ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 7, pp. 1288–1290. © Pleiades Publishing, Ltd., 2010.
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Synthesis 2-Ferrocenylpropan-2-ol under Conditions of Phase-Transfer Catalysis and Kinetic Relations Holding in This Reaction

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Received March 26, 2009

Abstract—2-Ferrocenylpropan-2-ol was synthesized by addition of ferrocene to acetone in the two-phase system petroleum ether–water using H_2SO_4–DEANaph as catalyst. Study on the kinetic parameters of the process showed that during the first two hours (conversion 87%) the reaction is of first order in ferrocene. The energy of activation of the addition of ferrocene to acetone under conditions of phase-transfer catalysis was estimated at 21 kcal mol^{-1}.

DOI: 10.1134/S1070363210070121

Aprotic catalysts are generally used in most laboratory and large-scale ferrocene alkylation processes. Hydroxy and hydroxyalkyl ferrocene derivatives are usually subjected to alkylation in the presence of protic catalysts [1, 2]. Interest in compounds belonging to the above series continuously increases for several reasons. First, these compounds are initial materials for the synthesis of antimicrobial agents and other medicines. Second, they are the base components for the preparation of composite antiknock additives to engine fuels [3], so that their synthesis is an important problem.

New catalytic systems for the synthesis of various hydroxyalkyl (carbinol) derivatives of ferrocene were proposed. These systems ensured facile addition of both symmetric and unsymmetric ketones to ferrocene under conditions of phase-transfer catalysis. Ferrocenyldimethylcarbinol $C_5H_4FeC_5H_4C(CH_3)_2OH$ (2-ferrocenylpropan-2-ol) was previously synthesized by reaction of ferrocene with acetone in the presence of sulfuric acid as catalyst [4, 5]. Factors affecting the hydroxyalkylation process were also studied. As noted in [4, 5], the reaction is accompanied by redox transformations of ferrocenylcarbocation Fc–C^+ generated during the process, which lead to various decomposition products; as a result, the yield of the target product strongly decreases.

With a view to minimize the contribution of side processes and raise the yield of the target product, 2-ferrocenylpropan-2-ol, kinetic parameters of the addition of acetone to ferrocene under conditions of phase-transfer catalysis were examined. The reaction was carried out in a two-phase system consisting of light petroleum ether (bp 40–70°C) and water. The substrate (ferrocene Fc) and alkylating agent (acetone) were placed into the organic phase, while the catalyst (sulfuric acid) resided in the aqueous phase. In addition, naphthenic acid diethylammonium salt (DEANaph), prepared by reaction of diethylamine with naphthenic acid, was used as phase-transfer agent which ensured transport of sulfuric acid to the organic phase.

The reaction of formylferrocene (cymantrene) with chloroform under conditions of phase-transfer catalysis was studied previously; it resulted in the formation of α-metallocenylglycolic acids LMC_5H_4–CH(OH)–COOH; benzyltriethylammonium chloride $Et_2PhCH_2N^+Cl^-$ was used as phase-transfer catalyst [6].

The addition of ferrocene to acetone was performed on a laboratory setup equipped with a reflux condenser. The optimal conditions included: ratio of the organic to inorganic phase 10 : 1, equimolar amounts of ferrocene and ketone 1 : 1, and 2 equiv of H_2SO_4 with respect to DEANaph. The corresponding reactants were introduced into the organic and aqueous phases, and phase-transfer catalyst (DEANaph) was then added. To accelerate the process, the inorganic phase

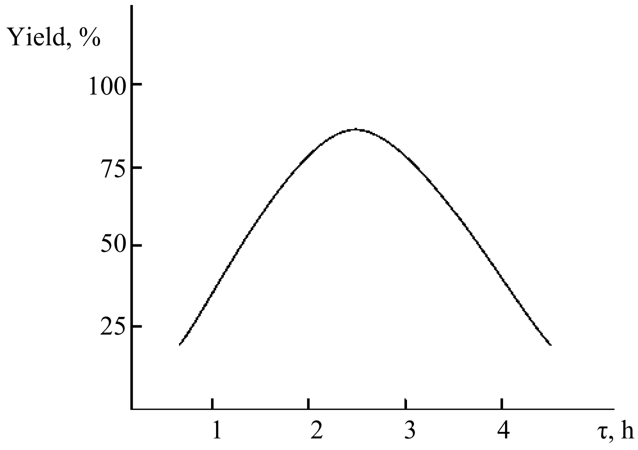

Fig. 1. Kinetics of the addition of ferrocene to acetone under conditions of phase-transfer catalysis.

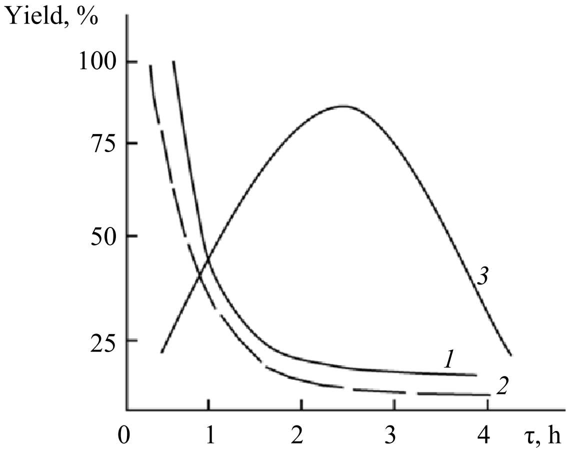

Fig. 2. Kinetics of consumption of (*1*) ferrocene and (*2*) acetone and (*3*) accumulation of the addition product.

was maintained as 20–60°C. The progress of the reaction was monitored as follows. A sample of the reaction mixture was withdrawn every 10 min, and carbonyl and hydroxyl numbers were determined according to standard procedures. In addition, the concentration of carbonyl compounds in the reaction solution was estimated by IR spectroscopy from the intensity of the carbonyl absorption bands.

Figure 1 shows how the yield of the ferrocene–acetone addition product changes with time. It is seen that in the presence of H_2SO_4–DEANaph (2:1) as catalytic system the yield of 2-ferrocenylpropan-2-ol increases during the first two hours, attaining a maximum value, and then slowly decreases (in 2–2.5 h). Figure 2 illustrates variations of the yield of the addition product and concentrations of the initial reactants (acetone and ferrocene) with time. It is seen that the conversion of ferrocene reaches 87% in 2–2.5 h. As the addition product accumulates in the reaction zone, the amount of reacting ferrocene sharply decreases. The addition of ferrocene to acetone is complete in 3 h. During that time, up to 87% of the initial amount of ferrocene is converted, while the remaining part of ferrocene undergoes oxidative decomposition. The contribution of the latter process depends on the order of addition of components to the catalytic system. To minimize this side process, sulfuric acid was initially added to the aqueous phase to a concentration of 88–94%. Ferrocene and acetone were then added to the organic phase, the organic phase was slowly added to the aqueous phase, quaternary ammonium salt DEANaph was added, and the mixture was heated to 60°C. The ratio H_2SO_4–DEANaph (2:1) is very important.

At initial ferrocene, H_2SO_4, and acetone concentrations of 1.86×10^{-3}, 9×10^{-7}, and 3.2×10^{-3} M, respectively, the product concentration attains 1.28×10^{-3} M in 2.5 h. The yield of the product reaches 87% in 2 h. These findings correspond to first-order kinetics:

$$\ln c = kt + \ln c_0.$$

When the conversion of the initial reactants attains 87%, the rate of addition appreciably decreases, and the reaction deviates from first-order kinetics. The energy of activation of the addition of ferrocene to acetone under conditions of phase-transfer catalysis was determined from the consumption of ferrocene at 40, 45, and 50°C; the rate constants k were 0.0013, 0.021, and 0.0015, respectively. From the dependence of log k versus $1/T$ we estimated the energy of activation at 21 kcal mol^{-1}.

The above data suggest the following mechanism of addition of ferrocene to acetone in a two-phase system in the presence of phase-transfer catalyst. The carrier DEANaph with H_2SO_4 (catalyst) forms intermediate complex [DEANaph]·H_2SO_4 at the phase boundary. The complex is transferred into the organic phase where it catalyzes the addition of ferrocene to acetone with formation of carbinol adduct.

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