radical scavenger. The reaction of $>NO^\bullet$ with peroxyl radicals leads to quinone–nitrone (QN), shows a strong absorption band in the visible spectral region [12].

Peroxide decomposition was carried out in a thermostated (37°C) quartz cell of an Ultrospec 1100 pro spectrophotometer. A peroxide solution (2.5 mL) in water or chlorobenzene was placed into the cell, kept for 10 min at 37°C, then a stock solution of surfactant and a stock solution of Q or $>NO^\bullet$ in ethanol were added via a microsyringe. To provide homogeneous

Table 1. Kinetic characteristics of radical formation in a 20 mM CHP + 1 mM surfactant system in chlorobenzene and aqueous solution at 37°C

Surfactant	W_i, mol/(L s)	$\varpi \times 10^3$, L/(mol s)	W_i, mol/(L s)	$\varpi \times 10^3$, L/(mol s)
	organic solvent		water	
Without surfactant	≈0	≈0	≈0	≈0
Cetyltrimethylammonium chloride, CTACl	6.4×10^{-8}	3.2	1.1×10^{-8}	0.55
Cetyltrimethylammonium bromide, CTABr	5.8×10^{-8}	2.9	5.6×10^{-9}	0.28
Cetyltrimethylammonium hydrogen sulfate, $CTAHSO_4$	0.5×10^{-8}	0.25	3.4×10^{-9}	0.17
Dicetyldimethylammonium bromide, DCDMABr	4.4×10^{-8}	2.2	8.4×10^{-9}	0.42
Cetylpyridinium bromide, CPBr	5.8×10^{-8}	2.9	1×10^{-8}	0.5
Sodium dodecyl sulfate, SDS	≈0	≈0	≈0	≈0
Aerosol OT, AOT	≈0	≈0	≈0	≈0

mixing of a 30% aqueous H_2O_2 solution with chlorobenzene, 250 μL of isopropyl alcohol per 2 μL of 30% aqueous H_2O_2 was added. After the addition of the scavenger, optical spectra within 310–450 nm range were recorded at certain time intervals. The consumption of the scavengers was monitored by measuring changes in the optical density at absorption maxima. The changes in the absorption spectra of the reaction mixture resulting from scavenger consumption in reactions with free radicals are exemplified in [13, 16].

RESULTS AND DISCUSSION

Effect of a Surfactant on the Yield of Radicals upon Decomposition of Cumyl Hydroperoxide

It was shown in [13] that the addition of CHP reduces the surface tension at the water–air interface; i.e., the hydroperoxide behaves as a surfactant but, like alcohols, forms no micelles in an aqueous solution. However, CHP can form mixed micelles in combination with micelle-forming surfactants. Direct and reverse micelles form in aqueous and organic solutions, respectively. The radical formation rate upon the CHP decomposition in the presence of a surfactant was measured using quercetin as a radical scavenger. Consumption rates for Q at $[Q] > 2 \times 10^{-5}$ M are independent of its initial concentration ($[Q]_0$) in both the organic solvent and aqueous solution. According to the theory of inhibition of radical chain reactions [14], such a concentration dependence is typical for the scavenger consumed in free radical reactions at the rate of their initiation W_i/f, where f is the stoichiometric coefficient of inhibition (for quercetin $f = 2$ [15]). Table 1 presents the results of measuring the rate of radical formation in a CHP–surfactant system in chlorobenzene and aqueous solutions.

In the absence of surfactants and in the presence of anionic SDS and AOT in hydroperoxide solutions, quercetin is almost not consumed during several hours. The consumption of Q is observed only when both the cationic surfactant and CHP are present together; the rate is on average six times greater in the organic solvent than in aqueous solutions, other conditions being equal. The study of the concentration dependence of initiation rate showed that W_i value is proportional to the CHP concentration in the range 0.5–70 mM, the linear dependence of W_i on the surfactant concentration occurring in a narrower range of 0.5–3.0 mM. Table 1 also shows the values of the average specific radical initiation rate ($\overline{\varpi} = W_i/[\mathrm{CHP}][\mathrm{surfactant}]$), which allow one to compare surfactants and assess the initiation rate when the reagent concentrations are known.

In order of decreasing activity in the radical decomposition of CHP, the studied cationic surfactants can be arranged as follows:

in the organic solvent in reverse micelles,

$$\mathrm{CTACl} > \mathrm{CTABr} = \mathrm{CPBr} \geq \mathrm{DCDMABr} > \mathrm{CTAHSO_4}; \quad (1)$$

in direct micelles in an aqueous solution,

$$\mathrm{CTACl} > \mathrm{CPBr} \geq \mathrm{DCDMABr} > \mathrm{CTABr} > \mathrm{CTAHSO_4}. \quad (2)$$

In both direct and reverse micelles, the highest rates are observed in the presence of CTACl, while the lowest ones are detected in the presence of $CTAHSO_4$. The activities of bromides with different polar heads and hydrophobic fragments are close.

Effect of the Surfactant on the Yield of Radicals upon the Decomposition of Limonene Hydroperoxide

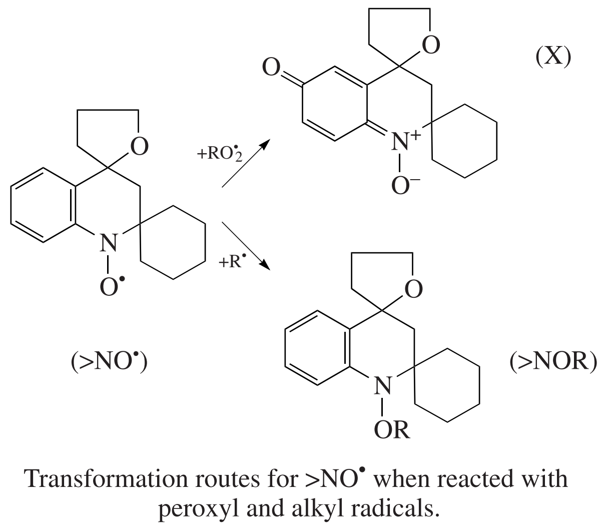
The formation of radicals in the limonene hydroperoxide–cationic surfactant system was studied with the

Table 2. Kinetic characteristics of radical formation in a system of 50 mM limonene hydroperoxide + 1 mM cationic surfactants at 37°C in chlorobenzene solution

Surfactant	$W_i \times 10^8$, mol/(L s), organic solvent	$\overline{\omega} \times 10^3$, L/(mol s), organic solvent
$C_{16}H_{33}(CH_3)_3N^+Cl^-$ (CTACl)	7.5	1.5
$C_{16}H_{33}(CH_3)_3N^+Br^-$ (CTABr)	5.4	1.1
$C_{16}H_{33}[C5H5N^+]Br^-$ (CPBr)	5.5	1.1
$(C_{16}H_{33})_2(CH_3)_2N^+Br$ (DCDMABr)	5.5	1.1
$C_{12}H_{25}SO_4^-Na^+$ (SDS)	0	0

use of stable nitroxyl radical 4-(spirotetrahydrofuryl-2')-2-spirocyclohexyl-1,2,3,4-tetrahydroquinoline-1-oxyl (>NO$^\bullet$), which is a selective trap for peroxyl radicals. The reaction of >NO$^\bullet$ with peroxyl radicals results in quinone–nitrone (QN), showing an intense absorption band in the visible spectral region (figure) [12].

The absorption maxima for QN (372 nm, extinction coefficient 1.9×10^4 L/(mol cm)) and >NO$^\bullet$ are in different spectral regions, which allows one to simultaneously monitor the consumption of the initial >NO$^\bullet$ (in solvents transparent at 280 nm) and the accumulation of its conversion product. The reaction of >NO$^\bullet$ with alkyl radicals R$^\bullet$ leads to hydroxamic ether >NOR, which absorbs in the UV spectral region.



Transformation routes for >NO$^\bullet$ when reacted with peroxyl and alkyl radicals.

The comparison of radical formation rates upon limonene hydroperoxide decomposition catalyzed by surfactants indicates that CTACl is also the most active catalyst of free-radical decomposition for this hydroperoxide. The comparison of data in Tables 1 and 2 shows that the $\overline{\omega}$ value for LHP is two times lower than that for CHP; i.e., CHP in combination with cationic surfactants produces radicals more actively. Anionic SDS is inactive in radical production. All studied bromides (CTABr, CPBr, and DCDMABr) exhibit similar activities in radical generation.

Effect of the Surfactant on the Yield of Radicals upon the Decomposition of Hydrogen Peroxide

Hydrogen peroxide is a surface-inactive substance. The surface tension (σ) of its 30% solution (75.2 mJ/m^2) is higher than that of water (72.8 mJ/m^2) [13]. Therefore, in microheterogeneous media formed by surfactant additives in a hydrocarbon environment, hydrogen peroxide is located in the polar core of reverse micelles [16].

In spite of this fact, cationic surfactants accelerate H_2O_2 decomposition to form free radicals both in an organic medium and aqueous solutions (Table 3). The rates of radical formation were measured from quercetin consumption. Quercetin is not consumed in a chlorobenzene medium and aqueous solutions in the presence of H_2O_2 (20–70 mM) without a surfactant. The simultaneous addition of H_2O_2 and a cationic surfactant leads to consumption of Q. As distinct from CHP, hydrogen peroxide in the presence of surfactant produces radicals at close rates in an organic medium and an aqueous solution, and H_2O_2 forms no radicals in the presence of cationic $CTAHSO_4$.

These data indicate that cationic surfactants in combination with a hydroperoxide can be used as lipophilic initiators of free radicals. These systems produce radicals also in aqueous solutions but at lower rates.

The measurement of the surface tension (σ) at the water–air interface upon the addition of cationic surfactants [13] showed that the surface activity of surfactants decreases in the series:

$$CTAHSO_4 > CPBr > CTABr > CTACl. \quad (3)$$

Dicetyldimethylammonium bromide, containing two long hydrocarbon fragments, taken alone almost does not decrease σ, which is due to its extremely low solubility. However, the decrease in σ down to 38.9 mJ/m^2 [13] and the formation of radicals is observed for a mixture of CHP with DCDMABr in water when aliquots of stock ethanolic solutions of the components are added to water.

The solutions of hydroperoxide and surfactant can be classified with mixed micellar solutions [17] in which only one component can produce micelles, whereas other amphiphilic components (alcohols, hydroperoxides) in the pure state form no micelles. The fact that the free-radical decomposition of hydroperoxides is accelerated only in combination with cationic surfactants (in contrast to anionic and nonionic) points out the possible role of peroxide orientation toward

Table 3. The rates of radical formation in the system of 20 mM H_2O_2 + 1 mM surfactant in chlorobenzene and aqueous solution at 37°C

Surfactant	W_i, mol/(L s)	$\varpi \times 10^3$, L/(mol s)	W_i, mol/(L s)	$\varpi \times 10^3$, L/(mol s)
	organic solvent		water	
Without surfactant	≈0	≈0	≈0	≈0
Cetyltrimethylammonium chloride, CTACl	2.0×10^{-8}	1.0	0.43×10^{-8}	0.21
Cetyltrimethylammonium bromide, CTABr	0.6×10^{-8}	0.3	0.42×10^{-8}	0.21
Cetyltrimethylammonium hydrogen sulfate, $CTAHSO_4$	≈0	≈0	≈0	≈0
Dicetyldimethylammonium bromide, DCDMABr	0.6×10^{-8}	0.3	0.4×10^{-8}	0.2
Cetylpyridinium bromide, CPBr	1.6×10^{-8}	0.8	0.32×10^{-8}	0.16
Sodium dodecyl sulfate, SDS	≈0	≈0	≈0	≈0
Aerosol OT, AOT	≈0	≈0	≈0	≈0

electric field in mixed hydroperoxide–surfactant micelles.

It should be noted that, other conditions being equal, the radical production rate is strongly dependent on the nature of the counterion in the surfactant. The series of surfactant activity (1) and (2) in this process do not coincide with variations in the surface activity of surfactants (3). For all studied peroxides, H_2O_2 including, CTACl shows the highest catalytic activity in both the organic medium and aqueous solution. Bromides CTABr, CPBr, and DCDMABr, which differ in surface and catalytic activity in aqueous solution, equally catalyze radical formation from hydroperoxides in the organic medium in the systems of reverse micelles.

One can suppose that the ability of cationic surfactants to produce radicals can be associated with the different degree of their dissociation in aqueous solutions. At a considerable content of positively charged surface-active cations, according to the known notions, the energy profit upon the formation of a mixed CHP–surfactant micelle increases due to excessive mutual attraction of ions of the components [18]. This, in turn, can affect the energetics of radical production reaction. This assumption is supported by the inertness of nonionic surfactant toward radical production and the enhanced ability of cationic surfactants to produce radicals in nonaqueous media.

The decrease in the dissociation degree at least for the series $CTAHSO_4$ > CTABr > CTACl is indirectly confirmed by the reduction of the surface activity in the same series, which is associated with the electrostatic repulsion of cetyltrimethylammonium ions upon the formation of an adsorption layer. Thus, the study on the dissociation of cationic surfactants is one of the areas of research on the features of liquid-phase oxidation in the presence of surfactants.

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