PERKIN 2

Inverse phase transfer catalysis *versus* interfacial catalysis. Effect of medium stirring in the epoxidation reaction of chalcone by hydrogen peroxide

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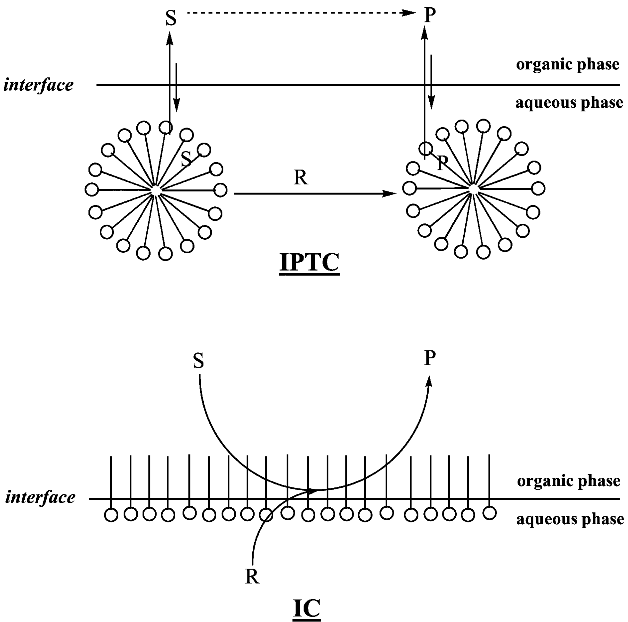
The epoxidation of chalcone by H_2O_2 has been investigated in a water–heptane two-phase system in the presence of a surfactant (dodecyltrimethylammonium bromide; DTAB) in order to analyse the role played by the rate and the type of stirring (magnetic and sonication). Under these conditions two catalytic processes have been proved to intervene: an inverse phase transfer catalysis (IPTC) or an interfacial catalysis (IC). This latter process appears to be very sensitive to stirring efficiency.

Introduction

We recently described[1] an alternative to phase transfer catalysis (PTC) which enables reactions in biphasic water–organic solvent systems. This new approach consists of substituting the quaternary lipophilic onium generally used as a transfer catalyst by a water soluble surfactant. Under these conditions, we proved that there were two competitive catalytic processes[2] (Scheme 1).



Scheme 1 Inverse phase transfer catalysis (IPTC) and interfacial catalysis (IC) principles involving a surfactant as catalyst (S: Substrate, P: Product and R: Reactant).

In the first process, the surfactant allows the transfer of the lipophilic substrate into the water phase by solubilizing it within micelles. The substrate reacts with the hydrophilic reagent in the micellar microenvironment. In that case the surfactant plays two roles:

i) it transfers and solubilizes the substrate into the aqueous phase

ii) it enables the micellar catalysis of the chemical step.

In contrast to PTC, the reaction takes place in the water phase and not in the organic one. This process is consistent with an inverse phase transfer catalysis (IPTC).[3]

The second mechanism that we displayed arises from the aptitude of a surfactant to reduce the interfacial tension by forming a monolayer at the interface. Under stirring, the interfacial area between water and the organic solvent can become very large. This increases the encounter probability of the lipophilic substrate with the hydrophilic reagent at the interface. Consequently, the reaction rate becomes greater. Thus, in this second case the surfactant also plays two roles:

i) it creates a large contact area between the phases

ii) it ensures the potential stabilization of the transition state formed at the interface in the microenvironment of the surfactant monolayer.

In this process, none of the species need to be transferred from one phase to another. The reaction takes place at the interface. We called this process interfacial catalysis (IC). IPTC and IC are two competitive catalytic pathways. We showed that while undergoing slow stirring (100 rpm), the reaction occurs mainly through an IPTC process. However, while undergoing vigorous stirring (1200 rpm), the IC process becomes predominant.[1]

Moreover, IPTC can occur only if the micellar concentration in the water phase is high enough to solubilize a significant fraction of the hydrophobic substrate. To be efficient, the surfactant concentration should be noticeably higher than the critical micellar concentration (cmc).

In contrast, IC can occur even if the surfactant concentration is lower than the cmc, since a small amount of surfactant is enough to promote a large interfacial area.

Therefore, IC appears to be a potentially interesting method for the following reasons:

i) IC can be applied to a greater variety of reactions than the usual PTC process. Indeed, this IC process can be applicable to any reaction, whatever the hydrophilic reagent (anionic, cationic or even non-ionic).

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ii) the surfactant can be used in a catalytic amount.

iii) at the end of the reaction, a hydrophilic surfactant is easier to eliminate than is a lipophilic quaternary onium salt used in PTC.

Due to the potentiality of this interfacial catalysis, we tried to better evaluate the influence of the area of the interface. In order to do this, we examined the role played by the rate and the type of stirring at several surfactant concentrations.

These different factors have been analysed through the use of the epoxidation reaction of chalcone as a model reaction.[1,2]

Results and discussion

Epoxidation of chalcone by hydrogen peroxide was achieved in water–heptane (1 : 1) under basic conditions. This was done using dodecyltrimethylammonium bromide (DTAB) as a catalyst.

The kinetic conditions used were the following:

$[\text{chalcone}]_0 = 0.1$ M in heptane

$[H_2O_2]_0 = 0.5$ M; $[\text{NaOH}]_0 = 0.5$ M; $[\text{DTAB}] = 0.1$ M in water.

The reaction was carried out at 25 °C. Equal volumes of the two phases were used. Magnetic stirring ranged from 100 to 1200 rpm. The variation of the initial epoxidation rate values is plotted on Fig. 1 as a function of the stirring speed.

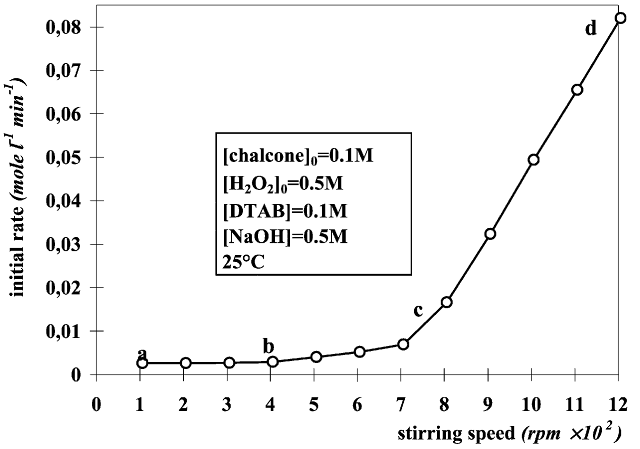

Fig. 1 Influence of the agitation rate on the initial reaction rate in the epoxidation reaction of chalcone.

The corresponding plot can be divided into three parts:

part a–b: at these low stirring speeds, the two phases are clearly separated. The reaction occurs mainly in micelles within the aqueous phase (IPTC). The IC pathway is very restricted, since the interface area is roughly equal to the section of the flask used.

part b–c: at the beginning of this section, the formation of a cloudy layer can be observed at the interface. The thickness of this zone increases with the speed of stirring, and at a stirring speed close to 800 rpm the biphasic system changes into an emulsion.

part c–d: as soon as an emulsion is formed, the reaction rate is markedly dependent on the stirring speed. From the strong increase observed, the following conclusions can be drawn:

i) the interface area increases markedly as soon as the stirring speed reaches 800 rpm or higher, which favors the IC process.

ii) in contrast to what has been observed in classical PTC,[4] a plateau cannot be reached even at 1200 rpm. This means that the surfactant is far from being completely at the interface.

Consequently, not only is the stirring effect much more sensitive in IC than in IPTC, but also we can expect that a more efficient stirring would provide a larger interfacial area. This in turn would amplify the efficiency of the IC process. To check this point, we compared two reactions. Both of them were carried out under the same conditions, except for their different methods of stirring. In one case, we used a magnetic stirring at 1200 rpm, while in the other case, we applied an ultrasonic stirring. The reaction was monitored at 300 nm ($\lambda_{\max}$ of chalcone). The absorbance variations are plotted in Fig. 2.

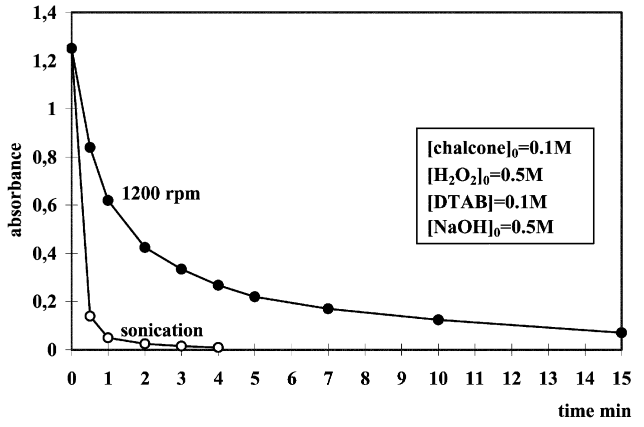

Fig. 2 Influence of the agitation type (magnetic stirring (1200 rpm) or sonication).

It clearly appears that the reaction proceeds faster under ultrasonic stirring. As expected, acoustic waves, which correspond to a stronger energy source, are more prone to creating a large interface area than a magnetic stirring. We have compared the influence of the DTAB concentration on the reaction rate in both types of stirring (Fig. 3).

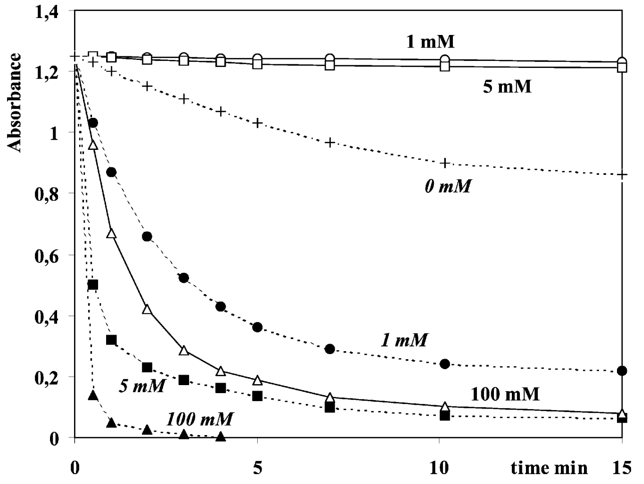

Fig. 3 Influence of the surfactant concentration on the epoxidation reaction carried out under sonication (dashed line) and magnetic stirring (1200 rpm; full line).

As observed in Fig. 3, if magnetic stirring (1200 rpm) is applied and if catalyst concentration varies from 100 to 5 mM, then the reaction rate decreases drastically. While in contrast, if ultrasonic stirring is used, then the rate is only weakly reduced. Moreover, even with 1 mM in DTAB (which is lower than cmc) the reaction remains rapid under ultrasonic stirring. Only the IC process is able to operate under these conditions. As a consequence, IC is efficient even with a tiny amount of catalyst.

Conclusion

We have shown that IC can be an interesting alternative to the classical PTC. Also, the biphasic medium must be efficiently stirred; we have shown that this could be achieved through the use of acoustic waves. Further studies on the application of the present IC process to additional reactions are in progress.

Experimental

Dodecyltrimethylammonium bromide (DTAB), chalcone, sodium hydroxide and 30% hydrogen peroxide were obtained from commercial sources.

UV studies were performed on a SAFAS DES-170 spectrophotometer.

Sonochemical reactions were conducted using a VIBRA-CELL sonicator equipped with a titanium tip with a frequency of 20 kHz.

Reactions in two-phase media were carried out according to the general procedure already described.[2]

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