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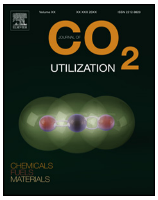

Effect of the CO_2-pressure on the hydrosilylation of CO_2 catalyzed by [Ir(NSiN)] species

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ABSTRACT

The iridium(III) complex $[Ir(H)(CF_3SO_3)(NSiN)(coe)]$ (NSiN = bis(pyridine-2-yloxy)methylsilyl, coe = cyclooctene) has demonstrated to be an active catalyst for the solvent-free and selective hydrosilylation of CO_2 with $HSiMe(OSiMe_3)_2$ to afford the corresponding silyl formate, namely $HC(O)OSiMe(OSiMe_3)_2$. The activity of this catalytic system depends on both parameters the reaction temperature and the CO_2-pressure. This work includes a kinetic study at variable temperature (from 25 °C to 75 °C) and pressure (from 1 bar to 8 bar) together with a kinetic modeling of this catalytic reaction. The best catalytic performances have been achieved at 75 °C and 8 bar of CO_2.

1. Introduction

The design of new catalytic processes that enable large-scale use of CO_2 as a chemical feedstock could be considered as one of the goals of catalysis in our times [1,2]. In particular, the catalytic CO_2 hydrosilylation represents a thermodynamically favorable process for the transformation of CO_2 into value added chemicals such as silyl formates (SFs) [3], which also presents the advantages that some hydrosilanes are easy-to-handle, readily available and environmentally harmless [4]. SFs, in situ prepared by catalytic hydrosilylation of CO_2, have been successfully used as C1 building blocks in the synthesis of formamides and amines [5]. However, the catalytic hydrosilylation of CO_2 faces two main challenges: (i) the lack of selectivity, which could afford not only SFs but mixtures of the corresponding SF together with variable amounts of the corresponding bis-silylacetal, methoxysilane, siloxane and methane [3,6], and (ii) the highly reactivity of SFs towards moisture to afford formic acid and silanols, making it difficult to handle and to store [7]. In this context, it is noteworthy that some examples of catalytic systems which are capable to promote the selective hydrosilylation of CO_2 to the corresponding SF have been reported. Among them, there are some homogeneous catalytic systems based on iron [8], ruthenium [9], rhodium [10], cobalt [11], zinc [4c,12][12] or copper [13] complexes and some examples of organocatalysts [14–17].

In this regard, it should be mentioned that we have reported that the iridium complex $[Ir(H)(CF_3SO_3)(NSiN)(coe)]$ (**1**) (NSiN = bis(pyridine-2-yloxy)methylsilyl, coe = cyclooctene) catalyzes the selective formation of the corresponding silyl formate (SF), namely $HC(O)OSiMe(OSiMe_3)_2$, by solvent-free catalytic hydrosilylation of CO_2 with $HSiMe(OSiMe_3)_2$ under mild reaction conditions (3 bar and temperatures below 75 °C) [18]. Theoretical studies at the DFT level showed that in this catalytic reaction the Si—H bond activation is a triflate ligand assisted process. The higher energy barrier of the catalytic process (calculated via DFT methods, $94.6\ kJ\ mol^{-1}$ [18a]; found experimentally, $73.8\ kJ\ mol^{-1}$ [18b]) corresponds to the activation of the CO_2 molecule, which proceeds via an outer-sphere mechanism through the transition state **TS1** showed in Fig. 1. The results from these preliminary studies suggest that an enhancement of the CO_2 pressure could have a positive effect on the activity of the catalytic system formed by complex **1**, CO_2 and $HSiMe(OSiMe_3)_2$.

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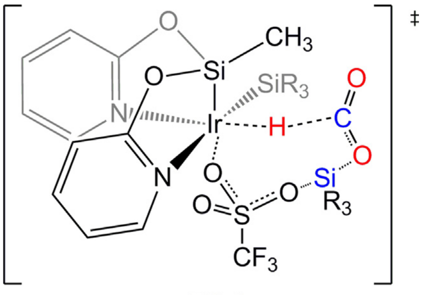


TS-1

Fig. 1. Transition state, **TS-1**, responsible for the rate-limiting step in the catalytic CO_2 hydrosilylation using complex **1** as catalyst precursor.

Herein, we report a kinetic study at variable temperature and pressure together with a kinetic modeling of the catalytic hydrosilylation of CO_2 with $HSiMe(OSiMe_3)_2$ in presence of catalytic amounts of compound **1**.

2. Experimental

2.1. General information

All manipulations were performed with rigorous exclusion of air at an argon/vacuum manifold using standard Schlenk-tube techniques or in a dry-box (MB-UNILAB). The catalytic experiments were carried out using a 25 mL batch reactor with Teflon lining inside. Gas chromatography–mass spectrometry (GC–MS) analyses were performed using Agilent 7890A GC system and Agilent 5975C inert MSD with Triple-Axis Detector MS system with DB1 capillary column (30 m × 320 μm, film thickness 1 μm). Oven parameters: initial temperature, 80 °C hold for 3.0 min, then increase the temperature up to 160 °C by heating rate of 5.0 °C min^{-1} hold for 1.0 min. Again heated up to 250 °C by rate of 5.0 °C min^{-1}. Carrier gas flow was 1.8 mL min^{-1} and injection volume was 0.1 μL. Inlet temperature was 250 °C and split ratio is 100:1. The iridium(III) complex **1** was prepared according to method reported in the literature [18a]. $HSiMe(OSiMe_3)_2$ and carbon dioxide (99.99% purity) were purchased from commercial sources. $HSiMe(OSiMe_3)_2$ was dried over 4A molecular sieves previously to use.

2.2. Catalytic reactions at variable temperature and pressure

A 25 mL batch reactor with Teflon lining inside was charged with dry $HSiMe(OSiMe_3)_2$ (3 mL, 11.04 mmol). Then the reactor was closed, purged with CO_2 gas few times and heated to the corresponding temperature. After stabilization to the corresponding temperature and CO_2 pressure, the reactor was opened under argon atmosphere and the iridium catalyst **1** (75 mg, 0.11 mmol), which was weighed in a glove box, was added. After closing the reactor, the system was purged few times using vacuum and CO_2 gas. Then the pressure of CO_2 gas was adjusted to the corresponding value. The reaction mixture was stirred with mechanical stirrer. The liquid samples were taken periodically after releasing the CO_2 pressure, without opening the reactor, using a long needle through sample withdrawal valve. The reactor was purged with vacuum and CO_2 several times after each sample withdrawal and the pressure was returned back to the desired value bar using CO_2.

2.3. GC–MS samples preparation

The collected samples were diluted in dry tetrahydrofuran (1.0 mL) and analyzed by quantifiable GC–MS. The product yield was obtained by comparison of the area corresponding to the peaks assigned to the reaction products with the area of the peak corresponding to $HSiMe(OSiMe_3)_2$.

2.4. Kinetic modeling of the catalytic hydrosilylation of CO_2 with $HSiMe(OSiMe_3)_2$

It was assumed that the volume of the reaction mixture remains constant during the catalytic process, which is reasonable since the density does not change appreciably. A power law model was proposed for the homogeneous reaction [19]. In addition, we have considered a first-order reaction with respect to $HSiMe(OSiMe_3)_2$. So, the rate of disappearance of $HSiMe(OSiMe_3)_2$ (Eq. (1)) can be written as:

$$-V\frac{dC_{sx}}{dt} = V\frac{dC_f}{dt} = k_i C_{sx} W_c \qquad (1)$$

where, C_{sx} and C_f are the molar concentrations of $HSiMe(OSiMe_3)_2$ and SF in the reaction mixture, respectively, V is the initial volume of $HSiMe(OSiMe_3)_2$,W_c is the weight of the catalyst, t is the time in hours and k_i is the rate constant.

MATLAB ODE45 subroutine, which utilizes the 4th order Runge–Kutta method, was used to solve the resulting equations and the parameters were estimated with the described non-linear regression. The values of k_0 and E were estimated using a non-linear regression. Only positive parameter values were determined. The sum of square error was minimal and a tight confidence interval for each parameter was ensured. Minimal correlations (γ) and the coefficient of determination (R^2) was almost unity. See supporting information for more details.

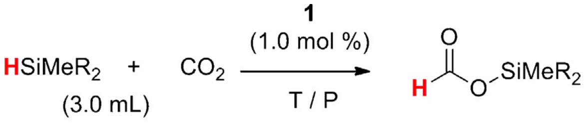
3. Results and discussion

3.1. Kinetic study of the catalytic hydrosilylation of CO_2 with $HSiMe(OSiMe_3)_2$

We have recently reported kinetic studies on the reaction of CO_2 with $HSiMe(OSiMe_3)_2$ in presence of a catalytic amount of complex **1** (1.0 mol%) at variable temperature and constant pressure (3 bar). These studies evidenced a clear positive effect of the temperature on the reaction performance [18b]. In this work we expand the scope of our kinetic studies to variable CO_2-pressures from 1 to 8 bar (Scheme 1).

The studies of this reaction at different CO_2-pressures and temperatures revealed that, as it was expected, the CO_2-pressure also exerts an effect on the activity of the catalytic system (Table 1). Indeed, an adjustment of the reaction temperature and the CO_2-pressure at 75 °C and 8 bar leads to reach a turnover frequency ($TOF_{1/2}$) value of 138 h^{-1} (Table 1, entry 12).

These results evidenced that at 25 °C the CO_2-pressure seems to have limited influence on the catalytic activity (Table 1, entries 1, 4, 7 and 10). At 55 °C, an enhancement of the CO_2-pressure from 1 to 3 bar slightly influences the activity of the catalytic system (Table 1, entries 2 and 5). In fact, at that temperature it was necessary to



T = 25ºC, 55ºC and 75ºC
P = CO_2-pressure of 1 bar, 3 bar, 6 bar and 8 bar
R = $OSiMe_3$

Scheme 1. Solvent-free catalytic CO_2 hydrosilylation with HMTS using **1** (1.0 mol%) as catalyst precursor.