RAPID PAPER

Selective Dimerization of *p*-Cresol in the Presence of Micelles of Cationic Surfactants

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Abstract : The oxidative coupling of *p*-cresol by FeCl_3 in aqueous solution was conducted in the presence of alkyltrimethylammonium bromide ($\text{C}_n\text{-TAB}$). Cationic surfactants greatly inhibited trimer production and increased the selectivity for dimer production. The dimer produced in the reaction system may possibly be incorporated into micelles and subsequently excluded from the aqueous oxidation system. With $\text{C}_{16}\text{-TAB}$, the dimer was selectively produced at a concentration above cmc. $\text{C}_{12}\text{-}$ and $\text{C}_{10}\text{-TAB}$ brought about selective dimerization, even below cmc.

Key words : selective dimerization, oxidative coupling, *p*-cresol, alkyltrimethylammonium bromide

The oligomers of *p*-cresol (1) are synthesized by the oxidative coupling of 1 using FeCl_3 in the aqueous solution^{1)~3)}. Because of the commercial availability of each *o-o* linked oligomer^{4)~6)}, the development of the reaction systems to control the degree of polymerization has been required. During the oxidation, the dimeric compound thus produced in the reaction system is partly precipitated, since it is insoluble in water unless it coordinates to an iron ion⁷⁾. Our recent study showed that the trimer production was efficiently depressed when the reactions were carried out in aqueous-hydrophobic two phase systems, since the dimer was efficiently transferred into the hydrophobic phases and excluded from the aqueous oxidation system where the oxidizing agent, the Fe^{3+} ion, was present^{8),9)}. This effect resulted in a depression of further oligomerization of the dimer, consequently, producing an enhancement of the selectivity of the dimer. In these studies, the water-insoluble organic solvents⁸⁾ and the cavity of γ -cyclodextrin⁹⁾ were shown to be efficient hydrophobic phases for the selective dimerization.

The use of organic solvents, however, is restricted since they are vaporized at temperatures above their boiling points. Cyclodextrin would also be inappropriate to be used in higher temperature conditions, since the oxidative coupling produces hydrochloride which causes the hydrolysis of cyclodextrin.

Alkyltrimethylammonium bromide could be aggregated in the aqueous solution to form micelles. The hydrophobic fields, the inner sphere of the micelles, are thus dispersed in the aqueous solution of the cationic surfactants. If the alkyltrimethylammonium bromide micelles could efficiently include the dimer during the reaction, they are useful materials for the selective dimerization, since they are robust in acidic and higher temperature conditions.

In the present study, the oxidative couplings were carried out in the presence of hexadecyltrimethylammonium bromide ($\text{C}_{16}\text{-TAB}$), dodecyltrimethylammonium bromide ($\text{C}_{12}\text{-TAB}$), or decyltrimethylammonium bromide ($\text{C}_{10}\text{-TAB}$). The influences of the cationic surfactants on the oxidative coupling reactions were determined.

The aqueous solution of 1 (5.0×10^{-2} M), FeCl_3 (5.0×10^{-2} M), and alkyltrimethylammonium

bromide was stirred for 24 h at 25°C. After the reactions were finished, methanol was added to the reaction mixture to dissolve precipitates. Iron ions and cationic surfactants were removed from the solution by passing it through a cation-exchange chromatograph (SP Sephadex C-25 Na⁺ form).

Surface tensions of aqueous solutions of the surfactants were measured in advance, and the critical micelle concentrations (cmc) were determined as 9.8×10^{-4} M, 5.0×10^{-3} M, and 2.2×10^{-2} M for C₁₆-TAB, C₁₂-TAB, and C₁₀-TAB, respectively.

The conversion of 1 and yields of the *o-o* dimer (2) and *o-o* trimer (3) shown in Fig. 1 in the presence of C₁₆-TAB are shown in Fig. 2.

Product distributions of oxidized compounds were scarcely influenced when the concentration of C₁₆-TAB was below the cmc. On the other hand, when the concentration was above the cmc, the trimer production was efficiently inhibited and the dimer was produced in high selectivity. These results indicate that the dimeric compound 2 thus produced in the reaction

Fig. 1 Structures of *o-o* Dimer (2) and *o-o* Trimer (3) of *p*-Cresol (1).

Fig. 2 Conversion of 1 and Yields of 2 and 3 in the Addition of C₁₆-TAB in the Oxidative Coupling Reaction System.

Fig. 3 Conversion of 1 and Yields of 2 and 3 in the Addition of C₁₂-TAB in the Oxidative Coupling Reaction System.

Fig. 4 Conversion of 1 and Yields of 2 and 3 in the Addition of C₁₀-TAB in the Oxidative Coupling Reaction System.

system was mostly transferred into the micelle of C₁₆-TAB. On the other hand, monomer 1, being more hydrophilic than 2, tended to be present in the aqueous phase where the substrates could be oxidized.

The conversion of 1 was drastically decreased when the concentration of C₁₆-TAB was more than ten times that of cmc. The ratio of 1 incorporated into the micelle would be increased under these conditions.

The results obtained when C₁₂-TAB and C₁₀-TAB were added are shown in **Fig. 3** and **4**.

The selective dimerization of 1 was also shown to occur by adding C₁₂-TAB or C₁₀-TAB to the reaction system. However, unlike the case observed for C₁₀-TAB, the trimer production was inhibited even though the concentrations of the surfactants were less than their cmc. The cmc values shown in advance were determined in the absence of any *p*-cresol derivatives. In the oxidation system, C₁₂-TAB and C₁₀-TAB would thus be aggregated at a lower concentration than the cmc by incorporating the substrates during the reaction.

The selective oxidative dimerization of 1 by the addition of alkyltrimethylammonium bromide is one of the simplest and low cost methods. It could thus significantly affect industrial processing.

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[ノート] 脱酸素剤による食用油の保存性向上 (第2報)

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市販の鉄系脱酸素剤をポリエステルフィルムやエチレン酢酸ビニルフィルムで密着被覆して、密栓したガラス容器または食用缶のヘッドスペースに添付または油中に浸漬することによって、容器内の魚油や大豆油の自動酸化をほぼ完全に抑制することができた。
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[ノート] CDM 試験による焼き菓子類の酸化安定性の評価

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市販の焼き菓子類の酸化安定性について、製品から油脂を抽出することなしに直接 CDM 試験で測定した。誘導期 (IP) の測定は Methrom Rancimat 679 型を用い、粉末試料 43 点について測定した。26 試料の IP は 50 h 以内に迅速に測定されたが、還元糖含有量が多い残りの 17 試料は、連続して緩やかに電導率が上昇するため測定できなかった。CDM は焼き菓子類の酸化安定性を相対的に評価できる実用的な方法である。
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[速報] カチオン界面活性剤ミセルの存在下における *p*-クレゾールの選択的二量化反応

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水溶液中での塩化第二鉄による *p*-クレゾールの酸化カップリング反応を、アルキルトリメチルアンモニウムブロミド型カチオン界面活性剤 (C_n -TAB) の存在で行った。カチオン界面活性剤の添加は三量体の生成を顕著に抑制し、二量体生成の選択性を向上させることが認められた。これは反応系に生成された二量体はミセル中に取り込まれ、酸化反応が進行する水相からは疎外されるためと考えられる。ヘキサデシルトリメチルアンモニウムブロミド (C_{16} -TAB) を添加した場合は、cmc 以上の濃度で二量体は高選択的に合成された。ドデシルトリメチルアンモニウムブロミド (C_{12} -TAB) あるいはデシルトリメチルアンモニウムブロミド (C_{10} -TAB) を添加した場合には、cmc 以下の濃度においても選択的二量化が起こることが見いだされた。

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