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ARTICLE TYPE

Solvent-Free Iridium-Catalyzed CO₂ Hydrosilylation: Experiments and Kinetic Modeling

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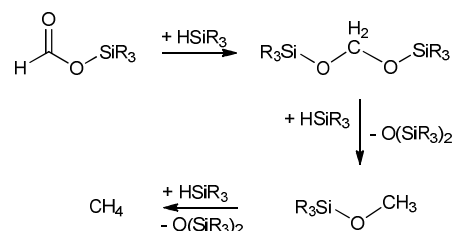
The iridium(III) complex [Ir(H)(CF₃SO₃)(NSiN)(coe)] (NSiN = bis(pyridine-2-yloxy)methylsilyl, coe = cyclooctene) has demonstrated to be an active catalyst for the solvent-free hydrosilylation of CO₂ with 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) under mild reaction conditions (3 bar). The activity of this catalytic system depends on the reaction temperature. The best catalytic performance has been achieved at 75 °C. A kinetic study at variable temperature (from 25°C to 75°C) and constant pressure (3 bar) together with a kinetic modeling has been carried out. The results from such study show a value of 73.8 kJ mol⁻¹ for the activation energy of the process.

1. Introduction

The development of sustainable processes for carbon dioxide (CO₂) reduction is a topic of general interest for the scientific community.¹ In particular, catalytic CO₂ hydrosilylation represents a thermodynamically favorable process for the transformation of CO₂ into value added chemicals,² which also presents the advantages that some hydrosilanes are easy-to-handle, readily available and environmentally harmless.³ This CO₂ fixation methodology allows formation of silylformates which have been successfully used as C1 building blocks in the synthesis of formic acid,⁴ formamides,⁵ amines,⁶ and methane.⁷ Selectivity is a relevant parameter to take into account when new catalysts for CO₂ hydrosilylation to silylformates have to be designed. This is due to the reactivity of silylformates, which under the reaction conditions could be hydrosilylated to afford the corresponding bis(silyl)acetal, which could react further with the excess of hydrosilane present in the reaction mixture to give methoxysilane and (R₃Si)₂O (Scheme 1).⁸ Additionally, the reaction of the corresponding methoxysilane with one additional equivalent of hydrosilane could lead to the formation of methane and (R₃Si)₂O (Scheme 1).⁷ It is worth to mentioning that some examples of transition metal catalysts as well as organocatalysts which selectively catalyze the hydrosilylation of CO₂ to silylformates have been recently reported.^{4b,9-12} Among of them, the phosphane-copper catalysts, using 1,4-dioxane as solvent, reported by Baba and co-workers are the most active known so far.⁴

On the other hand, the large-scale use of volatile organic solvents in industrial processes contributes to the impact of human activity on the environment.^{13, 14} Therefore, the development of solvent-free synthetic and catalytic processes has become of wide interest for the chemists.¹⁵ To the best of our knowledge only two solvent-free catalytic system effective for the hydrosilylation of

CO₂ to silylformate have been reported.^{12,16}

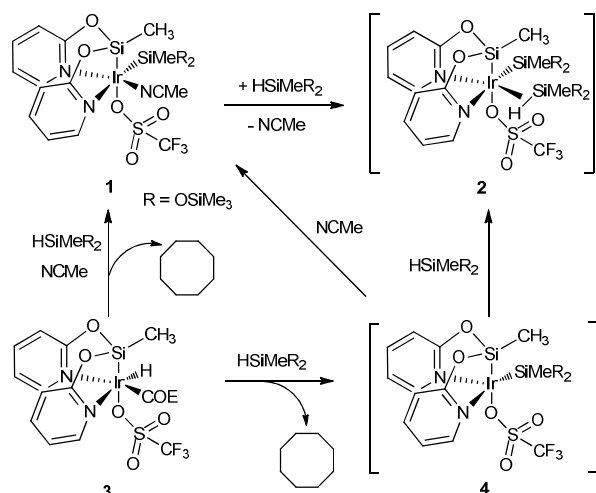


Scheme 1. Possible transformations of “*in situ*” generated silylformate during catalytic CO₂ hydrosilylation processes.

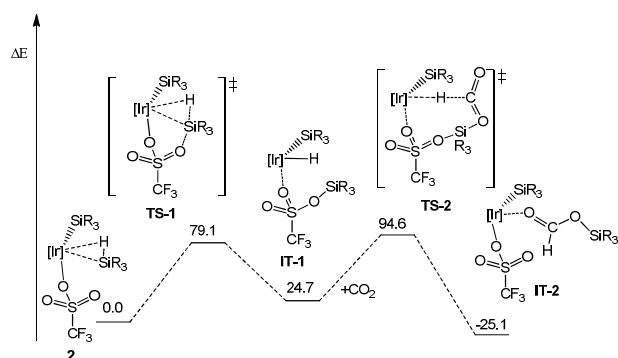
In this context, it has been previously communicated that complex [Ir{SiMe(OSiMe₃)₂}(CF₃SO₃)(NSiN)(NCMe)] (**1**) (NSiN = bis(pyridine-2-yloxy)methylsilyl, coe = cyclooctene) catalyzes the selective formation of silylformate by solvent-free hydrosilylation of CO₂ with 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) under mild reaction conditions (r.t. and 3 bar). Using complex **1** as catalyst precursor an activation step consisting in the replacement of the acetonitrile molecule by one molecule of HMTS to yield the corresponding active intermediate **2** containing a η²-(H-Si) coordinated HMTS molecule is required (Scheme 2).¹⁶ Theoretical studies at the DFT level showed that the Si-H bond activation is a triflate ligand assisted process via **TS1** and that the activation of the CO₂ molecule proceeds via an outer-sphere mechanism through the transition state **TS2** (Scheme 3).¹⁶

It is worth noting that the yield of the reaction of synthesis of **1** from **3** (Scheme 2) is relatively low due to purification difficulties. Subsequently, the use of an alternative catalyst precursor is of interest. In this regard, preliminary ¹H NMR

studies of the reaction of **3** with HMTS in CD_2Cl_2 , in the absence of acetonitrile, showed the formation of cyclooctane together with a mixture of not identified iridium-containing compounds. Interestingly, when the same reaction was carried out using a mixture of acetonitrile- d_3 and CD_2Cl_2 as solvents ^1H NMR studies evidenced the formation of cyclooctane and **1** (see supplementary information). These results are consistent with the formation of intermediate **4** which coordinates a molecule of acetonitrile to give **1** (Scheme 2). Therefore, it is reasonable to assume that working in solvent-free conditions complex **3** could afford directly the active species **2** via $\eta^2\text{-(H-Si)}$ coordination of a molecule of silane to **4**.



Scheme 2. Examples of the reactivity of complex **3**.



Scheme 3. Energetic profile for the outer-sphere mechanism of the hydrosilylation of CO_2 using complex **1** as catalyst precursor ($[\text{Ir}] = \text{Ir}(\text{NSi}n)$; $R = \text{Me}$; energy in kJ mol^{-1}).

Aforementioned background motivates us to explore the potential application of compound **3** as catalyst precursor in solvent-free CO_2 hydrosilylation processes. Herein, we report a detailed kinetic study at variable temperature together with a kinetic modeling of the catalytic hydrosilylation of CO_2 with 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) using complex **3** as catalyst precursor.

2. Experimental

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 HP5-MS capillary column (30 m \times 250 μm , film thickness 0.25 μm). Oven Parameters: Initial Temperature, 45 $^\circ\text{C}$ hold for 1.0 min, then increase the temperature up to 160 $^\circ\text{C}$ by heating rate of 8.0 $^\circ\text{C min}^{-1}$ hold for 1.0 min. Again heated up to 250 $^\circ\text{C}$ by rate of 8.0 $^\circ\text{C min}^{-1}$. Carrier gas flow was 1.2 mL min^{-1} and injection volume was 0.1 microliter. Inlet temperature was 250 $^\circ\text{C}$ and Split Ratio is 100:1. The iridium(III) complex **3** was prepared according to method reported in the literature.¹⁶ NMR spectra were recorded on a Bruker ARX 300 or a Bruker Avance 300 MHz. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H , $^{13}\text{C}\{^1\text{H}\}$). Coupling constants, J , are given in hertz. 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) and carbon dioxide (99.99 purity) were purchased from commercial sources. HMTS was dried over 4A molecular sieves.

Catalytic reactions at variable temperature and 3 bar. A 25 mL batch reactor with Teflon lining inside was charged with dry HMTS (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, the reactor was opened under argon atmosphere and the iridium catalyst **3** (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 3 bar. 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 pressure was returned back to 3 bar using CO_2 . **GC-MS samples preparation.** The collected samples were diluted in dry tetrahydrofuran (0.5 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 HMTS.

Kinetic modeling of the catalytic reaction. Power law model was proposed as descriptor of the kinetic of the first order reaction¹⁷ of CO_2 with HMTS. The rate of the disappearance of HMTS (Equation 1) and the rate of the formation of silylformate (Equation 2) can be written as:

$$-\frac{V}{W_c} \frac{dC_{SX}}{dt} = (k_f C_{SX}) \quad (1)$$

$$\frac{V}{W_c} \frac{dC_F}{dt} = (k_f C_{SX}) \quad (2)$$

where C_{SX} , C_F are the molar concentration of HMTS and silylformate in the system, V is the volume of the reactor, W_c is the weight of the catalyst, t is the time in hours and k_f is the rate

constant. The reaction rate constants are related to temperature through Arrhenius equation.¹⁸ A nonlinear regression algorithm (MATLAB; ODE 45-4th order Runge-Kutta method and LSQCURFIT) was used to evaluate the model equations and to obtain the kinetic parameters. The details of the regression analysis are similar to those previously described in Waziri et al.¹⁹

3. Results and Discussion

Reaction of CO₂ with HMTS at 298 K using catalytic amounts

of **3**. We have found that the catalytic solvent-free reaction of CO₂ (298 K, 3.0 bar) with HMTS to produce the corresponding silylformate was faster when complex **3** (1.0 mol %) was used, instead of **1**, as catalyst precursor. Indeed, using complex **3**, the total consumption of HMTS to give a yellow oil identified by ¹H, ²⁹Si{¹H} NMR spectroscopy and GC-MS as the silylformate, HCOOSiMe(OSiMe₃)₂, (in approximately 89 % yield) was observed after three and a half days of reaction, while six days were needed to achieve the full conversion of HMTS using complex **1** (1.0 mol %) as catalyst precursor under the same reaction conditions.

¹H NMR spectra of CD₂Cl₂ solutions of the reaction mixture confirm that at the end of the reaction HCOOSiMe(OSiMe₃)₂ is the major reaction product (see supplementary information). Interestingly, in these spectra we always observed the presence of a minor resonance at δ 1.54 ppm which shows a direct C-H bond correlation in the heteronuclear single quantum correlation (HSQC) with one signal that appears at δ 27.3 ppm in the ¹³C{¹H} NMR spectra of the reaction samples, and subsequently has been assigned to the CH₂ moieties of cyclooctane. The formation of cyclooctane supports that the “in situ” generation of the active species **2** by reaction of **3** with HMTS could be proposed as the activation step of the catalytic process (Scheme 2). Furthermore, ²⁹Si{¹H} NMR spectra of CD₂Cl₂ solutions of the reaction product also confirm the formation of HCOOSiMe(OSiMe₃)₂ as the major reaction product. These spectra show two single resonances at δ 11.0 ppm and at δ -58.4 ppm corresponding to the OSiMe₃ and HCOOSiMe silicon atoms, respectively.^{16,20} Additionally, traces of others no-identified silicon containing minor species were observed (see Figure 1 and Figure S8 in supplementary information).

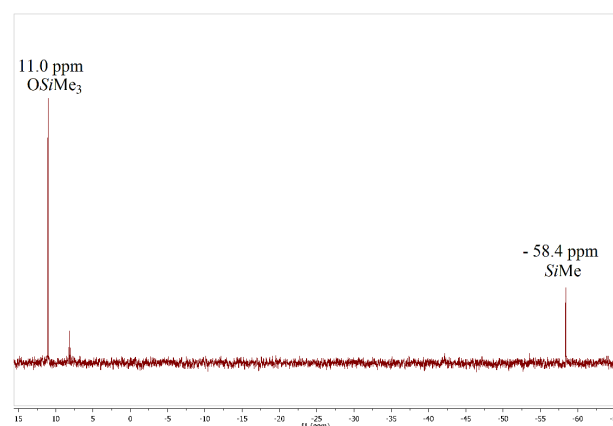


Figure 1. ²⁹Si{¹H} NMR (79.5 MHz, CD₂Cl₂) spectrum of the product of the reaction of CO₂ (3 bar) with HMTS after 3.5 days at 25 °C using **3** (1.0 mol %) as precatalyst.

GC-MS spectra of the reaction samples taken after 3.5 days of reaction at 25 °C evidenced the full consumption of the starting HMTS and the presence of a peak with a retention time of 7.74 min corresponding to a major reaction product (close to 89 % yield) (Figure 2 and Table 1). The mass pattern found for that peak agrees with that expected for HCOOSiMe(OSiMe₃)₂ (see supporting information). An additional peak due to {(Me₃SiO)₂MeSi}₂O appears at 14.02 min (9.4 %). The presence of {(Me₃SiO)₂MeSi}₂O could be attributable to further reactions of the silylformate, and its derivatives, with HMTS under the reaction conditions²¹ (Scheme 1) or to some iridium-catalyzed hydrolysis of the starting hydrosilane.²²

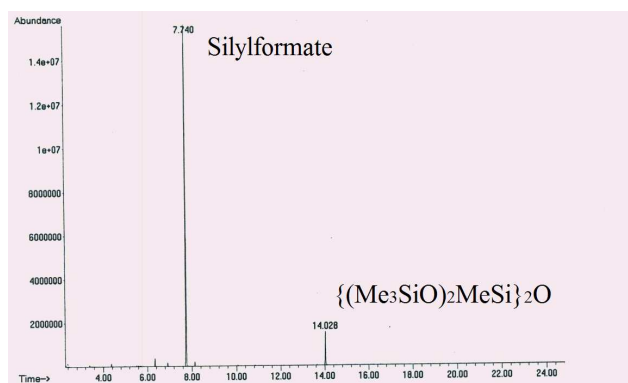


Figure 2. GC of the product of the reaction of CO₂ (3 bar) with HMTS after 3.5 days at 25 °C using **3** (1.0 mol %) as precatalyst.

These results compare well with the work reported by Mizuno and co-workers using the catalytic system [Rh₂(OAc)₄] (0.25 mol %) / K₂CO₃.¹⁰

Kinetic study of the catalytic hydrosilylation of CO₂ with

HMTS. Kinetic studies of the reaction of hydrosilylation of CO₂ with 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) in presence of a catalytic amount of **3** (1.0 mol %) show that the rate of this process is temperature dependent. The results from the kinetic studies of the reaction are depicted in Figure 3. The points in that Figure 3 represent the conversion of HMTS versus time. The

dotted lines in Figure 3 have no mathematic meaning and uniquely represent a continuous path between the experimental data points. These results evidenced that an increasing of the temperature of the reactor from 25 °C to 75 °C produces an enhancement of the catalytic activity.

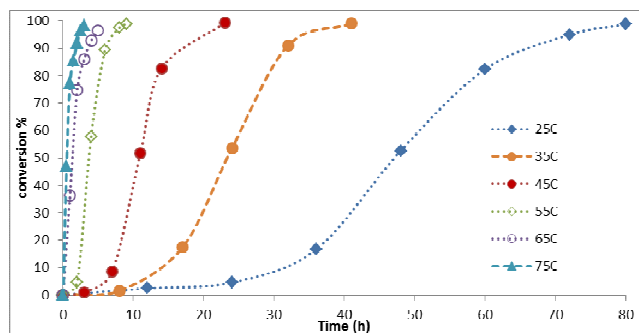


Figure 3. Representation of the experimental data obtained for HMTS conversion by GC-MS studies.

Table 1. Temperature dependence of the turnover frequency (TOF) value obtained for the catalytic hydrosilylation of CO₂ with HMTS using **3** (1.0 mol %) as precatalyst.

Temperature (°C)	Time (h)	Product (mmol) ^a	Yield (%) ^b	TOF (h ⁻¹)
25	80	9.8	88.8	1.1
35	41	10.0	90.6	2.2
45	23	10.0	90.6	3.9
55	9	9.6	87.0	9.7
65	5	9.5	86.1	17.3
75	3	9.6	87.0	29.1

(a) mmol of silylformate obtained by quantitative GC-MS analysis. (b) [(mmol of silylformate / initial mmol of HMTS) x 100].

The higher catalytic activity was found at 75 °C. GC-MS studies of the reaction evidenced that after 3 hours at that temperature most of the starting HMTS has been consumed and HCOOSiMe(OSiMe₃)₂ (87.0 %) is the major reaction product together with traces of {(Me₃SiO)₂MeSi}₂O (Figure 4 and Table 1).

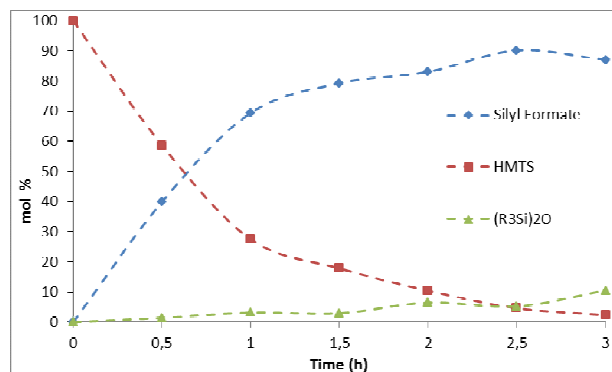
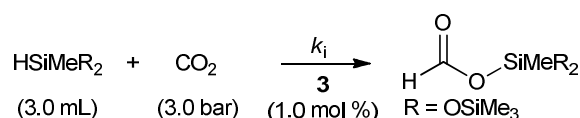


Figure 4. Time dependence of the composition of the reaction samples taken from the solvent-free hydrosilylation of CO₂ (3.0 bar) with HMTS using **3** (1.0 mol %) as catalyst precursor at 75 °C. Data obtained by quantitative GC-MS studies.

Table 1 shows that at temperatures higher than 45 °C there is a slightly falloff of the reaction yield. In addition, it has been observed that at these temperatures the silylformate is partially transformed into {(Me₃SiO)₂MeSi}₂O (see Figure 4 and Table S1 in supplementary information). This observation is compatible with the known reactivity of silylformates (see Scheme 1).²¹ The catalytic activity found for **3** in this work is higher than the previously reported for complex **1** and compares well with the catalytic activity of the zinc-based catalytic system reported by Sattler and Parkin for the solvent-free hydrosilylation of CO₂ with HSi(OEt)₃.¹² In addition, complex **3** shows better catalytic activity in the range of 55 °C and 75 °C (Table 1).

Kinetic modeling of the Ir-catalyzed CO₂ hydrosilylation.

Kinetic modeling of the iridium-catalyzed hydrosilylation of CO₂ with HMTS has been developed based on the equation represented in Scheme 4 and on the approximation of that the rate of disappearance of HMTS (Equation 1) is equal in absolute terms but opposite in sign to the rate of formation of HCOOSiMe(OSiMe₃)₂ (Equation 2).



Scheme 4. Solvent-free catalytic CO₂ hydrosilylation with HMTS using **3** (1.0 mol %) as catalyst precursor.

Power law model¹⁷ was proposed as descriptor of the kinetic of the first order reaction shown in Scheme 4. The reaction rate constants are supposed to be related to temperature through the Arrhenius equation.¹⁸ The mole balance equations (Equations 1 - 2) incorporating with the Arrhenius relation between k_i and E_a (see supplementary information) were evaluated by a least square fitting of the kinetic parameters using the experimental data obtained from the GC-MS studies of the reaction of hydrosilylation of CO₂ with HMTS using **3** (1.0 mol %) as precatalyst at different temperatures (see supplementary information). Experimental data were used to optimize the model parameters. In order to select the acceptable model the following criteria were considered: (i) all the kinetics parameters (specific reaction rates and activation energies) should be consistent with

physical principles, (ii) coefficient of determination (R^2), (iii) lower SSR (sum of the squares of the residuals), (iv) lower cross-correlation coefficient (γ), and (v) smaller individual confidence intervals for the model parameters.

As a result of this kinetic study values of $73.8 (\pm 2.9) \text{ kJ mol}^{-1}$ and of $3.1 \cdot 10^{-2} (\pm 0.03) \text{ s}^{-1}$ have been found for the activation energy of the process (E_a) and for the Arrhenius pre-exponential factor, respectively. This E_a value is consistent with the activation energy theoretically calculated at the DFT level for the outer-sphere mechanism proposed in Scheme 3.¹⁶

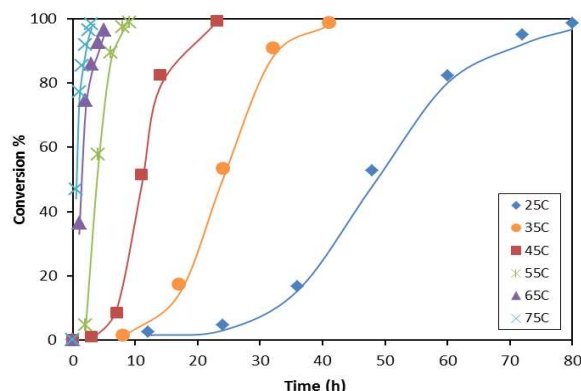


Figure 5. Temperature dependence of the consumption of HMTS predicted by the kinetic model (continuous lines). HMTS conversion obtained from GC-MS experimental studies (points).

A comparison of the experimental data with the model predictions is plot in Figure 5. The temperature dependence of the consumption of HMTS predicted by our model (the continuous lines in Figure 5) fit in an excellent manner with the experimental data obtained from the GC-MS studies of the reaction samples (data points in Figure 5).

4. Conclusions

The iridium(III) complex $[\text{Ir}(\text{H})(\text{CF}_3\text{SO}_3)(\text{NSiN})(\text{coe})]$ (**3**) (NSiN = bis(pyridine-2-yloxy)methylsilyl, coe = cyclooctene) has demonstrated to be an active catalyst precursor for the solvent-free hydrosilylation of CO_2 with 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) under mild reaction conditions (25 °C to 75 °C and 3 bar) allowing preparation of the corresponding silylformate in gram scale and high yield. The best catalytic performance has been achieved at 75 °C (TOF = 29.1 h^{-1}). A kinetic study at variable temperature together with a kinetic modeling of the catalytic hydrosilylation of CO_2 with HMTS using complex **3** as catalyst precursor has been carried out. The results from this study showed a value of 73.8 kJ mol^{-1} for E_a (activation energy of the process).

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Notes and references

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