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Dramatic Enhancement of Enone Epoxidation Rates in Nonionic Microemulsions

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Abstract: The ability of microemulsions to dissolve polar and non-polar components with a huge internal interface can overcome the reagent incompatibilities frequently encountered in organic reactions. We investigated model epoxidation reactions of α,β-unsaturated enones and alkaline hydrogen peroxide in different nonionic microemulsions, both in the presence and absence of a phase-transfer agent (PTA). The obtained reaction profiles were compared with those for the corresponding surfactant-free two-phase systems. In addition, we defined a time constant τ as a measure for the rate of turnover. The epoxidation of *trans*-chalcone using an *n*-alkyl-polyoxyethylene surfactant based microemulsion was fastest in the system with the PTA ($\tau = 66$ min) and slightly slower without the PTA ($\tau = 77$ min). It was still slower in the two-phase system with a PTA ($\tau = 114$ min) and extremely sluggish without a phase-transfer agent. With *n*-alkyl β-D-glucopyranoside as the surfactant the conversion was twice as fast than in the former microemulsion systems, but the PTA did not accelerate the reaction further ($\tau = 35$ and 33 min). The epoxidation of vitamin K_3, the second model system, was extremely accelerated. It proceeded a factor of approximately 35 faster in the microemulsion ($\tau = 1.44$ min) than in the corresponding two-phase system ($\tau = 57$ min).

Keywords: enones · epoxidation · kinetics · microemulsions · phase-transfer catalysis

Introduction

Organic Synthesis lies at the heart of the production of fine chemicals, pharmaceuticals and other valuable products from readily available and cheap starting materials. However, reagent incompatibility, that is, dramatically different solubility properties are frequently encountered in organic reactions (i.e., inorganic salts and organic substrate). In many cases, water-soluble reactants such as inorganic salts need to be reacted with water-insoluble organic compounds. Many reactions, for instance, the alkaline hydrolysis of esters, oxidative cleavage of olefins or nucleophilic substitution on benzylhalides with inorganic salts are typical examples. It is current practice to solve the problem of the pure phase contact by choosing as solvents polar protic or polar aprotic liquids such as DMSO (dimethyl sulfoxide) and DMF (dimethyl formamide), offering the possibility of solubilizing both the organic and the inorganic compound. These solvents are excellent media; however, they have three main drawbacks: they are expensive, toxic and have high boiling points, which makes them difficult to remove once the reaction is completed.[1]

As an alternative approach, the reactants can be dissolved in two immiscible solvents, and the contact area between the phases is increased by either intensive mechanical mixing or better by the use of a phase-transfer agent (PTA). These PTAs, in most cases quaternary ammonium salts and crown ethers, act as phase-transfer catalysts (PTCs) and are widely used in two-phase reactions. Such compounds are capable of carrying the ionic reactant into the organic phase, where the low degree of solvation increases the reactivity remarkably. PTCs have been intensively used for oxidation reactions in general.[1–3] The catalytic epoxidation of enones,[4] in particular the epoxidation of *trans*-chalcone using alkaline hydrogen peroxide (Weitz–Scheffer conditions) as oxidant,[5] is of special interest in this field. Jew et al. found an enhancement of the enantioselectivity and the reaction rate in epoxidations of *trans*-chalcone using enantiomeric pure PTAs and catalytic amounts of technical

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grade surfactants.[6] In 2000, Maruoka and co-workers reported a significant rate enhancement of phase-transfer catalyzed enone epoxidations and alkylations by the combination of a non-chiral PTC and ultrasonic irradiation.[7]

Microemulsions are thermodynamically stable, optically isotropic mixtures of at least the three components water, oil[1] and surfactant.[8,9] These ternary systems offer various nanosized and complex microstructures, with a huge internal interface that can vary from droplets of oil dispersed in a continuous water phase over a bicontinuous "sponge" phase to water droplets dispersed in a continuous oil phase.[10–13] Regardless of the structure, the surfactant generates the internal surface which is positioned as a monolayer between water and oil. Much effort has been devoted to the utilization of these macroscopically homogeneous but microscopically nanosized two-phase systems as reaction media.[14] Nanoparticle designing,[15–17] polymerizations,[18,19] enzymatic reactions[20] and, of course in our interest, organic synthetic transformations[21] are suitable applications of microemulsions. These ternary systems have the ability to dissolve a broad spectrum of water-soluble and water-insoluble compounds. An organic reaction occurs at the very large water–oil interface and, in contrast to the use of PTAs, the ionic reactant is not transported into the oil phase. Additionally, these solutions are highly dynamic with a surfactant monolayer fluctuating on the time scale of less than milliseconds. This effect, as well as the high local reactant concentrations inside the water and oil sub-volumes influence and increase the reaction rates.

A number of reactions show enhanced reaction rates in microemulsions, for example, the oxidation of different hydrophobic substrates by Caron and co-workers,[22] alkylation of phenol,[23] nucleophilic substitution reactions[24] as well as catalytic, enantioselective oxidations of olefins[25] by Egger et al. The microemulsion approach and the PTA approach can be combined by adding a specific ionic surfactant to a microemulsion system, yielding together the highest reaction rates.[26–28] However, only a few reports have dealt with this powerful method so far.

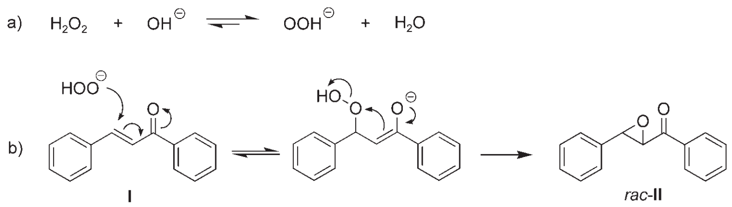
In our approach, we used this combined method, that is, using a one-phase microemulsion formulation based on the well-known nonionic surfactants *n*-alkyl-polyglycol ether (C_iE_j) with a cationic quaternary ammonium PTA. As a model reaction, we studied the epoxidation of the enone *trans*-chalcone (**I**) by alkaline hydrogen peroxide as a mild, inexpensive and environmentally benign oxidant. As microemulsion system we used H_2O–*n*-octane–$C_{10}E_4$/$C_{10}E_5$ with and without phase-transfer agent. We employed dodecyltrimethylammonium bromide (DTAB) as PTA because it was already shown by Boyer and co-workers that this PTA accelerates the transformation of enones to epoxides under Weitz–Scheffer conditions in heterogeneous two-phase systems.[5] For comparison, the same reaction was performed in a second nonionic microemulsion based on the rather hydrophilic nonionic surfactant *n*-octyl β-D-glucopyranoside (C_8G_1). The phase behaviour of this rather temperature insensitive surfactant was tuned by using a medium-chain alcohol as cosurfactant, resulting in the quaternary system H_2O–*n*-octane–C_8G_1–1-octanol (C_8E_0). In the second part of this work, the epoxidation of vitamin K_3 (**III**) by alkaline hydrogen peroxide was performed in the nonionic microemulsion system H_2O–toluene–$C_{10}E_8$, and analyzed kinetically by UV/Vis measurements.

[1] The term "oil" stands for hydrophobic liquids in general.

Results

Epoxidation of *trans*-chalcone (I)

The reaction scheme of the epoxidation of *trans*-chalcone (**I**) is shown in Scheme 1. As can be seen in Scheme 1, deprotonation of H_2O_2 by NaOH in the aqueous phase determines the concentration of the reactive species OOH^-. Due to the fact that the pK_a of H_2O_2 is 11.65,[29] the formation of the hydrogen peroxide anion is favored. The reaction B between the substrate *trans*-chalcone (**I**) and OOH^- can then take place at the interfacial area of the microemulsion and consumes one molar equivalent of hydrogen peroxide. As already discussed by Boyer and co-workers, both nucleophilic reagents OH^- and OOH^- were not able to open the epoxide ring of *rac*-**II**.[5]



Scheme 1. Weitz–Scheffer epoxidation of *trans*-chalcone (**I**), yielding the epoxide *rac*-**II**.

The H_2O/NaOH/H_2O_2–*n*-octane/*trans*-chalcone–$C_{10}E_4$/$C_{10}E_5$-(–DTAB) system: The phase behaviour of ternary and pseudo-ternary systems is usually studied in $T(\gamma)$ phase diagrams at a constant mass ratio α of oil-to-water plus oil, which is a representative cut through the corresponding phase prism.[10,30,31] Figure 1 shows a $T(\gamma)$ section of the pseudo-ternary system H_2O/NaOH/H_2O_2–*n*-octane/*trans*-chalcone–$C_{10}E_4$/$C_{10}E_5$ (-DTAB, 10 mol%) at $\delta = m_{C_{10}E_5}/(m_{C_{10}E_5} + m_{C_{10}E_4}) = 0.225$ and $\alpha = 0.4120$, which corresponds to equal volumes of water and oil. The concentrations of the solutes in the water phase were $c(H_2O_2, NaOH) = 0.30$ M and of the substrate in *n*-octane c(*trans*-chalcone) = 0.15 M.

The phase boundaries resemble the shape of a "fish-tail".[11] It shows a one-phase region (1) which contains a la-

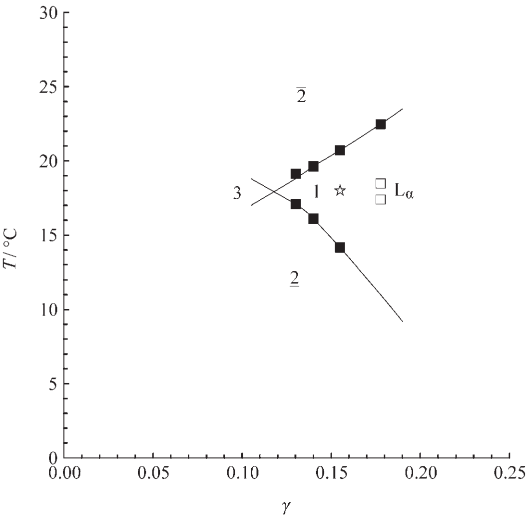


Figure 1. Phase diagram of the pseudo-ternary system H_2O/NaOH/H_2O_2–*n*-octane/*trans*-chalcone–$C_{10}E_4$/$C_{10}E_5$ (-DTAB, 10 mol %) at $\alpha=0.4120$ and $\delta_{C_{10}E_5}=0.225$ containing c(*trans*-chalcone) = 0.15 м in the oil phase and c(NaOH) = 0.30 and $c(H_2O_2)=0.30$ м in the aqueous phase. The star shows the reaction composition.

mellar phase (L_α) at higher surfactant mass fractions (open squares). At lower temperatures, a two-phase area ($\underline{2}$) exists where an oil-in-water microemulsion coexists with an oil excess phase. A second two-phase area ($\bar{2}$) exists at higher temperatures where a water-in-oil microemulsion coexists with a water excess phase. Considering the one-phase region it can be seen that it shrinks with decreasing surfactant mass fraction γ. The point where the phase boundaries meet is referred to as the X-point or "fishtail" point. This X-point is a reference point for each system and describes the minimum mass fraction of surfactant which is necessary for the complete solubilization of water and oil at a specific temperature (denoted as $\tilde{\gamma}$, $\tilde{T}$). Decreasing γ further a three-phase body (3) appears, in which the microemulsion phase coexists with a water and an oil excess phase. The X-point of the pure ternary system H_2O–*n*-octane–$C_{10}E_4$ is located at $\tilde{T}$ = 24.3 °C.[31] The addition of NaOH shifts the X-point to lower temperatures. In our case, this effect was partially compensated by the addition of the more hydrophilic surfactant $C_{10}E_5$. We chose the specific mass ratio of $\delta_{C_{10}E_5}$ = 0.225 in order to adjust the X-point temperature at $\tilde{T}$ = 18 °C since organic reactions with sensitive starting materials (i.e., the decomposition of H_2O_2) and products should be performed at low temperatures. Furthermore, all following transformations of *trans*-chalcone (**I**) to the epoxide *rac*-**II** are carried out at T = 18 °C in order to avoid different temperature effects on the reaction profiles. Addition of 10 mol % DTAB as PTA (with respect to the substrate concentration) does not influence the phase boundaries noticeably. The conversion of *trans*-chalcone (**I**) was investigated without and with DTAB. The reaction compositions are designated by the star in Figure 1 and Table 1.

Figure 2 shows the reaction profiles in the different media monitored by HPLC. Here, the epoxide yield is shown as a function of time. The reaction was also performed in the appropriate two-phase system with addition of 10 mol % DTAB (relative to the substrate concentration). The compositions and the measurement conditions of the three reactions are compiled in Table 1. The time constants τ of all profiles were calculated as the reciprocal slope of an exponential function fitted to the experimental data and are also compiled in Table 1.

The use of a microemulsion with DTAB (curve 1) in the epoxidation of *trans*-chalcone (**I**) resulted in a substantial acceleration of the reaction rate compared to both the microemulsion without DTAB (curve 2), and even more compared to the heterogeneous two-phase system with DTAB (curve 3). Nevertheless, the reaction in the microemulsion without DTAB proceeded still faster than the reaction in the heterogeneous two-phase system with DTAB. In all three systems the conversion was quantitative after six to ten hours. In contrast, the product *rac*-**II** was not detected in the heterogeneous two-phase system without DTAB after t = 24 h. As a measure for the reaction rate a time constant is extracted

Table 1. Compositions of the epoxidation reaction of *trans*-chalcone (**I**) in the system H_2O/NaOH/H_2O_2–*n*-octane/*trans*-chalcone–$C_{10}E_4$/$C_{10}E_5$ at $\alpha=0.4120$ and T = 18.00 °C.

	Equivalents			c [м]						
No.	H_2O_2	NaOH	*trans*-chalcone	H_2O_2	NaOH	*trans*-chalcone	τ [min]	γ	$\delta_{C_{10}E_5}$	DTAB
1	2	2	1	0.30	0.30	0.15	66.19	0.155	0.225	with[a]
2	2	2	1	0.30	0.30	0.15	77.06	0.155	0.225	without
3	2	2	1	0.30	0.30	0.15	114.07	–	–	with[a]

[a] 10 mol %.

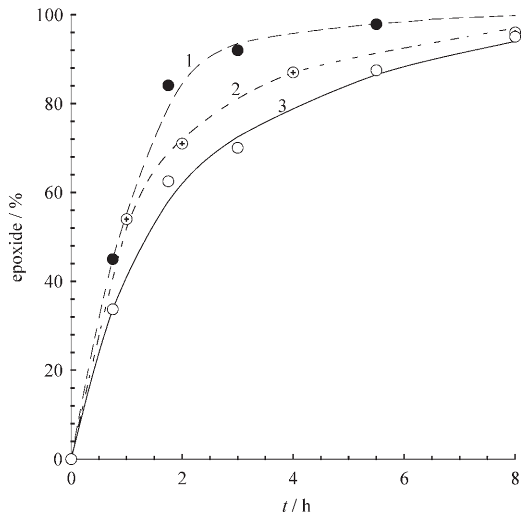


Figure 2. Reaction profiles for the epoxidation of *trans*-chalcone (**I**) to the epoxide *rac*-**II** at T = 18.00 °C, α = 0.4120 in the microemulsion system H_2O/NaOH/H_2O_2–*n*-octane/*trans*-chalcone (**I**)–$C_{10}E_4$/$C_{10}E_5$ with 10 mol % (with respect to the substrate concentration) DTAB (full circles, curve 1), without DTAB (dotted circles, curve 2), as well as the reaction in the two-phase system H_2O/NaOH/H_2O_2–*n*-octane/*trans*-chalcone with 10 mol % DTAB (open circles, curve 3). Lines shown are guides to the eye.

from the exponential fit to the experimental data (given in minutes and seconds). For the microemulsion with DTAB, without DTAB and of the heterogeneous two-phase system with DTAB it amounts to $\tau=66$, $\tau=77$ and $\tau=114$ min, respectively. Consequently, the reaction in the microemulsion with and without PTA is approximately twice as fast as in the two-phase system with PTA.

The H_2O/NaOH/H_2O_2–*n*-octane/*trans*-chalcone–C_8G_1(–DTAB) system: The pseudo-quaternary microemulsion studied contains the four components H_2O/NaOH/H_2O_2 (A), *n*-octane/*trans*-chalcone (B), *n*-octyl β-D-glucopyranoside(C_8G_1) (C), and as cosurfactant 1-octanol (D). The weak temperature sensitivity of the surfactant C_8G_1 in this system makes it difficult to influence the phase behaviour by varying the temperature. Instead, the hydrophobic cosurfactant 1-octanol (C_8E_0) was used for tuning the system in the same fashion as if the temperature was increased. Considering a four component system, the phase behaviour has to be represented in a phase tetrahedron at constant pressure and temperature.[32,33] The characterization of the phase behaviour is most conveniently done performing two-dimensional sections through the phase tetrahedron at a constant oil to oil-plus-water mass fraction of $\alpha=0.4120$. Figure 3a and b show the phase diagrams of the system H_2O/NaOH/H_2O_2–*n*-octane/*trans*-chalcone–C_8G_1–1-octanol (C_8E_0) at this α and a constant temperature of $T=18.00$ °C. The ordinate and the abscissa mirror the overall C_8E_0 mass fraction and the overall C_8G_1 mass fraction, respectively.

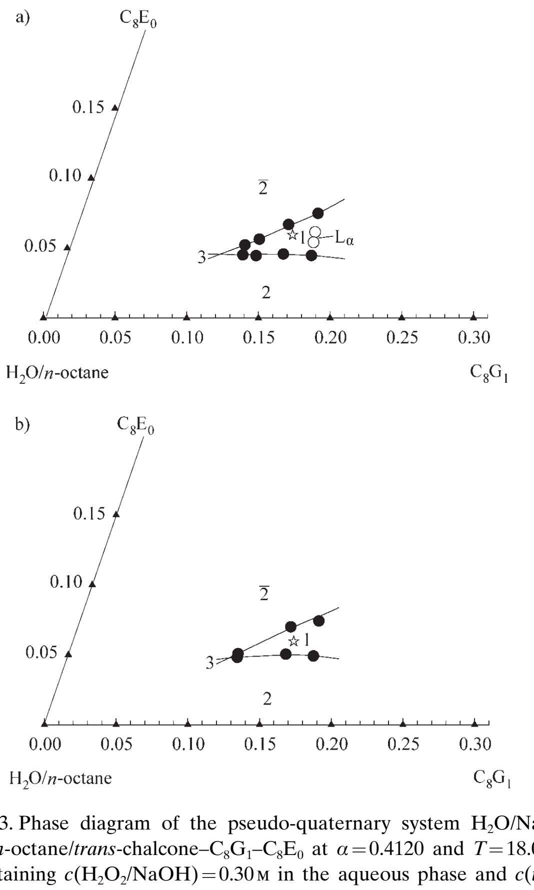


Figure 3. Phase diagram of the pseudo-quaternary system H_2O/NaOH/H_2O_2–*n*-octane/*trans*-chalcone–C_8G_1–C_8E_0 at $\alpha=0.4120$ and $T=18.00$ °C. a) Containing $c(H_2O_2/NaOH)=0.30$ M in the aqueous phase and c(*trans*-chalcone (**I**)) = 0.15 M in the oil phase. b) Containing $c(H_2O_2)=4.50$ M and $c(NaOH)=0.45$ M in the aqueous phase and c(*trans*-chalcone (**I**)) = 0.15 M in the oil phase. The stars indicates the reaction compositions.

In Figure 3a, the concentrations of *trans*-chalcone (**I**) in *n*-octane, H_2O_2 in water and NaOH in water were chosen to be c(*trans*-chalcone) = 0.15 M, $c(H_2O_2)=0.30$ M and $c(NaOH)=0.30$ M. In Figure 3b c(*trans*-chalcone) equals 0.15 M, $c(H_2O_2)=4.50$ M and $c(NaOH)=0.45$ M.

The phase boundaries in both diagrams resemble the shape of a "fishtail" with the phase progression $\underline{2}$–3–$\bar{2}$ for low mass fractions of surfactant while for high mass fractions of surfactant the progression $\underline{2}$–1–$\bar{2}$ is observed with increasing amount of 1-octanol. Comparing Figure 3a and b it is obvious that the *X*-points coincide well with each other. Consequently, both reactants H_2O_2 and NaOH appear to do not affect the phase behaviour noticeably. Note that $c(H_2O_2)$ is increased by a factor of 15 from 0.30 to 4.50 M.

The reaction profiles within the two microemulsions containing $c(H_2O_2)=0.30$ M, $c(NaOH)=0.30$ M in the aqueous phase and c(*trans*-chalcone) = 0.15 M in the organic phase were determined. One of them comprises additional 10 mol% of DTAB as PTA (again with respect to the substrate concentration) which does not influence the phase behaviour remarkably. The composition of both samples is designated by the star in Figure 3a. The reaction profile of the system containing $c(H_2O_2)=4.50$ M, $c(NaOH)=0.45$ M in the aqueous phase and c(*trans*-chalcone) = 0.15 M in *n*-octane was monitored at the sample composition exhibited by the star in Figure 3b. The reaction profiles of the epoxidation in the different reaction media are shown in Figure 4 while Table 2 compiles the compositions of the reaction media. For comparison, the time profile of the reaction in the heterogeneous two-phase systems with 10 mol% of DTAB is also given. All time constants τ of the reactions were obtained as discussed above and they are compiled in Table 2.

The microemulsion containing 30 equivalents H_2O_2 with respect to the substrate showed the fastest reaction rate and quantitative conversion after $t=150$ min (curve 4, $\tau=27$ min). The reaction proceeded more slowly in the two microemulsions with lower peroxide concentrations (curve 5 and 6) while one of them contained 10 mol% DTAB (filled circles). The time constants τ for curve 5 ($\tau=35$ min) and 6 ($\tau=33$ min) show no substantial difference in the reaction rates. In both cases, the conversion of *trans*-chalcone (**I**) is quantitative finished after $t=300$ min. In fact, all three microemulsion systems described show a considerable enhancement of the reaction rate compared to the two-phase system with 10 mol% DTAB ($\tau=114$ min). In the latter case, the conversion is not quantitative after $t=420$ min (curve 3). Hence, the reaction acceleration in the microemulsion with a large excess of oxidant is four-fold compared with the two-phase system with DTAB. It is three-fold in the microemulsions both with and without DTAB using two equivalents of peroxide.

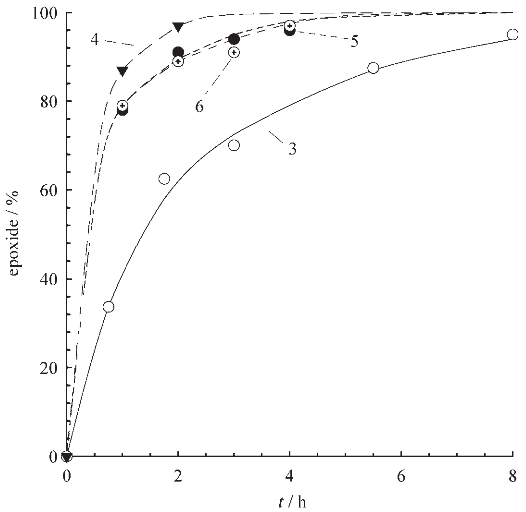


Figure 4. Reaction profiles for the transformation of *trans*-chalcone (**I**) to the epoxide *rac*-**II** at $T=18.00\,°C$ in the microemulsion system H_2O/NaOH/H_2O_2–*n*-octane/*trans*-chalcone–C_8G_1–C_8E_0 with and without 10 mol % DTAB (with respect to the substrate concentration). The filled triangles (curve 4) show the conversion in the microemulsion system without DTAB containing $c(H_2O_2)=4.50\,\text{M}$ and $c(\text{NaOH})=0.45\,\text{M}$ in the aqueous phase and c(*trans*-chalcone) $=0.15\,\text{M}$ in the oil phase. The filled and dotted circles show the profile in the microemulsion containing $c(H_2O_2)=0.30\,\text{M}$ and $c(\text{NaOH})=0.30\,\text{M}$ in the aqueous phase and c(*trans*-chalcone) $=0.15\,\text{M}$ in *n*-octane with and without DTAB, respectively. The open circles exhibit the reaction course of the two-phase system containing $c(H_2O_2)=0.30\,\text{M}$ and $c(\text{NaOH})=0.30\,\text{M}$ in the aqueous phase and c(*trans*-chalcone) $=0.15\,\text{M}$ in *n*-octane. Lines shown are guides to the eye.

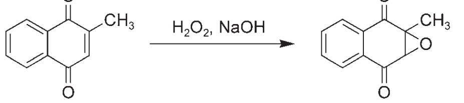
Table 2. Compositions of the epoxidation reaction of *trans*-chalcone (**I**) in the system H_2O/NaOH/H_2O_2–*n*-octane/*trans*-chalcone–C_8G_1–C_8E_0 at $\alpha=0.4120$ and $T=18.00\,°C$.

	Equivalents			c [M]						
No.	H_2O_2	NaOH	*trans*-chalcone	H_2O_2	NaOH	*trans*-chalcone	τ [min]	$\frac{m_{C_8G_1}}{\sum m}$	$\frac{m_{C_8E_0}}{\sum m}$	DTAB
4	30	3	1	4.50	0.45	0.15	27.44	0.154	0.06	without
5	2	2	1	0.30	0.30	0.15	35.22	0.154	0.06	with[a]
6	2	2	1	0.30	0.30	0.15	33.13	0.154	0.06	without
3	2	2	1	0.30	0.30	0.15	114.07	–	–	with[a]

[a] 10 mol %.

Epoxidation of vitamin K_3 (III)

The epoxidation of **III** to the epoxide *rac*-**IV** is shown in Scheme 2. The reaction of **III** to the corresponding epoxide *rac*-**IV** requires the same deprotonation of H_2O_2 as already shown in Scheme 1. The subsequent reaction between the enone **III** and OOH^- takes place at the interfacial area.



III   *rac*-IV

Scheme 2. Reaction scheme for the epoxidation of **III** to the epoxide *rac*-**IV**.

The H_2O/NaOH/H_2O_2–toluene/III–$C_{10}E_8$ system: Due to the low solubility of vitamin K_3 (**III**) in *n*-alkanes, the aromatic oil toluene was chosen as organic solvent in the pseudo-ternary system H_2O/NaOH/H_2O_2–toluene/**III**–$C_{10}E_8$. The ternary base system H_2O–toluene–$C_{10}E_8$ was investigated previously.[34] It was shown that the already known phase behaviour of the systems H_2O–*n*-alkane–C_iE_j is transferable to ternary systems comprising H_2O–toluene–$C_{10}E_8$.

Figure 5 shows a $T(\gamma)$ phase diagram of the system H_2O/NaOH/H_2O_2–toluene/**III**–$C_{10}E_8$ at constant $\alpha=0.4120$. The concentrations of H_2O_2 and NaOH with respect to the water phase and vitamin K_3 (**III**) with respect to the oil phase are $c(H_2O_2)=4.50\,\text{M}$, $c(\text{NaOH})=0.45\,\text{M}$ and $c(\textbf{III})=0.15\,\text{M}$, respectively. Because the volumes of oil and water are not equal at $\alpha=0.4120$, the molar ratio of **III** to NaOH to H_2O_2 is 1 to 3.7 to 37.3.

The phase diagram shows the typical "fishtail" behaviour with an X-point at $\tilde{\gamma}\approx 0.12$ and $\tilde{T}\approx 14\,°C$ and a pronounced lamellar phase L_α at slightly higher mass fractions of surfactant.

The reaction in the microemulsion, the composition of which is indicated by the star in Figure 5 ($\gamma=0.13$ and $T=14.00\,°C$) was to fast to be monitored by GC. The color change from the yellow vitamin K_3 (**III**) to the colorless epoxide *rac*-**IV** points to a complete conversion after a few minutes. No substrate (**III**) could be detected after $t=4$ min. Throughout the reaction the system was in the one-phase area, indicating low impact of the substrate or H_2O_2 on the phase behaviour.

In order to slow down the reaction rate the aqueous concentrations of H_2O_2 and NaOH were reduced to $c(H_2O_2)=0.36\,\text{M}$ and $c(\text{NaOH})=0.06$, 0.03 or 0.012 M, respectively. Figure 6 shows a series of $T(\gamma)$ phase diagrams of the system H_2O/NaOH/H_2O_2–toluene/**III**–$C_{10}E_8$ at $\alpha=0.4120$ containing different concentrations of H_2O_2, NaOH and **III**. As expected, the phase boundaries resemble the shape of a "fishtail", and all systems exhibit the typical X-point.

Phase diagram **A** shows the ternary system H_2O–toluene–$C_{10}E_8$ without H_2O_2, NaOH and **III**. In phase diagrams 7, 8 and 9 the concentrations of H_2O_2 in the aqueous phase and **III** in toluene are $c(H_2O_2)=0.36\,\text{M}$ and $c(\textbf{III})=0.15\,\text{M}$, respectively. Furthermore, the concentration of NaOH is increased from 9, 8 and 7 to $c(\text{NaOH})=0.012$, 0.03 and 0.06 M, respectively. As can be seen from Figure 6, low concentrations of the substrate and alkaline hydrogen peroxide shift the X-point only slightly to lower temperatures. Comparison with Figure 5 reveals that even the strong increase of the H_2O_2 and NaOH concentrations to $c(H_2O_2)=4.50\,\text{M}$ and $c(\text{NaOH})=0.45\,\text{M}$ drops the X-point only from $\tilde{T}\approx 24\,°C$ (pure ternary system) to $\tilde{T}\approx 14\,°C$ while the mass fraction of

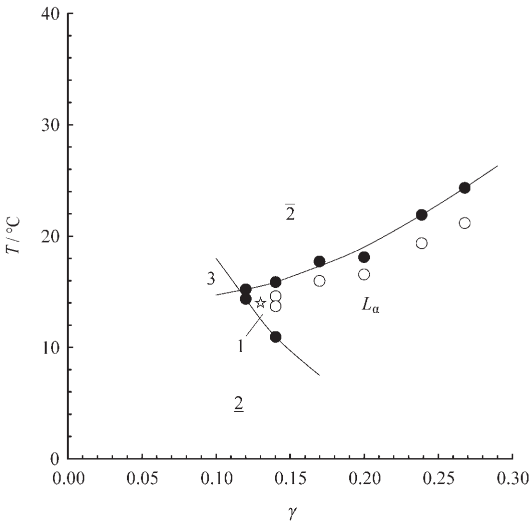


Figure 5. Phase diagram of the system H_2O/NaOH/H_2O_2–toluene/**III**–$C_{10}E_8$ system at $\alpha = 0.4120$ containing $c(H_2O_2) = 4.50$ M and c(NaOH) = 0.45 M in the aqueous phase and c(**III**) = 0.15 M in the oil phase. A significant lamellar phase exists in the one-phase region. The reaction composition and temperature is designated by the star.

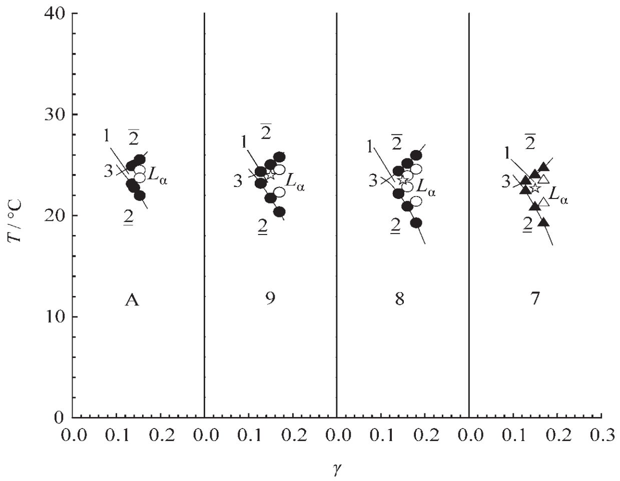


Figure 6. Phase diagrams of the H_2O/NaOH/H_2O_2–toluene/**III**–$C_{10}E_8$ system at $\alpha = 0.4120$. In diagram A the system contains no substrate. Diagram 7, 8 and 9 contain c(**III**) = 0.15 M in toluene and $c(H_2O_2) = 0.36$ M and c(NaOH) = 0.012, 0.03 and 0.06 M, respectively, in water. The X-point drops to some extend in temperature while the concentration of NaOH is increased. The reaction compositions are designated by the star in 7, 8 and 9.

surfactant at the X-point stays approximately constant at $\tilde{\gamma} \approx 0.12$. The shift of the phase behaviour to lower temperatures is due the effect that H_2O molecules have to hydrate the starting materials and thus are not available for the hydration of the surfactant head groups.[35]

The epoxidation of **III** in the microemulsion systems was monitored by UV/Vis measurements, following the transmittance of the incident light at $\lambda = 415$ nm, as described in the Experimental Section. Three reaction profiles were recorded at a constant $\alpha = 0.4120$, using the one-phase microemulsion H_2O/H_2O_2/NaOH–toluene/**III**–$C_{10}E_8$ as reaction medium. The concentration of H_2O_2 in the aqueous phase, and **III** in toluene were set at $c(H_2O_2) = 0.36$ M and c(**III**) = 0.15 M, whereas the concentration of NaOH was varied: c(NaOH) = 0.012, 0.03 and 0.06 M. Each profile was monitored in the one-phase region just in front of the lamellar phase area at $\gamma = 0.15$ and at the temperature of the X-point of $\tilde{T} \approx 24.00$ °C (23.50, 22.70 °C) for c(NaOH) = 0.012 M (0.03, 0.06 M). The transformation was also performed in the appropriate two-phase system H_2O–toluene at $T = 22.70$ °C where the concentration of **III** in toluene and of H_2O_2 and NaOH in water are c(**III**) = 0.15 and $c(H_2O_2) = 0.36$ and c(NaOH) = 0.06 M, respectively. In the three microemulsion systems the UV transmittance of **III** was continuously measured during the reaction. Figure 7 shows the transmittance

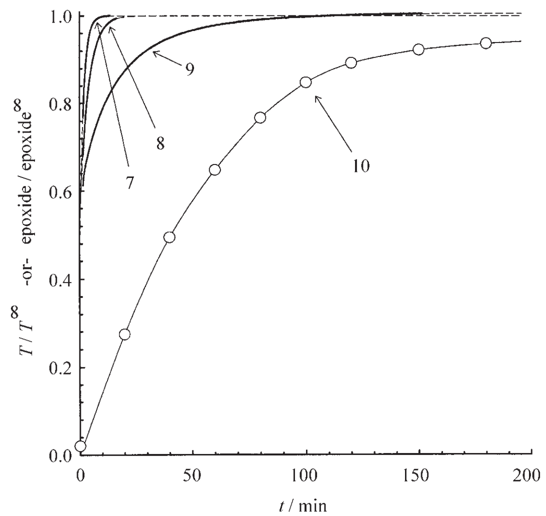


Figure 7. Reaction profiles (curves 7, 8 and 9, axis: T/T^{∞}) for the transformation of **III** to the epoxide *rac*-**IV** measured in the system H_2O/NaOH/H_2O_2–toluene/**III**–$C_{10}E_8$ by UV/Vis spectroscopy. The wavelength which transmittance has been observed as a function of time is $\lambda = 415$ nm (d_{cell} = 1 mm). Curves 7, 8 and 9 correspond to conditions specified in Table 3 and Figure 6. Curve 10 shows the normalized reaction profile for the formation of the epoxide *rac*-**IV** in the heterogeneous two-phase system with $c_{toluene}$(**III**) = 0.15 M, c_{H_2O}(NaOH) = 0.06 M and $c_{H_2O}(H_2O_2) = 0.36$ M (axis: epoxide/epoxide$^{\infty}$) at $T = 22.7$ °C. The dashed lines (7–9) and the solid line (10) shown are guides to the eye.

normalized onto the transmittance at quantitative transformation (axis T/T^{∞}) as function of time. On the other hand, the transformation of **III** in the two-phase system was measured by GC. Consequently, this reaction profile was given by data points that are assigned to the axis epoxide/epoxide$^{\infty}$ of Figure 7, that is, the normalized yield of the epoxide. As discussed above, all time constants were obtained by fitting an exponential function to the experimental data. Table 3 summarized the sample compositions and reaction conditions of the reaction shown in Figure 7.

The reaction was extremely fast in all microemulsion systems. Using 50 mol % NaOH with respect to the substrate concentration (c(NaOH) = 0.06 M, curve 7), the reaction was quantitative after $t = 5$ min. With 25 mol % NaOH (c(NaOH) = 0.03 M, curve 8), the reaction was nearly as fast

Table 3. Compositions of the epoxidation reaction of **III** in the system H_2O/NaOH/H_2O_2–toluene/**III**–$C_{10}E_8$ at $\alpha = 0.4120$.

	Equivalents			c [M]					
No.	H_2O_2	NaOH	**III**	H_2O_2	NaOH	**III**	τ [min]	γ	T [°C]
7	3	0.50	1	0.36	0.06	0.15	1.44	0.15	22.70
8	3	0.25	1	0.36	0.03	0.15	3.51	0.15	23.50
9	3	0.10	1	0.36	0.012	0.15	19.05	0.15	24.00
10	3	0.50	1	0.36	0.06	0.15	56.57	–	22.70

and the transformation was completed after $t = 12$ min. With 10 mol% NaOH (c(NaOH) = 0.012 M, curve 9) the reaction still proceeded extremely well, but the quantitative product was obtained after $t = 90$ min. This result is in line with the time constants τ which increase from $\tau = 1.44$, 3.51 to 19.05 min for curves 7, 8 and 9, respectively.

In contrast to the above results, in the two-phase system H_2O/NaOH/H_2O_2–toluene/**III** without $C_{10}E_8$ with c(NaOH) = 0.06 M and $c(H_2O_2) = 0.36$ M in the aqueous phase and c(**III**) = 0.15 M in toluene at $T = 22.70$ °C, the conversion to the product proceeds sluggishly. The conversion of **III** to the epoxide *rac*-**IV** is not quantitatively after $t = 180$ min ($\tau = 57$ min). Thus, the corresponding reaction rate in the microemulsion is a factor of approximately 35 faster than in the heterogeneous two-phase system.

Discussion

Epoxidation of *trans*-chalcone (I)

The solubility of *trans*-chalcone (**I**) in water and that of hydrogen peroxide and sodium hydroxide in *n*-octane is extremely low. Accordingly, the epoxidation reaction can only take place at the water–*n*-octane interface within the two-phase system. Due to the fact that the interfacial tension between water and *n*-octane is very high (~50 mNm^{-1}), the interfacial area, even with intensive mechanical stirring, is extremely small. No conversion of the enone **I** to the epoxide *rac*-**II** was obtained after 24 h.

Furthermore, it is not surprising that the reaction in the two-phase system without PTA is slower than in the system with 10 mol% of DTAB. As can be seen in Figures 2 and 4 (curve 3), the epoxidation proceeds reasonably fast under these conditions. DTAB acts simultaneously as ionic surfactant and as PTA by carrying the anionic reactant into the oil phase. The ionic surfactant decreases the interfacial tension between water and *n*-octane. Therefore, the interfacial area where the contact between the reagents is facilitated increases noticeably. In addition, the positively charged DTAB which adsorbs at the oil–water interface may well attract the negatively charged hydrogen peroxide anion. Due to DTAB acting as PTA, a favorable extraction equilibrium is established, namely, the equilibrium between the PTA in the water and in the oil phase, carrying the hydroperoxide anion. Once carried into the oil, the nucleophilic reagent (OOH^-) becomes poorly solvated, and thus highly reactive.

As can be seen in Figure 2 (curve 2) a significant increase in the reaction rate was obtained by using the nonionic microemulsion system H_2O/NaOH/H_2O_2–*n*-octane/*trans*-chalcone–$C_{10}E_4$/$C_{10}E_5$. The total surfactant mass fraction of $\gamma = 0.155$ leads to a significantly larger total interfacial area, which in turn results in an enhancement of the reaction rate (Figure 2, curve 2). The observation that the reaction rates are different in the heterogeneous two-phase system with 10 mol% DTAB and in the microemulsion indicates that in the rate-limiting step, close contact between the two reactants is facilitated. As a consequence, the epoxidation of *trans*-chalcone (**I**) proceeds very quickly and efficiently. Considering the model S_N2 reaction between 4-*tert*-butylbenzyl bromide and potassium iodide the situation can be different.[27] They found that the conversion within a two-phase system with addition of a PTA is just as fast as in a microemulsion system with PTA. In this case the total interfacial area does not determine the reaction rate and one may assume a fast and efficient extraction equilibrium, whereby the "chemical" reaction itself is the rate determining step.

As can be seen in Figure 2, addition of 10 mol% DTAB to the microemulsion system further increases the reaction rate (curve 1). The amount added is so low (0.24 wt%) that the total interfacial area between water and *n*-octane is not enhanced significantly. Hence, the effect of the surface enhancement can be neglected while the function as PTA must be taken into account. Furthermore, this result supports the assumption that bringing the two reactants in close contact to each other (either by increasing the interfacial area or by using a PTA) is the rate-limiting, that is, and not the "chemical" reaction between the enone and the oxidant.

The reaction proceeds faster in the similar nonionic microemulsion system H_2O–*n*-octane–C_8G_1–C_8E_0, based on the rather hydrophilic surfactant *n*-octyl β-D-glucopyranoside, and using 1-octanol as cosurfactant. As can be seen in Figure 4, the conversion to the epoxide is slowest for the heterogeneous two-phase system (curve 3) as already discussed above, faster in the microemulsion with and without 10 mol% DTAB (curve 5 and 6, respectively), and fastest when a large excess of H_2O_2 was employed (curve 4). With equal concentrations of oxidant and base, the reaction proceeds faster in the C_8G_1/C_8E_0 system without DTAB (Figure 4, curve 6) than in the $C_{10}E_4$/$C_{10}E_5$ system without DTAB (Figure 1, curve 2). This behaviour is reflected in the time constants of the reaction profiles which are $\tau = 77$ min for the $C_{10}E_4$/$C_{10}E_5$ based systems and more than twice as fast ($\tau = 33$ min) for the C_8G_1/C_8E_0 based system, respectively. In both systems, the reactions were conducted under very similar conditions, only different surfactants and surfactant amounts were used. This indicates a correlation of the reaction rate with the specific interfacial area on one hand, which is mainly determined by the amount of surfactant and cosurfactant in the system and the molecular composition of the interfacial film on the other hand. The specific interfacial area, SV^{-1}, which is the area created by the surfactant and the cosurfactant molecules can, as a first approximation, be calculated as shown in equation (1)[32]

$$\frac{S}{V} = \sum \frac{a_C}{v_C}\phi_{C,i} + \sum \frac{a_D}{v_D}\phi_{D,i} \qquad (1)$$

where a_C and a_D are the areas and v_C and v_D the volumes of the surfactant and cosurfactant molecules, respectively, $\phi_{C,i}$ and $\phi_{D,i}$ are the overall volume fractions of the surfactants and cosurfactants in the interfacial layer. The molecular areas and volumes of the surfactant and cosurfactant molecules and their overall volume fractions in the internal interface are given in Table 4.[32,36] The total interfacial areas between water and oil are compiled in Table 5. Therefore, the monomeric solubilities of the surfactants and cosurfactants in water and oil have been taken into account.[31,34]

Table 4. Molecular areas and volumes of the surfactant and cosurfactant molecules.

Surfactant	a_C [Å^2]	v_C [Å^3]
$C_{10}E_4$	52.8	579
$C_{10}E_5$	58.9	646
$C_{10}E_8$	77.1	841
C_8G_1	52.0	429
Cosurfactant	a_D [Å^2]	v_D [Å^3]
C_8E_0	29.3	260

The surface area increases from $SV^{-1} = 122\,m^2mL^{-1}$ in the $C_{10}E_4/C_{10}E_5$ system to $SV^{-1}=212\,m^2mL^{-1}$ in the C_8G_1/C_8E_0 system. DTAB was neglected in the calculation of the total specific interfacial area due to its considerably low amount in the solution. Thus, we conclude that the larger interfacial area of the C_8G_1/C_8E_0 system in comparison with the $C_{10}E_4/C_{10}E_5$ system is associated with the observed enhancement of the reaction rate of a factor slightly higher than two. However, the total interfacial area SV^{-1}, as discussed above, is not twice as high, and hence, the enhancement of the reaction rate cannot be explained exclusively by the larger interfacial area. Most likely, the composition of the interfacial film and the molecular structures of the surfactants give rise to considerable differences in the reaction rates.

The very polar structure of C_8G_1 causes a difference in the dielectrical constant at the interface, compared with the system containing $C_{10}E_4/C_{10}E_5$. This effect was already discovered by Drummond et al. for micelles of sugar-based and of ethoxylate-based surfactants.[37] The conversion of *trans*-chalcone (**I**) to the corresponding epoxide *rac*-**II** proceeds via a charged transition state in which the epoxide ring closure is not yet completed (Figure 1)[38] (and references therein). It is well known that charged transition states are stabilized by polar solvents. Therefore, the reaction proceeds faster the higher the polarity of the solvent is. The same holds true when one compares the epoxidation reaction in sugar-based and ethoxylate-based microemulsion systems. Due to the fact that the reaction takes place at the interfacial film, the high polarity of the surface stabilizes the charged transition state and accelerates the reaction when the carbohydrate-surfactant is employed. Otherwise, as in case of the $C_{10}E_4/C_{10}E_5$ system, the reaction proceeds more slowly.

As can be seen by comparison of curves 5 and 6 in Figure 4, 10 mol% of DTAB does not influence the course of the reaction noticeably. This is surprising because an enhancement of the reaction rate was observed in the nonionic $C_{10}E_4/C_{10}E_5$ system. However, it may be assumed that the already very polar surface of the C_8G_1-based systems is not polarized further. Furthermore, the conversion in the C_8G_1-based microemulsion is already very rapid and for that reason, the effect will be extremely small compared to the "background" reaction.

Epoxidation of vitamin K_3

Because the solubility of vitamin K_3 in water and that of hydrogen peroxide and sodium hydroxide in toluene is also low, one can assume that the epoxidation reaction takes place only at the water–toluene interface, too. However, the small solubility of toluene in water[39] and water in toluene[40] results in a slow conversion of **III** (Figure 7, curve 10). The reaction turns into completion after $t \approx 360$ min and the time constant of the reaction is $\tau = 57$ min. This is in contrast to the absence of any conversion of *trans*-chalcone (**I**) in the two-phase system H_2O/NaOH/H_2O_2–*n*-octane/*trans*-chalcone.

The addition of $C_{10}E_8$ to the system H_2O/NaOH/H_2O_2–toluene/**III** changes the situation substantially. As can be seen in Figure 7 curves 7, 8 and 9, the reaction did take place quantitatively within $t=5$, 12 and

Table 5. Summary of the different reaction profiles including the total interfacial area SV^{-1} and the time constants τ of the fitted exponential functions.

No.	System	DTAB 10 mol%	Interface/ [m^{2}mL^{-1}]	τ [min]	Equivalents H_2O_2	NaOH	Substrate
1	H_2O/*n*-octane/$C_{10}E_4/C_{10}E_5$	with	122	66.19	2	2	1
2	H_2O/*n*-octane/$C_{10}E_4/C_{10}E_5$	without	122	77.06	2	2	1
3	H_2O/*n*-octane	with	n/a	114.07	2	2	1
4	H_2O/*n*-octane/C_8G_1/C_8E_0	without	212	27.44	30	3	1
5	H_2O/*n*-octane/C_8G_1/C_8E_0	with	212	35.22	2	2	1
6	H_2O/*n*-octane/C_8G_1/C_8E_0	without	212	33.13	2	2	1
n/a	H_2O/*n*-octane	without	n/a	no conv.	2	2	1
n/a	H_2O/toluene/$C_{10}E_8$	without	55	<1.44	37.2	3.70	1
7	H_2O/toluene/$C_{10}E_8$	without	74	1.44	3	0.50	1
8	H_2O/toluene/$C_{10}E_8$	without	74	3.51	3	0.25	1
9	H_2O/toluene/$C_{10}E_8$	without	74	19.05	3	0.10	1
10	H_2O/toluene	without	n/a	56.57	3	0.50	1

90 min, respectively. This is in accordance with their time constants $\tau = 1.44$, 3.51 and 19.95 min. The conversion rate decreased with the concentration of sodium hydroxide ($c =$ 0.06, 0.03 and 0.012 M). This observation indicates that the concentration of NaOH is decisive for the reaction rate. Acting as a "catalyst", the concentration of base mainly determines the reaction rate. Compared with the conversion without surfactant and 50 mol% base ($\tau = 57$ min, curve 10), the conversion of **III** is a factor of approximately 35 faster than in the corresponding microemulsion system (Figure 7, curve 7).

Table 5 summarizes the total interfacial areas between water–toluene, calculated by Equation (1), and by taking into account the monomeric solubility of $C_{10}E_8$ in toluene.[34] The specific interfacial area for the system containing $\gamma =$ 0.13 is $SV^{-1} = 55\,m^2 mL^{-1}$ and of the systems containing $\gamma =$ 0.15 is $SV^{-1} = 74\,m^2 mL^{-1}$. Compared with the values calculated for the $C_{10}E_4/C_{10}E_5$ ($122\,m^2 mL^{-1}$) or the C_8G_1/C_8E_0 system ($177\,m^2 mL^{-1}$), it is not possible to explain the rapid reaction rate by the interfacial area alone. In addition, the interfacial area is less polar than that of the C_8G_1-based one, but only slightly more polar than that of the $C_{10}E_4/C_{10}E_5$-based surfactant. Consequently, the β-peroxyenolate adduct, resulting from the addition of hydroperoxide to **III** will not be stabilized significantly better by the $C_{10}E_8$ interfacial layer compared with the interface of the C_8G_1/C_8E_0 and $C_{10}E_4/C_{10}E_5$.

However, microemulsion formulations with strongly penetrating "polar" oils as toluene have been thoroughly investigated.[34] It was found that the mass fraction of monomeric-dissolved $C_{10}E_8$ in toluene is 15.6 wt%. The molecular structure of $C_{10}E_8$ is rather similar to the structure of cyclic polyoxyethylenes (crown ethers) which, in turn, are known to act as PTAs. This leads to the conclusion that *n*-alkyl-polyoxyethylene-based surfactants such as $C_{10}E_8$ have a reasonable extraction equilibrium in the organic phase. The surfactant carries—depending on the quality of $C_{10}E_8$ as PTA—the reactive species in the organic phase and, hence, the reaction rate is increased appreciably. This "crown ether effect" is less pronounced in non-polar oils such as *n*-alkanes since under these conditions, the monomeric solubility is only in the dimension of 2 wt%. Nevertheless, this point is not sufficient to explain the striking acceleration of the reaction rate compared to the conversion of *trans*-chalcone (**I**). Toluene is not only crucial for the reaction rate due to the monomeric solubility of the surfactant, but rather the penetration into the interfacial film is decisive for the reaction rate. It appears that the penetration of toluene brings the reactants closer to each other compared with the H_2O–*n*-octane–$C_{10}E_4/C_{10}E_5$ and the H_2O–*n*-octane–C_8G_1–C_8E_0 systems. This effect increases the reaction rate dramatically as a closer contact of the substrates is provided over the total interfacial area.

The above two aspects are crucial for the rate enhancement. The very strong penetration is assumed to cause an enhancement of the reaction rate, while the influence of the monomeric solubility of $C_{10}E_8$ is rather secondary. The rather polar interfacial area generated by the surfactant $C_{10}E_8$ is also of minor importance.

Conclusion

The reaction between *trans*-chalcone (**I**) and the alkaline hydrogen peroxide proceeds at an appreciable rate in nonionic microemulsions based on H_2O, *n*-octane and $C_{10}E_4/C_{10}E_5$ or, alternatively, C_8G_1 and C_8E_0. PTC was effective in the heterogeneous two-phase system as well as in the $C_{10}E_4/C_{10}E_5$ based systems. In general, the reaction proceeded fastest in the systems based on the carbohydrate surfactant. This is probably due to the fact that the charged intermediate in the reaction cycle is stabilized better within the very polar interfacial area. Furthermore, the specific interfacial area is larger than that in the ethoxyethylate-based systems. Moreover, we found that the reagents NaOH, H_2O_2 and *trans*-chalcone (**I**) did not show a considerable impact on the phase behaviour of the carbohydrate surfactant based system. For this reason, these nonionic microemulsions are suitable for large scale applications.

The reaction between vitamin K_3, hydrogen peroxide and catalytical amounts of base proceeded strikingly fast in the system H_2O, toluene and $C_{10}E_8$. We found a quantitative conversion of vitamin K_3 after $t = 5$ min (50 mol% base) whereas the reaction in the heterogeneous two-phase system H_2O–toluene is quantitative after $t \approx 6$ h. The time constants reveal that the conversion in the latter system is approximately 35-fold slower than in the corresponding microemulsion.

Both results are of practical interest for organic synthesis where the reagent incompatibility is frequently encountered. Transfer of this oxidation methodology to further enones is currently under investigation.

Experimental Section

Materials: The surfactants polyoxyethylene *n*-alkylethers (C_iE_j), namely $C_{10}E_4$, $C_{10}E_5$ and $C_{10}E_8$ were purchased from Nikko Chemicals (Tokyo, Japan) and Fluka (Buchs, Switzerland), respectively (> 98% purity in all cases). *n*-Octyl β-D-glucopyranoside (C_8G_1) was obtained from Bachem (Bubendorf, Switzerland) with a purity > 99%. The phase-transfer agent dodecyltrimethylammonium bromide (DTAB), 2-methyl-1,4-naphthoquinone (**III**) and *trans*-chalcone were purchased from Fluka (Buchs, Switzerland) with a purity of > 98%. As oils, *n*-octane from Fluka (Buchs, Switzerland) and toluene from Sigma-Aldrich (Milwaukee, USA) with a purity of > 99.5 and > 99.8%, respectively, were used. The cosurfactant 1-octanol (C_8E_0) was purchased from Sigma-Aldrich (Milwaukee, USA) with a purity of > 99.4%. Water was double-distilled using a quartz column. Sodium hydroxide with a purity of > 99% and a 30% w/w solution of hydrogen peroxide were purchased from Merck (Darmstadt, Germany). All components were used without further purification.

Phase diagrams: Meaningful experiments on microemulsions can only be conducted if the phase behaviour is well known. Thus, we studied at first the phase behaviour of all microemulsions used as reaction media. Thereby the phase behaviour is studied in two different ways. While for the temperature dependent ternary (i.e., pseudo-ternary) systems the isoplethal (constant composition) method is used, the temperature invariant quaternary (i.e., pseudo-quaternary) systems are studied at isothermal conditions. Accordingly the phase diagrams of the ternary systems are determined as a function of temperature and the overall surfactant mass fraction. The polar component (A), the non-polar component (B), the nonionic surfactants C_iE_j (C) and, if required, the PTA DTAB were weighed into test tubes which were then sealed with polyethylene stoppers. The occurring phases were investigated at a constant sample composition and as a function of temperature in a water bath with a temperature control of $\Delta T = \pm 0.02$ K. The number and kind of coexisting phases are studied by visual inspection of both transmitted and scattered light. Using crossed polarizers the existence of anisotropic phases, as for example, the lamellar phase (L_α) can be detected. To characterize fixed compositions, it is useful to define the mass fraction of the non-polar component in the mixture of the polar and non-polar component

$$\alpha = \frac{m_B}{m_A + m_B}, \tag{2}$$

the overall mass fraction of the surfactant and cosurfactant

$$\gamma = \frac{\sum m_C + \sum m_D}{m_{total}}, \tag{3}$$

and the mass fraction of one surfactant in the surfactant mixture

$$\delta = \frac{m_D}{m_C + m_D}. \tag{4}$$

The amount of all starting materials is given in molar concentrations and of DTAB in mol % with respect to the molar amount of the substrate. Thereby it is assumed that the concentration of DTAB is so small that the total interfacial area between water and *n*-octane is not enhanced considerably.

To determine the phase diagrams of the quaternary temperature invariant systems all components were weighed into a test-tube as stated above. The samples were placed in a water bath at constant temperature $T = 18.00 \pm 0.02$ °C. When temperature equilibrium was reached, the stopper was lifted and the mixture was titrated with the cosurfactant C_8E_0 (D) using a calibrated microliter syringe. The amount added was controlled by weight with an accuracy of $\Delta m = \pm 0.001$ g. After stirring, the system was allowed to equilibrate and the occurring phases were monitored. The composition of these quaternary systems was characterized by Equations (2), (3) and (4).

Chemical reactions: Two different epoxidation reactions were carried out as follows:

I: The epoxidation of the α,β-unsaturated enone *trans*-chalcone (**I**) with alkaline hydrogen peroxide was performed in various microemulsions and in heterogeneous two-phase systems in test tubes using vigorous agitation. Different ratios of the substrate, of the base and of hydrogen peroxide were employed. To this end, stock solutions of the substrate **I** (0.15 M) in *n*-octane and of NaOH (0.60 and 0.90 M) and H_2O_2 (0.60 and 9.00 M) in water were prepared. If required, the surfactants $C_{10}E_4$, $C_{10}E_5$ and DTAB or analogously C_8G_1, C_8E_0 and DTAB, were added. The influence of the reactants on the phase behaviour of the corresponding microemulsion was determined. The reactions were all carried out at $T = 18.00$ °C.

Thereby it was assured that the microemulsion system stayed in the one-phase state during the complete course of the reaction. After a given period of time, samples were withdrawn and the reaction was stopped by addition of aqueous sodium thiosulfate (excess, to ensure complete reduction of hydrogen peroxide). The reaction mixture was evaporated to dryness, and the crude product was purified by flash chromatography (*c*-hexane/diethyl ether 9:1). The course of the reaction was monitored by HPLC.

The product was exemplarily isolated following the procedure described above, and 2,3-epoxy-1,3-diphenylpropanone (*rac*-**II**) was isolated in 99 % yield.

For the two-phase reaction, a solution of *trans*-chalcone (**I**) (46.9 mg, 1.00 equiv, 225 μmol) in *n*-octane (1.50 mL) and an aqueous solution (1.50 mL) containing hydrogen peroxide (30 % aqueous solution; 37.2 μL, 15.3 mg, 2.00 equiv, 450 μmol) and sodium hydroxide (18.0 mg, 2.00 equiv, 450 μmol) were combined. After a given time 100 μL samples of the organic phase were withdrawn and the reaction was stopped by addition of aqueous sodium thiosulfate solution (excess, to ensure complete reduction of hydrogen peroxide). The organic phase was dried over magnesium sulfate, and the crude product was purified by flash chromatography (*c*-hexane/diethyl ether 9:1). The course of the reaction was monitored by HPLC.

II: The epoxidation of **III** with alkaline hydrogen peroxide was performed in the microemulsion H_2O–toluene–$C_{10}E_8$ and in the two-phase system H_2O–toluene. To this end, stock solutions of the substrate **III** in toluene (0.15 M) and of NaOH (0.12, 0.06, 0.024 and 0.90 M) and H_2O_2 (0.72 and 9.00 M) in water were prepared. Sodium hydroxide and hydrogen peroxide were used in different ratios, whereas the concentration of **III** in toluene was kept constant at c(**III**) = 0.15 M. To formulate the microemulsion the surfactant $C_{10}E_8$ was added and the influence of the reactants on the phase behaviour was determined.

In the microemulsion containing $c(H_2O_2) = 4.50$ and c(NaOH) = 0.45 M in the aqueous phase, the reaction was carried out in the one-phase region at $T = 14.00$ °C. In the microemulsion systems containing c(**III**) = 0.15 M, $c(H_2O_2) = 0.36$ M and c(NaOH) = 0.06 M (0.03, 0.12 M) in the aqueous phase, the substrate conversion was investigated at $T = 22.70$ °C (23.50, 24.00 °C). The course of the reaction was monitored by measuring the transmittance of the incident light through the microemulsion at $\lambda =$ 415 nm where **III** exhibited a very low transmittance and the product **III** epoxide *rac*-**IV** was almost transparent. UV/Vis measurements were performed with a Perkin Elmer Lambda 19 spectrophotometer. For temperature control, the cell (of 1 mm optical pathway) was placed in a thermostated cell holder with an accuracy of $\Delta T = 0.02$ °C.

Product isolation (reaction conditions according to Figure 7, curve 7) was performed as follows: The reaction was stopped at $t = 5$ min by the addition of a large excess of ethyl acetate and water. The phases were separated and the aqueous phase was extracted with ethyl acetate. The combined organic phases were evaporated, and the crude product was purified by flash chromatography (ethyl acetate/*c*-hexane 3:1). The 2,3-epoxy-2-methyl-1,4-naphthoquinone (*rac*-**IV**) was isolated in 94 % yield.

Two-phase reaction conditions: **III** (38.7 mg, 1.00 equiv, 225 μmol) and diphenyl ether (internal standard) (38.3 mg, 1.00 equiv, 225 μmol, 35.7 μL) were dissolved in toluene (1.50 mL) at 22.70 °C. After addition of sodium hydroxide (4.50 mg, 0.50 equiv, 113 μmol) and hydrogen peroxide (68.9 μL, 76.5 mg, 3.00 eq, 675 μmol) in water (1.85 mL) the reaction was stirred for three hours. After a given time 100 μL samples of the organic phase were withdrawn. The reaction was stopped by the addition of an aqueous sodium thiosulfate solution. After drying over magnesium sulfate, the organic phase was analyzed by GC.

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