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MICELLAR CATALYSTS IN THE $CoBr_2$ CATALYZED OXIDATION OF p-XYLENE IN WATER

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Cationic and nonionic surfactants enhance cobalt bromide catalyzed oxidation of p-xylene by molecular oxygen in aqueous system at 120-140 °C and 0.9 MPa oxygen. Micellar catalytic effect is proposed for this reaction.

1. Introduction

The oxidation of methylsubstituted benzenes by molecular oxygen to corresponding carboxylic acids, catalyzed by cobalt and bromide catalysts, is, in commercial processes, realized preferably in acetic acid as a solvent. When water is used instead of corrosive acetic acid, a two-phase (aqueous and organic) reaction system is formed. However cobalt bromide catalyst is preferably dissolved in the aqueous phase and thus oxidation of p-xylene does not proceed [1].

In our previous studies [1,2] it has been shown that, in the presence of catalytic amounts of lipophilic quaternary ammonium or phosphonium compounds cobalt bromide catalysts possess high activity in such a two-phase reaction system. Thus, quaternary cations with relatively short alkyl chains (e.g. tetrabutylammonium cations) which are poor surfactants, act as phase-transfer agents for Br^- between aqueous and organic phases. The increase of Br^- concentration in the organic phase shifts the equilibria of Co-Br complexes towards catalytically higher active one and therefore increases their concentration in the organic phase [2]. Also, quaternary ammonium cations which are good surfactants, e.g. R_3N^+R', where R is short alkyl chain (C_1–C_3) and R′ is long alkyl chain (C_{14}–C_{16}) are catalytically active in the above-mentioned oxidation reaction. Besides these quaternary ammonium compounds the nonionic surfactants are also catalytically active. The catalytic activity of both these types of surfactants is the subject of the present study.

2. Experimental

p-xylene was purfied by distillation. A series of quaternary ammonium bromides were prepared by alkylation of corresponding tertiary amine (Triethylamine, N-methylmorpholine, N-methylpiperidine and pyridine) by alkylbromides. Slovasol 205 and Slovasol 6018 are commercial nonionic surfactants (CHZWP Novaky, Czechoslovakia), produced by reaction of ethylene oxide with C_{14}–C_{18} alcohols. Their HLB values are 8.4 and 15.0, respectively.

The reaction rates were measured by following the oxygen consumption. All reaction components and catalysts were put into a 50 cm^3 glass-lined stainless steel reactor connected with flexible metal capillary to the apparatus for measuring of oxygen consumption under constant pressure. Reaction mixture was mixed by shaking the vessel of the reactor in a thermostatted oil bath using a vibrator. The reaction rates were measured over the range of speed of agitation, where transport phenomena do not limit the reaction rates.

3. Results and discussion

Experimental data of p-xylene oxidation in the presence of water, $CoBr_2$ and cationic or nonionic surfactants are shown in table 1. The maximum reaction rates were calculated from linear parts of the plots of absorbed oxygen versus time. As is seen from table 1, the reaction rates depend on the structure and type of surfactant.

Table 1
Catalytic activity of surfactants./ Conditions: p-xylene 60 mmol, water 111 mmol, $CoBr_2$ 0.2 mmol and 0.4 mmol of quaternary onium salt or 0.1 g of nonionic surfactant/

Catalyst	t (°C)	$r_{max} \times 10^4$ (mol O_2 $dm^{-3}s^{-1}$)
none		0
dodecyl-MMB	125	8.9
tetradecyl-MMB	125	9.4
hexadecyl-MMB	125	9.6
dodecyl-MPB	125	9.2
tetradecyl-MPB	125	9.7
hexadecyl-MPB	125	9.4
1-hexadecylpyridinium bromide	140	11.7
dodecyltriethylammonium bromide	140	35.5
tetradecyltriethylammonium bromide	140	35.0
hexadecyltriethylammonium bromide	140	36.1
Slovasol 6018	140	17.6
Slovasol 205	140	21.7

In the range of 12–16 carbon atoms in alkyl chain in alkyltriethylammonium bromide, N-alkyl-N-methylpiperidinium bromide (alkyl-MPB) and N-alkyl-N-methylmorpholinium bromide (alkyl-MMB) reaction rates are only slightly influenced by the length of alkyl chain. This fact and observed catalytic activity of cationic and nonionic surfactants indicate that, in the studied reaction system, they act as micellar catalysts [3]. Positive effect of such catalysts can be explained on the base of (i) changes of the characteristics of the interphase area and (ii) the assumption that formation of micelles strongly influences the local concentrations of reactants and cobalt bromide catalytic species. Previously [2] we have found that the concentration of Co(II) and Br^- ions in the bulk organic phase is very low and insufficient for catalytic efficiency in the absence of any phase transfer agent. In the micellar reaction system local concentrations of Co(II) and Br^- in/or around the micelle containing p-xylene and intermediates, are different from concentrations in the above mentioned bulk organic phase.

The described reaction system is an example of catalysis where two types of catalysts–micellar and Co-Br complexes are present. This is the main difference from previously studied micellar catalytic reactions, where only reactants and micellar catalyst is present.

References

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