Communications to the Editor

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REACTIONS USING MICELLAR SYSTEMS: BIOMIMETIC TYPE OXYGENATION OF INDOLES CATALYZED BY COBALT(II)-SCHIFF'S BASE COMPLEXES

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Bis(salicylidene)ethylenediaminatocobalt(II) solubilized in a micellar system, such as 3% aq. sodium dodecylsulfate, catalyzed oxygenation of indoles at highly diluted concentrations of the substrate, resulting in a high rate of acceleration and/or reaction selectivity which are attributable to the condensation effect and/or distribution effect of micelles.

KEYWORDS-biomimetic oxygenation; micelle; sodium dodecylsulfate; cobalt(II) schiff's base; indole derivative

Taking into account the structure and catalytic property of micelles, we have been interested in reactions using micellar systems in relation to "the reaction field simulating the biological system."[2] Also, synthesizing metal complexes mimicking biological catalysts has become one of the most important objectives in bioinorganic and bioorganic chemistry. Cobalt(II)-Schiff's base complexes, for example, have been investigated as synthetic oxygen carrying models[3] and their reactivities have been studied in chemical reactions using organic solvents as the reaction media.[4] Oxygenation of the indoles in methanol catalyzed by bis(salicylidene)-ethylenediaminatocobalt(II)[Co(salen)] has been studied as a tryptophan 2,3-dioxygenase model by Nishinaga.[5] We now report the first example of the oxygenation of indoles catalyzed by a micelle-solubilized metal complex mimicking a biological reaction.

We selected sodium dodecylsulfate(SDS), the best surfactant to solubilize Co(salen) and methanol, as a homogeneous solvent to compare with the micellar system. The experimental results are shown in the Table. The structures of oxygenation products obtained from each substrate are also shown in Fig. 1. The oxygenation reactions were carried out as follows: 3% aq. SDS and methanolic solutions of Co(salen)[6](1.1 mM) and indoles (10 and/or 1.25 mM) [(**1**), (**2**), (**3**), (**4**), and (**5**)] were bubbled with a fine stream of oxygen at room temperature for 24 h. The reaction mixture was concentrated in vacuo and the concentrated residue was separated on a silica gel preparative plate.

The Table shows two charactaristic features: i) in SDS the reaction rates are greatly accelerated, 2.5 - 7 times more than those in methanol due to the condensation effect of micelles (Exp. 1-3 and 6); ii) the oxygenation of (**4**) and (**5**) in SDS show the marked difference in their conversion rates, whereas those in methanol proceed practically in the same order (Exp. 5 and 6). The rate differences of the oxygenation of (**4**) and (**5**) in SDS may be accounted for by different distribution of

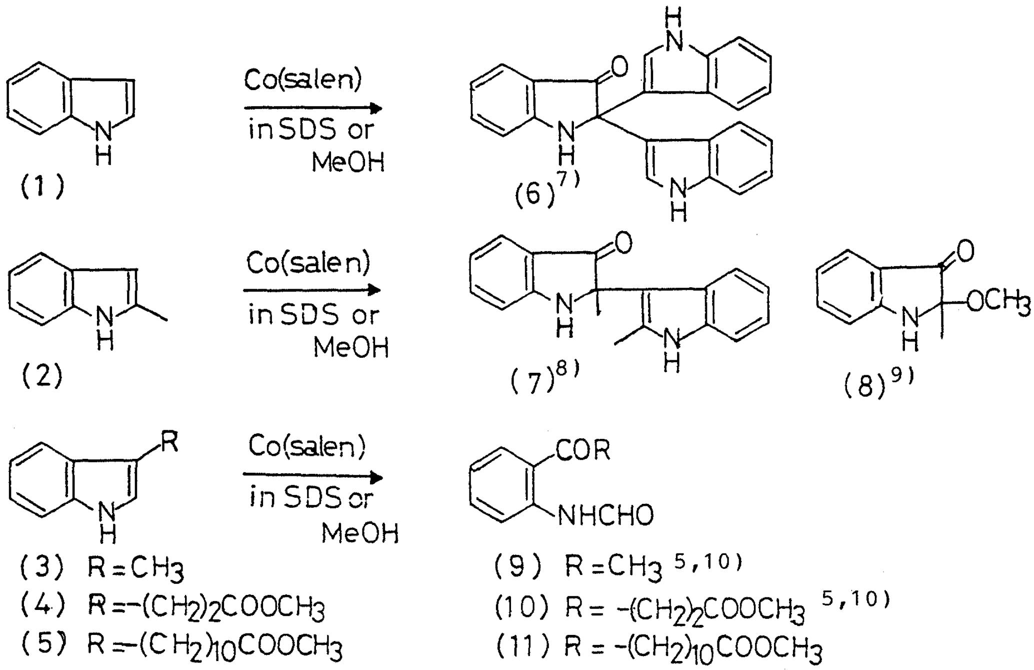

Fig. 1

Table. Co(salen)-Catalyzed Oxygenation of Indoles in SDS and Methanol[a)]

Exp.	Substrate	Concentration		Reaction media					
		Substrate	Co(salen)	MeOH			SDS		
				Conv.[b)]	Product	Yield[c)]	Conv.[b)]	Product	Yield[c)]
		(mM)	(mM)[d)]	(%)		(%)	(%)		(%)
1	**(1)**	10	1.1	15	**(6)**	5	50	**(6)**	44
2	**(2)**	10	1.1	11	**(7)**	3	80	**(7)**	70
					(8)	4		-----------	
3	**(3)**	10	1.1	14	**(9)**	10	67	**(9)**	49
4	**(4)**	10	1.1	10	**(10)**	5	6	**(10)**	3
5	**(4)**	1.25	1.1	23	**(10)**	10	19	**(10)**	9
6	**(5)**	1.25[e)]	1.1	23	**(11)**	10	57	**(11)**	26

a) The oxygenation was undertaken using 100 ml (Exp. 1 - 4) and 200 ml (Exp. 5, 6) reaction solutions in each medium as described in the text. The catalytic activity of Co(salen) was checked each time before use by the following method reported in the literature.[5)] To a 20 ml methanolic solution of **(3)** (50 mM) was added Co(salen)(12.5 mM) and the suspension was bubbled with O_2 at room temperature for 5 h. Samples of Co(salen) showing more than 85% conversion of **(3)** in the reactions, were used throughout the experiments.

b) Conversion is expressed in terms of the percentage of the treated substrate.

c) Expressed as the absolute yield calculated on the basis of the amount of initial substrate.

d) The maximum concentration of Co(salen) in 3% aq. SDS.

e) The maximum concentration of **(5)** in 3% aq. SDS.

the substrate between aqueous bulk phases and micellar phases, and by the contribution of an orientation effect of the micelles (see Fig. 2). Judging from the fact that the oxygenation of the more hydrophilic substrate (**4**) in SDS is decelerated (Exp. 4 and 5), it may be that Co(salen) is solubilized in the central aggregation part of the micelle (see Fig. 2).

The experiments results obtained by using a micellar system demonstrate that i) a hydrophobic metal complex, such as Co(salen), can be used in aqueous media, ii) the reaction rate can be increased due to the condensation effect of micelles, iii) substrate-dependent selective oxygenation is made possible by using different distributions of substrates into micelles and/or by the alignment effect of micelles (micelle-controlled reaction).

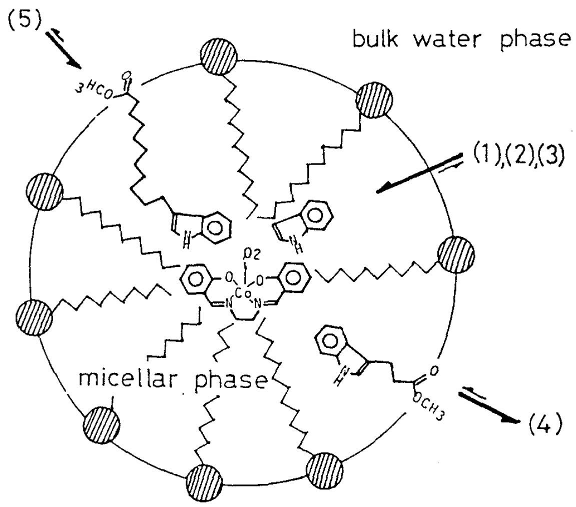

Fig. 2. Distribution of Indoles and Co(salen) in a Micelle

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