

EFFECT OF SURFACTANTS ON THE CLEAVAGE
OF THE N-O BOND
IN O-(2,4-DINITROPHENYL)-CYCLOHEXANONE OXIME

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Kinetics of cleavage of N-O bond in O-(2,4-dinitrophenyl)-cyclohexanone oxime with hydroxide ions both in the presence and absence of surfactants has been studied. The reaction is accelerated by cationic micelles, slightly by non-ionic micelles and there is no effect of anionic micelles. A plot of the rate constant vs. [surfactant] shows a maximum corresponding to the CMC of surfactant.

Была исследована кинетика расщепления связи NO в O-(2,4-динитрофенил)циклогексанон-оксиме с помощью гидроксильных ионов как в присутствии, так и в оксутствии поверхностно-активных веществ (ПАВ). Реакция может быть ускорена с помощью катионных мицелл, слегка ускорена с помощью неионных мицелл, а анионные мицеллы не оказывают какого-либо эффекта. На графике зависимости константы скорости от концентрации ПАВ наблюдается максимум, соответствующий ККМ ПАВ.

INTRODUCTION

Micellar catalysis has attracted the attention of various workers due to its relationship with enzymatic processes /1-4/. Also there is a similarity between micellar surfaces and lipid-protein interfaces and, consequently, micelle catalyzed reactions are of great help in elucidating the mechanism of electrostatic hydrophobic interactions in biological systems /5, 6/. During the last decade catalysis by micelles has contributed significantly to our insight in the importance of micro-environmental and proximity effects /7-10/. The micelle catalyzed hydrolysis of oxime-O-ethers, resulting in the cleavage of the N-O bond, is of interest because of its use in biological systems /11-14/.

Various studies have been made to investigate the effect of surfactants on the reaction kinetics. The behavior of surfactant is highly dependent upon the nature of the reaction. The rate of proton-catalyzed hydrolysis of N-benzylideneaniline has been shown to be strongly retarded in the presence of cationic detergent n-CTAB, by Van Sendew and Koningsberger /15/. Reactions between charged ions are reported to be affected by the addition of a surfactant having the opposite charge /16/.

EXPERIMENTAL

O-(2,4-dinitrophenyl)cyclohexanone oxime was prepared by the method described earlier /17, 18/. All reagents used were of BDH Analar grade. Solvents were redistilled before use. For kinetic studies deoxygenated water was used. All solutions were prepared in 50 : 50 (v/v) MeOH-water mixture.

The solvent system employed in the kinetic studies was 50 : 50 (v/v) MeOH-water at 40 ± 0.1 °C. The reaction was studied under pseudo first order conditions and followed in a Carl-Zeiss UV-VIS recording spectrophotometer at λ -400 nm corresponding to the formation of the product 2,4-dinitrophenoxide ion. The reaction was followed up to three half-lives and the final reading was noted after about ten half-lives.

RESULTS AND DISCUSSION

The rate of reaction was affected by the addition of cationic surfactants. A plot of the second order rate constant against the surfactant concentration is shown in Fig. 1. In both cases there is a maximum which arises because the increasing concentration of surfactant increases the micelle concentration, therefore, the amount of reactants in the micellar phase, too. But a further increase in surfactant concentration means that the reactants are distributed over a large amount of micelles which leads to 'dilution' of the reactants in the micellar phase and the rate is decreased. The reaction is catalyzed only at a particular concentration of surfactant equal to its CMC, below or above which there is no catalytic effect. Below CMC, when no micelles are formed, all the hydroxide ions are dispersed in the medium and the rate is not affected. The increase of surfactant concentration as soon as micelle formation starts, makes the surfactant QBr^* to exchange its bromide ions with hydroxide ions to give QOH. The concentration of hydroxide ions at the

* QBr = cetylpyridinium bromide or cetyltrimethylammonium bromide

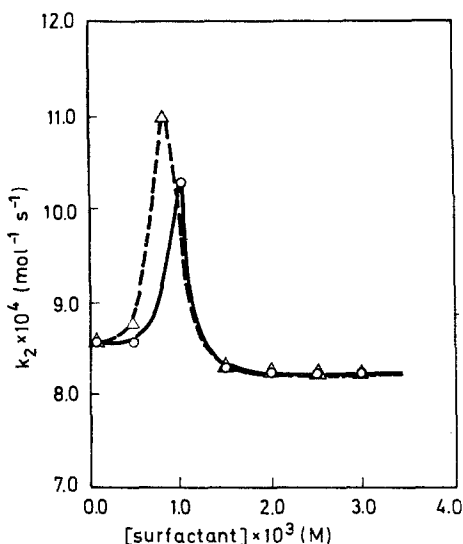


Fig. 1. Plot of second order rate constant vs. surfactant concentration, -- Δ -- cetylpyridinium bromide; — ○ — cetyltrimethylammonium bromide

micelle surfaces, therefore, increases and the rate is enhanced. As the concentration of QBr increases above its CMC, more and more micelles are formed, and hydroxide ions are distributed all over the system and there is no net increase but rather a decrease in hydroxide ion concentration at the micelle surface, hence the rate is decreased.

The catalytic effect is more pronounced with cetylpyridinium bromide than with cetyltrimethylammonium bromide. Cetylpyridinium bromide is a planar molecule and the cationic nitrogen is free for attack from both sides and is in a better position for reducing the charge density in the transition state, while cetyltrimethylammonium bromide is a sterically hindered tetrahedral molecule, which cannot effectively stabilize transition state (I) to the extent cetylpyridinium bromide can.

Similar experiments using sodium dodecylsulfate produce no significant change in the rate, suggesting that it is the charge on the micelle that is responsible for the enhancement of the rate.

The effect of micellar catalysis on bimolecular reactions depends upon the incorporation of reactants into the micelle and the rate in the micellar phase. The dependence of the overall rate constant upon the surfactant concentration can be attributed to the distribution of reactants between aqueous and micellar phase. For micelle catalyzed bimolecular reactions, the observed rate constants go through a

maximum with increasing surfactant concentration and the observed second order rate constant near the maximum is dependent on the reactant concentration.

This catalytic effect of micelles may offer a method for determining the CMC of surfactants.

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