Asian Journal of Chemistry; Vol. 28, No. 1 (2016), 27-29

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19157

Oxidation Reaction of 4-Carboxaldehyde-5-amino Pyrazole in Olive Reversed Microemulsions Catalyzed by Phase Transfer Catalyst

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Received: 7 March 2015; *Accepted*: 16 August 2015; *Published online*: 5 October 2015; AJC-17540

Synthesis of 4-carboxyl, 5-amino pyrazole was performed in both W/O microemulsions and two-phase system in presence of a phase transfer agent. The micro-structure of used microemulsions was determined by self-diffusion NMR. The reaction was fast in surfactantless microemulsion, slower in microemulsion with an anionic surfactant and sluggish in two phase system.

Keywords: Microemulsion, Olive oil, Phase transfer agent, 4-Carboxyl, 5-Amino pyrazole, Oxidation reaction.

INTRODUCTION

Incompatibility between hydrophobic organic molecules and inorganic salts is a commonly faced challenge in organic synthesis. The undesirable side reactions and low reaction rates may be resulted from incomplete phase contact of the reagents. The reaction of alkyl chloride with sodium sulfite to form alkyl sulfonates, hydrolysis of esters with sodium hydroxide and oxidative cleavage of olefins with permanganate are examples for incompatibility between reactants [1]. Such reactions may be performed in toxic aprotic polar solvents like dimethyl formamide, dimethyl sulfoxide or in a two phase system in the presence of a phase transfer agent such as a quaternary ammonium salt or a crown ether. The role of the phase transfer agent is to transfer the nucleophilic anion from the aqueous to the organic phase. However, water-in-oil (W/O) microemulsions or reverse micelles technique is one of the most recognized methods to overcome reactant solubility problems because of its ability to solubilize both oil and water. Use of a microemulsion as a reaction medium constitutes an alternative to phase transfer catalysis [2,3]. The interest in microemulsions as reaction media for organic synthesis is derived from their ability to dissolve, in a one-phase system, both lipophilic organic molecules and inorganic species and because of their large internal interfacial area. The lipophilic molecules go into the oil domains and the water-soluble species go into the aqueous domains. Since the interface between the two compartments is so large and since the system is a highly dynamic one with interfaces disintegrating and reforming at the timescale of milliseconds, there are ample opportunities for the two otherwise incompatible reagents to meet and react at the interface.

In this work, we have developed a method to produce 4-carboxyl, 5-amino pyrazole from 5-amino pyrazole 4-carboxaldehyde and potassium permanganate using new microemulsion systems with or without surfactant. These mixtures consisting of an inexpensive non-toxic oil (olive oil), a short chain-alcohol (1-butanol) and water represent thermodynamically stable dispersion of nanometer-sized water drops in a continuous oil medium. Reaction profiles are determined and compared with those obtained in two-phase system with benzyl triethylammonium chloride.

EXPERIMENTAL

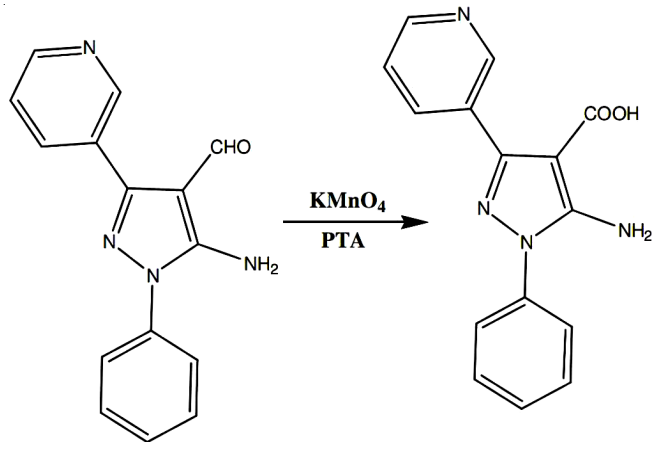
1-Phenyl, 3-pyridyl, 5-amino pyrazole 4-carboxaldehyde was prepared from the appropriated phenyl hydrazones *via* the Vilsmeier-Haack reaction [4]. Virgin olive oil was obtained from the local market. Sodium dodecyl sulfate (SDS) and 1-buanol (99 % pure) was purchased from Sigma. Benzyl triethylammonium chloride was supplied by Aldrich.

These reagents were used as received. Deionized Millipore Milli-Q water was used in all the experiments.

Methods: Phase diagrams were constructed as described in a previous work [5,6]. Self-diffusion coefficients of individual components of microemulsions were measured by the pulsed field gradient spin-echo method [7] on a Bruker FX-600 apparatus operating at ν_o = 600 MHz for protons. The time

separation of the gradient pulse was 140 ms and the length of the gradient pulse was 1-18 ms.

Reaction in two phases in presence of phase transfer agent was performed as follows: Benzyl triethylammonium chloride (0.33 mmol) was added to a solution of pyrazole, 4-carboxaldehyde in dichloromethane (0.74 mmol in 15 mL) placed in 50 mL round-bottom flask. The flask was immersed in water bath preheated to 60 °C, then (15 mL) an aqueous solution of potassium permanganate (1 mmol) was added dropwise under stirring. Four samples were run at the same time and at the same rpm. Stirring was discontinued after 30, 60, 90, 120 min, respectively. Dichloromethane was replaced by a mixture of olive oil/SDS/1-butanol or olive oil/1-butanol when the reactions were carried out in microemulsions (**Scheme-I**). The reaction was monitored by TLC (7:2 CH_2Cl_2:CH_3OH) and consumption of the aldehyde was quantified by ^1H NMR, using a 600 MHz BRUKER FX-600 apparatus and GC-mass (BRUKER Scion 456 GC-MS).



Scheme-I

RESULTS AND DISCUSSION

The phase diagram of the system SDS/1-butanol/olive oil/water solution is constructed in Fig. la. Fig. lb exhibits a phase diagram of the identical system without addition of a surfactant (SDS). From single phase region of both phase diagrams, two compositions A of Fig. la and B of Fig. lb have been selected to investigate their potential uses as media for oxidation reaction. Self-diffusion NMR is used to examine the micro-structure at compositions A and B. The values of the self-diffusion coefficients (D), for the main components at these compositions are shown in Table-1. The D/D° values at compositions A and B are indicative of W/O microemulsions. The D/D° values show that the water diffusion is more restricted than that of olive, indicating an interfacial curvature towards water, *i.e.* a water-in-oil (WO) structure. As is seen from the table, the self-diffusion coefficient (D) value of water in microemulsion A is higher than that of B. This is probably due to the absence of surfactant at composition A [7].

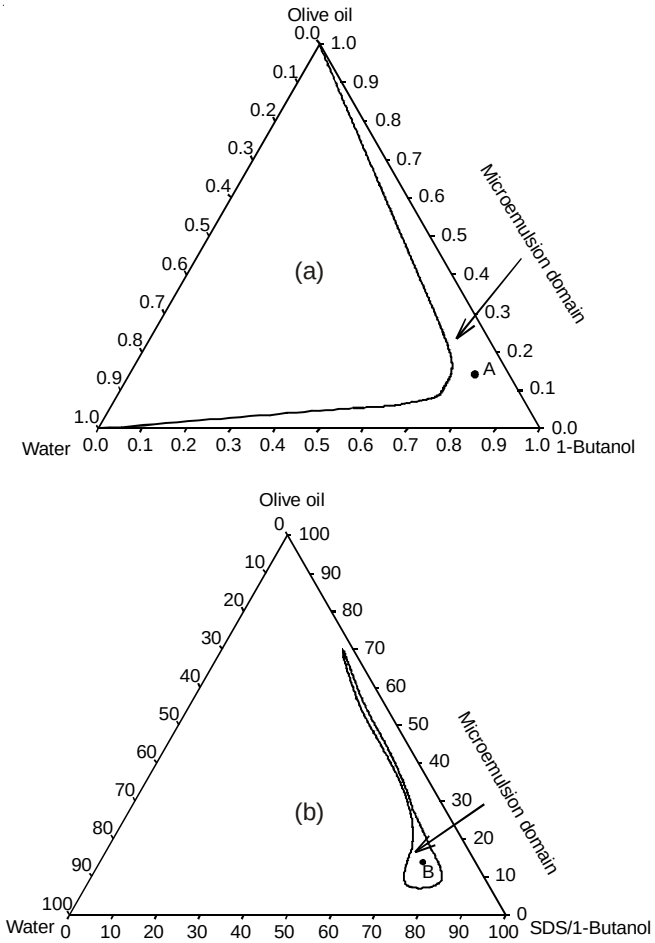


Fig. 1. Phase diagrams for the system 1-butanol/oil/$KMnO_4$ solution (a) and for the same with addition of SDS (b) both at 25 °C

In a microemulsion system, the rate reaction depends on the transfer of reactants across the interface. A kinetic model has been worked out in which the three pseudophases; oil, water and interface, are taken into account [8].

The reactions were carried out at compositions B and A of Fig. l, representing a W/O microemulsion with or without surfactant respectively in presence of phase transfer agent. Reactions were also conducted in two-phase system with added phase transfer agent kept under stirring. The reaction profiles obtained are represented in Fig. 2. As can be seen, the reaction is relatively fast in the microemulsion A, slower in microemulsion B and extremely sluggish in two-phase systems. The same general trend of higher reactivity in the microemulsions than in the two-phases system was obtained at all ratios. This

TABLE-1
SELF-DIFFUSION COEFFICIENTS (D) ($m^2 s^{-1}$) FOR THE MAIN COMPONENTS OF MICROEMULSION A (Fig. 1a) AND MICROEMULSION B (Fig. 1b) AT 25 °C.
SELF DIFFUSION OF PURE WATER (D°) (HDO) = 2.3×10^{-9} $m^2 s^{-1}$ AND PURE OLIVE OIL (D°) (OLIVE) = 1.48×10^{-9} $m^2 s^{-1}$

	Microemulsion A			Microemulsion B		
	HDO	1-Butanol	Olive	HDO	1-Butanol	Olive
$D \times 10^9$	0.366	0.586	0.750	0.110	0.457	0.435
D/D°	0.159	–	0.506	0.048	–	0.294

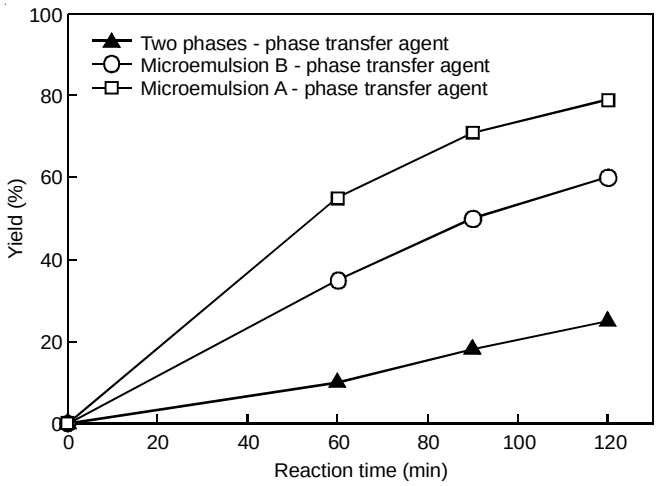


Fig. 2. Effect of type of system on reaction profile

observation agrees with that of Holmberg *et al*. [9]. The lower reaction rate in two-phases system is probably related to the high rigidity of this structure as compared with microemulsions. Diffusion of reactants across the interface of microemulsion is likely to be favoured by highly dynamic and flexible microstructures.

Reaction was performed in presence of anionic surfactant (SDS), which produces negative charge at the oil water interface causes a decrease in the reaction rate [9]. This is the expected result since electrostatic double-layer forces will render approach of the sulfite ion into the interfacial region more difficult.

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