



The concentration effects of reactants and components in the Pd(OAc)₂/p-toluenesulphonic acid/trans-2,3-bis(diphenylphosphinomethyl)-norbornane catalytic system on the rate of cyclohexene hydrocarbomethoxylation

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ABSTRACT

The reactants and components of a catalytic system were studied for their effects on the rate of Pd-catalysed cyclohexene hydrocarbomethoxylation. First-order reaction rate dependences were established for cyclohexene and Pd(OAc)₂, while non-monotonic rate dependences were determined for the diphosphine and p-toluenesulphonic acid concentrations and the CO pressure. The reaction was shown to follow first-order kinetics when the methanol concentration was below 0.4 mol/L; however, the reaction rate slowed upon a further increase in the methanol concentration. The obtained results were interpreted by considering a hydride mechanism supplemented with ligand exchange reactions, which decreased the activity of the catalyst, and with hydride complex annihilations by p-toluenesulphonic acid, resulting in complete loss of catalytic activity. Treatment of the proposed mechanism using the quasi-equilibrium concentration method gave a kinetic equation for the reaction that was consistent with the experimental data.

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1. Introduction

Olefin carbonylation catalysed by a transition metal complex is a promising process for the production of various organic compounds, particularly pharmacological and agrochemical agents [1]. An important carbonylation process is the palladium-catalysed hydrocarbomethoxylation of alkenes, which is suitable for the one-step conversion of widely available alkenes to various esters [2,3] (Scheme 1).

This process has already found use in industry. For example, in 2008, Lucite commercialised the ethylene hydrocarbomethoxylation process [4]. However, the hydrocarbomethoxylation of cyclohexene to produce cyclohexylcarboxylates is also of interest for commercialisation, as various cyclohexylcarboxylates are used as plasticisers [5], intermediates in the synthesis of pharmacological agents [6], liquid crystals [7], and in cosmetics [8]. The particular synthetic value of cyclohexene hydrocarbomethoxylation comes from the fact that this process is not complicated by the formation of a

pair of products with linear and branched structures and is almost free from cyclohexene and CO copolymerisation.

Among the catalytic systems used in alkene hydrocarbomethoxylation, palladium derivatives promoted by strong protic acids and free phosphines are of particular interest [3,9–13]. In the series of phosphines, diphosphines are used increasingly frequently. Diphosphines are able to form chelates with the palladium centre of the catalyst, which are more stable than standard monophosphine derivatives and allow for more pronounced effects on the kinetics and regioselectivities of the alkene hydroalkoxycarbonylation reactions [4,14–16].

Previously, we undertook a special study to determine how the structures of various diphosphines affect the rate of cyclohexene hydrocarbomethoxylation [17]. That study revealed the highest promoting activities known for trans-diphosphines with four-membered carbon bridges; specifically, trans-2,3-bis(diphenylphosphinomethyl)norbornane (TBDPN, Scheme 2) was the most effective diphosphine studied for the promotion of this process [17].

Based on the investigation on the effects of the Pd-catalysed carbonylation components on the reaction route and the remarkable catalytic performance of trans-2,3-bis-

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