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SURFACTANT CONTROL OF BROMINATION PRODUCTS

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Abstract The product distribution in the bromination of cyclohexene is almost completely controlled by the addition order of the reactants to the surfactant, the obtained bromohydrin being 99% pure. Water seems to be present all around the micelles head groups.

There have recently been many attempts to obtain product or regioselectivity [1] control by the use of micelles or similar submicroscopic aggregates, and limited success has been achieved.

We have observed almost total product control in the reaction of cyclohexene with bromine by using aqueous cetyltrimethylammonium bromide (CTABr). In water this reaction gives largely trans-1,2-dibromocyclohexane |1| and an intermediate bromonium ion is trapped by Br^{-}*, [2] but if Br_2 is added to CTABr, followed by cyclohexane the product is almost exclusively trans-2-bromocyclohexanol-1 |2|. However, the products depend upon the order of mixing because if Br_2 is added to a mixture of cyclohexene and CTABr considerable amounts of |1| are formed (See table). These results depend not only upon the order of mixing of the reagents but also upon the inert salt or amphiphile. For example trans dibromide is the major product if reaction is carried out in water and is significant product in sodium dodecyl sulfate (SDS) regardless of the order of mixing. The product specificity is essentially independent of temperature in the range 25 ÷ 90°C. Products were analyzed by g.l.c. (OV 17 or OV 101 5% on Chromosorb HP 80-100 1/8"6'); Varian Vista 6000, integrator HP 3390A and product yields were > 90%.Changes in the stirring rate had no effect.

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* Other nucleophilic anions can trap the bromonium ion.[2]

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nucleophile, the water.* Formation of less bromohydrin in reverse addition or in reactions in SDS suggests that the cyclohexene is located in a region of the micelle in which the amount of water is limited, so that the bromonium ion is captured largely by bromide. Reaction is SDS gives $|\underline{2}|/|\underline{1}| \cong 7$, regardless of the order of addition of reactants, despite the paucity of bromide at the micellar surface.

The products in reactions in which cyclohexene is added to CTABr/Br_2 can be controlled by addition of bromide or inert anions. Addition of Br^- increases the amount of $|\underline{1}|$, but inert anions, e.g. NO_3^-, $SO_4^=$ displace Br^- [6] from the micellar surface and decrease formation of dibromide (See table).

The markded product selectivity which we observe seems to depend upon the location of the reactant site, which for normal addition is the outer region of the micelle, or aggregate, and the very short life of the bromonium ion, although despite this short life there are no cis-products. Our results suggest that control of product or regioselectivity by micelles or similar aggregates will be achieved most readily in reactions which involve very short-lived intermediates, which are converted with products in diffusion-controlled reactions. Consistently we do not, to date, find micellar product control in the bromination of 1-octene, that is known to react with bromine slower than cyclohexene [2] Thus the migration of these intermediates is not faster than their conversion with products. With this stipulation we believe that micellar effects may be synthetically useful, and we observe similar results for chlorination of cyclohexene, which in CTACl or cetylpyridinium chloride gives largely chlorohydrin.

Under preparative conditions $|\underline{2}|$ can be extracted with ether and bromine and then cyclohexene added to the residual aqueous CTABr, so that the surfactant is reusable and product separation is easy.

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* The micelle model proposed by Menger [5] has water all around the surfactant head groups.

Table

Dependence of Products on the Order of Addition of Reactants

Salt[a]	|2|/|1| Normal Addition[b]	Reverse Addition[c]
CTABr	10	5
$CTANO_3$	20	6
$(CTA)_2SO_4$	30	7
NBu_4Br	0.1	0.1
CTABr	20[d]	4[d]
CTABr	90[d e]	10[d e]
CTABr	100[e]	-
CTABr	4[f]	-

a) At 25°C, unless specified, $[Salt] = 5 \times 10^{-2}$ N; bromine equimolar with ammonium ion, and cyclohexene in 5 ÷ 10% molar excess over bromine.

b) Br_2 added first.

c) Cyclohexene added first.

d) $[Br_2]/[Salt] = 0.5$.

e) At 90°C.

f) In 5×10^{-2}M NaBr.

This results are unexpected because the surface of a CTABr micelle is saturated with Br^-[3], but nevertheless the first-formed bromonium ion is captured almost completely by water, if bromine is added first, despite the nucleophilicity of many micellar bound anions[3,4].

Several factors are involved in this control of product specificity. First, bromine binds very strongly to CTA micelles and is not expelled by heating a CTA Br Solution at 90°C, and we assume it binds in the Stern layer. Micelles of SDS do not strongly bind bromine. Second, the bromonium ion is very short-lived, and in a cationic micelle may be so short-lived that is reacts, from the rear, almost exclusively with the most abundant

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