

A DFT Study of the Conversion of CO₂ in Dimethylcarbonate Catalyzed by Sn(IV) Alkoxides

Renata C. de Souto,^a Nilton Rosenbach Jr.^b and Claudio J. A. Mota^{*,a,c}

^aEscola de Química, Universidade Federal do Rio de Janeiro, Av Athos da Silveira Ramos 149, CT Bl E, 21941-909 Rio de Janeiro-RJ, Brazil

^bCentro Universitário Estadual da Zona Oeste, Avenida Manuel Caldeira de Alvarenga, 1203, Campo Grande, 23070-200 Rio de Janeiro-RJ, Brazil

^cINCT Energia e Ambiente, Universidade Federal do Rio de Janeiro, 21941-909 Rio de Janeiro-RJ, Brazil

Foram realizados cálculos de teoria do funcional da densidade (DFT) de intermediários e estados de transição da reação entre o CO₂ e metanol sobre catalisadores do tipo R₂Sn(OCH₃)₂. A interação da molécula de CO₂ com o catalisador de estanho é controlada pelo termo entrópico, sendo desfavorecida à temperatura ambiente e pressão atmosférica. Por outro lado, a inserção da molécula de CO₂ na ligação Sn–OCH₃ é termodinamicamente favorecida para todos os catalisadores estudados. A energia livre de ativação calculada varia com a natureza do substituinte R. Grupos fenila apresentam a menor barreira, enquanto que os átomos de halogênio, as mais elevadas. Os grupos alquila apresentam barreiras intermediárias. Os cálculos estão de acordo com resultados experimentais recentes, que indicaram uma maior frequência de rotação da reação (TON) para a formação de dimetil carbonato (DMC) quando Ph₂SnO foi usado como catalisador. O esquema mecanístico completo foi calculado para os substituintes fenila e metila, considerando uma espécie de estanho dimérica.

Density functional theory (DFT) calculations of intermediates and transition states of the reaction between CO₂ and methanol over different R₂Sn(OCH₃)₂ catalysts (R = alkyl, phenyl and halogens) were carried out. The interaction of the CO₂ molecule with the tin catalyst was controlled by the entropic term, being disfavored at room temperature and atmospheric pressure. On the other hand, the insertion of the CO₂ molecule into the Sn–OCH₃ bond is thermodynamic favorable for all the catalysts studied. The computed free-energy of activation varied with the nature of the substituent R. Phenyl groups exhibit the smallest barrier, whereas halogen atoms the highest. Alkyl groups present intermediate barriers. The results are in agreement with recent experimental results that indicated a higher turnover number (TON) for dimethylcarbonate (DMC) formation when Ph₂SnO was used as catalyst. The whole mechanistic scheme was then computed for phenyl and methyl as substituents, considering a dimer tin species.

Keywords: CO₂, dimethylcarbonate, tin alkoxides, DFT

Introduction

Carbon dioxide (CO₂) is essential to maintain optimal temperature conditions for life on our planet, because it is the main responsible for the greenhouse effect. However, due to the burning of fossil fuels, the concentration of CO₂ in the atmosphere is dramatically increasing, causing problems related with the global warming and climate

changes. If no action is made to control or reduce the emission of CO₂ to the atmosphere, it is expected that the Earth temperature may increase by up to 6 °C until the end of this century.¹

There are many studies for capturing, storing and using the CO₂ emitted from the burning of fossil fuels.² One alternative is the use of CO₂ as feedstock in sustainable processes to produce fuels and chemicals.³ Today, the industrial utilization of carbon dioxide is limited. It is used in the production of urea and salicylic acid. Methanol can

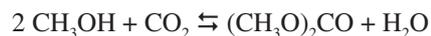
*e-mail: cmota@iq.ufrj.br

also be produced from CO₂, through hydrogenation over Cu and Zn based catalysts.⁴ An industrial plant using this route has been recently started up in Iceland, using hydrogen produced from geothermal source. Cyclic organic carbonates can be produced through the reaction of CO₂ with epoxides.⁵ Ethylene carbonate is industrially produced by the reaction of ethylene oxide with carbon dioxide. This route avoids the emission of 1730 ton of CO₂ to the atmosphere for each 10000 ton of polymer produced.⁶ The cyclic carbonates can react with methanol to produce dimethylcarbonate (DMC), an important and versatile chemical.

DMC is mainly used as a polar solvent in the manufacture of pharmaceuticals, agrochemicals, paints, coatings and fragrances.⁶ It is also used⁷ as a carbonylation and alkylation reagent in organic synthesis, substituting toxic reagents such as COCl₂ (phosgene), CH₃OCOCl (methyl chloroformate), (CH₃)₂SO₄ (dimethylsulfate) and methyl halides (MeX). Yet, DMC is used in the production of polycarbonates and polyurethanes, which are important polymers of versatile applications. DMC can also be used as oxygenated additive in gasoline, improving the octane number and reducing the emission of pollutants.

DMC can be prepared by the reaction of methanol with phosgene.⁸ However, this method has been gradually phased out, mainly due to the high toxicity of phosgene. The oxidative carbonylation⁹ of methanol and transesterification routes are, today, the most used pathways to DMC, but also have environmental concerns.

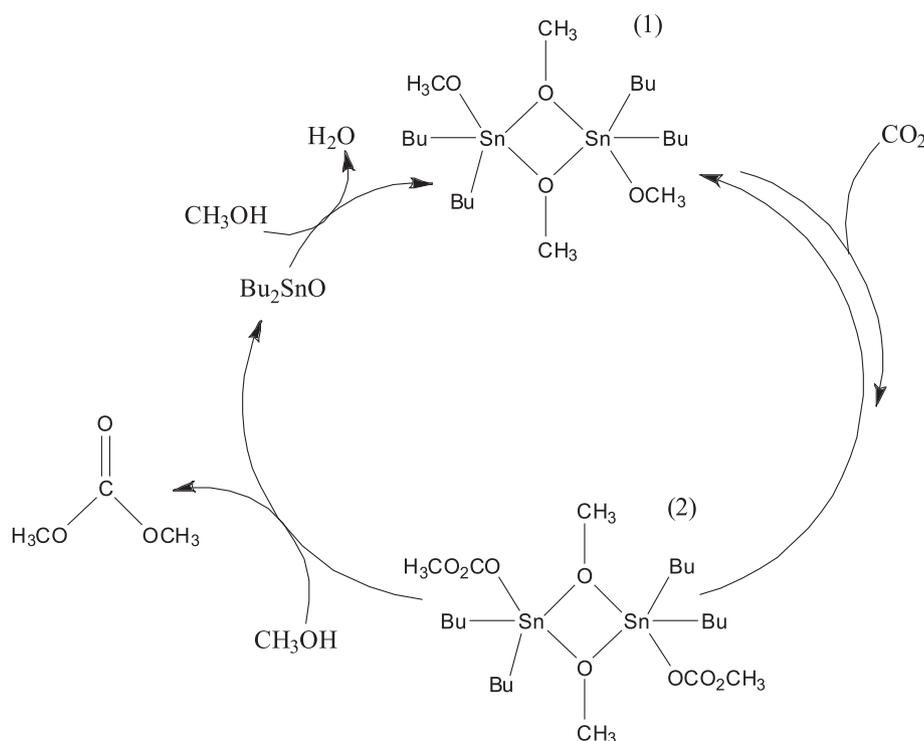
One alternative for a green synthesis of DMC is the direct carbonylation of methanol with CO₂ (Scheme 1). Apart from being a cleaner route, this process may also contribute to a reduction in the amount of carbon dioxide released into the atmosphere.



Scheme 1. Direct carbonylation of methanol with CO₂.

The conversion of CO₂ to DMC has been extensively investigated.¹⁰ Organometallic compounds, such as Sn(IV) alkoxides, are capable of catalyzing the reaction.¹¹ Different pathways may be envisaged to describe the role of Sn(IV) alkoxides in catalyzing the reaction of CO₂ with methanol to afford DMC and water. The most accepted¹² mechanistic pathway is shown on Scheme 2, involving a tin dimer species as catalyst. The dimerization increases the nucleophilicity of the Sn–OCH₃ oxygen atom and the electrophilicity of the tin atom. Kinetic studies show that the DMC yield increases smoothly and does not depend on the presence of methanol in the reaction medium. In fact, the alcohol can react with the product of the reaction between CO₂ and the catalyst (distannoxane), after formation of the DMC, to regenerate the catalyst.

The initial step of the mechanism is the insertion of the CO₂ molecule into the Sn–OCH₃ bonds of the catalyst, which involves a nucleophilic attack at the carbon atom of



Scheme 2. Simplified mechanistic pathway for the conversion of CO₂ and CH₃OH into DMC catalyzed by Sn(IV) alkoxides.

the CO₂ molecule by the oxygen atom of the tin alkoxide, affording a methoxy carbonate (**2**). This intermediate has already been isolated from the reaction medium, supporting the mechanistic pathway.¹³ The formation of the methoxy carbonate (**2**) is followed by an isomerization step, to afford an intermediate where the tin atom has an expanded valence shell, which then decomposes into DMC and regenerates the methoxyalkyltin species (**1**) upon reaction with methanol, restarting the catalytic cycle. In this last step, H₂O is released and may contribute to the deactivation of the catalyst, as well as it may react with the formed DMC to yield CO₂ and methanol. In all transition states, the Sn atom provides electrophilic assistance, binding to the oxygen atom of the CO₂ molecule or the carbonate group. Therefore, electron withdrawing or releasing groups may influence the Lewis acidity of the Sn atom, affecting the electrophilic assistance which may modify the kinetic profile of the reaction.

Our aim in this contribution is to carry out a theoretical study to understand the electronic effect of the R₁ and R₂ substituents on the thermodynamics and kinetic parameters of the conversion of CO₂ and methanol into DMC.

Computational methodology

Although the reaction of CO₂ and methanol to afford DMC and water is proposed to involve a dimeric Sn(IV) alkoxide species, we considered only the monomer, which is always in equilibrium with the dimer, to reduce the computational costs. This procedure may give a trend of the electronic effect of the substituents (R₁ and R₂) on the thermodynamics and kinetic parameters of the first step (formation of the methoxy carbonate **2** through insertion of CO₂ molecule into Sn–OCH₃ bond). In addition, steric effects are more significant in the dimeric form, which, in principle, may override the electronic effects in the presence of bulky substituents. Based on these results, we, subsequently, evaluated the thermodynamics and kinetic parameters for all steps of those catalysts that present the best performance in the activation of the CO₂ molecule, using the same methodology, but considering a dimeric form of the catalysts. For comparison purposes, we also performed the same calculations for the methyl-substituted catalyst, as a reference case.

Geometry optimizations were performed with the Gaussian 09 package¹⁴ using the meta-GGA functional M06-2x developed by Truhlar.¹⁵ The double-zeta polarized basis set 6-31G(*d,p*) was used to describe all atoms except Sn, for which the LANL2DZ effective core potential and basis set were applied. Vibrational analysis in the harmonic approximation (HO) was performed for all optimized

structures at same level to correct for the zero-point energy (ZPE) and thermal effects at 298.15 K and 1 atm. Furthermore, all transition state structures were checked using the intrinsic reaction coordinate (IRC) method.

The rate constants $k(T)$ were calculated using transition state theory with

$$k(T) = (c^0)^{1-m} \frac{k_b T}{h} \exp\left(-\frac{\Delta H^\ddagger - T\Delta S^\ddagger}{RT}\right)$$

in which c^0 is the inverse of the reference volume assumed in translational partition function calculation, k_b is the Boltzmann constant, T is temperature, h is plank's constant, R is the universal gas constant, m is the molecularity of the reaction and ΔS^\ddagger and ΔH^\ddagger are entropy and enthalpy of activation, respectively. ΔH^\ddagger is given by $\Delta H^\ddagger = (E^0 + ZPVE + \Delta\Delta H)_{TS-R}$, where $\Delta\Delta H$ is a temperature correction; ZPVE is the difference in zero-point vibrational energy between the transition state and the reactants; and E_0 is the difference in electronic energy of the transition state and the reactants. We also calculated the activation energy with: $E_a = \Delta H^\ddagger + mRT$ and frequency factor with

$$A = (c^0)^{1-m} \frac{k_b T}{h} \exp\left(\frac{mR + \Delta S^\ddagger}{RT}\right).$$

Results and Discussion

Figure 1 shows the structures of the transition state and intermediates for the insertion of the CO₂ molecule in the Sn–OCH₃ bond of the (CH₃)₂Sn(OCH₃)₂ monomer. The calculated thermodynamics and kinetic data are also reported in Figure 1 at 298.15 K and 1 atm (Gibbs free energies with the enthalpic and entropic contributions). The structures for the same species in the presence of other catalysts do not present significant differences.

Table 1 shows the thermodynamic and kinetic parameters for all catalysts studied. According to the results, the interaction between the CO₂ molecule and the tin monomer to afford the interaction complex is not thermodynamically favorable for all the substituents (R₁ and R₂) at room temperature and atmospheric pressure. This results show the weak interaction between the species, not capable of overcoming the entropic term at room temperature. On the other hand, the CO₂ insertion in the Sn–OCH₃ bond is thermodynamically favorable for all catalysts and involves energy barriers in the range of 30 to 50 kJ mol⁻¹. The weak interaction between CO₂ and the tin complex may explain the use of high pressures in the experimental studies related with the formation of DMC. The interaction is basically of non-dispersive nature

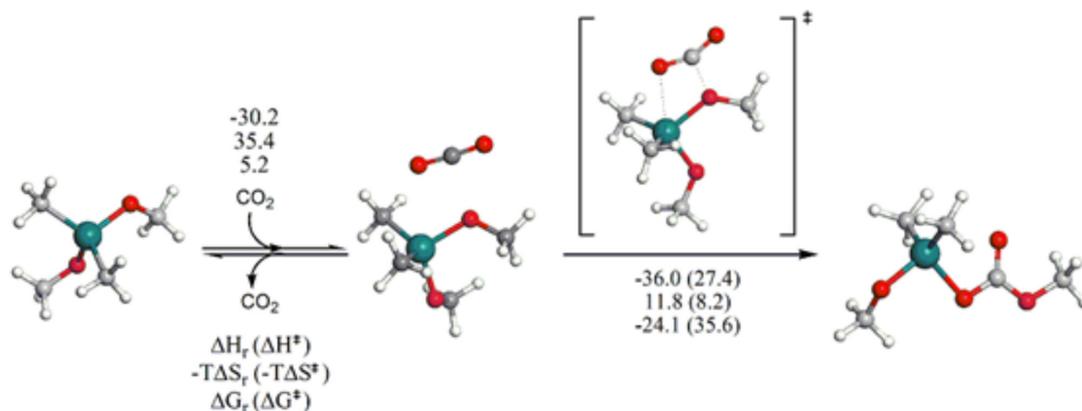


Figure 1. Calculated structure of the transition state and intermediates of the insertion of CO₂ into Sn–OCH₃ bond of (CH₃)₂Sn(OCH₃)₂ (thermodynamic and kinetic parameters are in kJ mol⁻¹ and refer to 298.25 K and 1 atm).

(VDW), with carbon atom faced to the oxygen atom of the OCH₃ moiety, whereas the tin atom interacts with the oxygen atom of the CO₂ molecule.

Figure 2 shows the effect of the substituents on the kinetic parameter (ΔG[‡]) for the insertion of CO₂ molecule in the Sn–OCH₃ bond of the (CH₃)₂Sn(OCH₃)₂ monomer. Phenyl substituents are the most effective groups to enhance nucleophilic/electrophilic assistance of the catalyst in the activation of the CO₂ molecule, because the reaction in the presence of Ph₂Sn(OCH₃)₂ has the lowest energy barrier. The Sn–OCO distance on the Ph₂Sn(OCH₃)₂ catalyst is shorter (*d*_{Sn–OCO} = 2.56 Å) than on (CH₃)₂Sn(OCH₃)₂ (*d*_{Sn–OCO} = 2.70 Å), showing that CO₂ is more strongly bounded with the phenyl-substituted catalyst. Butyl

groups also present quite similar results, with activation parameters close to what was calculated for the phenyl substituents. Although the difference is not significant, the others alkyl groups (methyl, ethyl and *n*-propyl) present higher activation energy compared to the *n*-butyl group. The results of calculations with the phenyl and butyl groups are in agreement with recent experimental results, that showed that these catalysts presented higher turnover frequencies (TON) for DMC formation in the reaction between methanol and CO₂, supporting the present calculation model.¹⁶

The free-energy of activation of fluorine, chlorine and bromine substituents are larger, compared with the alkyl groups. The order among the halogen atoms may

Table 1. Thermodynamic (kinetic) parameters for the insertion of CO₂ into Sn–OCH₃ bond, computed at M062x/6-31G(d,p) level of theory

R ₁ /R ₂ /R ₃ /R ₄	Step ^a	ΔH (ΔH [‡]) / (kJ mol ⁻¹)	-TΔS (-TΔS [‡]) / (kJ mol ⁻¹)	ΔG(ΔG [‡]) / (kJ mol ⁻¹)	<i>k</i> / s ⁻¹
Me/Me/OCH ₃ /OCH ₃	A→B	-30.2	35.4	5.2	3.58 × 10 ⁰⁵
	B→C	-36.0 (27.4)	11.8 (8.2)	-24.1 (35.6)	
Et/Et/OCH ₃ /OCH ₃	A→B	-37.4	39.9	2.4	2.98 × 10 ⁰⁵
	B→C	-36.8 (19.2)	15.3 (16.9)	-21.5 (36.1)	
Pr/Pr/OCH ₃ /OCH ₃	A→B	-37.6	38.0	0.4	7.88 × 10 ⁰⁴
	B→C	-36.5 (20.6)	13.1 (18.8)	-23.3 (39.4)	
Bu/Bu/OCH ₃ /OCH ₃	A→B	-40.3	47.5	7.2	1.57 × 10 ⁰⁶
	B→C	-33.9 (22.4)	6.0 (9.6)	-27.9 (31.9)	
Ph/Ph/OCH ₃ /OCH ₃	A→B	-33.3	42.2	8.9	2.25 × 10 ⁰⁶
	B→C	-42.9 (19.1)	11.0 (12.0)	-31.9 (31.1)	
F/F/OCH ₃ /OCH ₃	A→B	-30.9	39.6	8.7	7.36 × 10 ⁰⁴
	B→C	-5.8 (30.7)	9.3 (8.8)	3.5 (39.5)	
Cl/Cl/OCH ₃ /OCH ₃	A→B	-20.6	38.6	18.0	2.28 × 10 ⁰⁴
	B→C	-23.2 (26.9)	11.1 (15.5)	-12.1 (42.4)	
Br/Br/OCH ₃ /OCH ₃	A→B	-29.7	36.2	6.5	9.31 × 10 ⁰²
	B→C	-14.2 (38.1)	9.0 (12.2)	-5.2 (50.4)	

^aA→B refers to the interaction of CO₂ with the tin monomer; B→C refers to the insertion in the Sn–OCH₃ bond.

be explained by the electronegativity, which affect the electrophilicity of the Sn atom. As the electronegativity of the halogen decreases, the free-energy of activation increases.

Based on these results, we evaluated the thermodynamics and kinetic parameters for the whole mechanistic pathway considering the dimeric form of Ph₂Sn(OCH₃)₂ and (CH₃)₂Sn(OCH₃)₂, as a reference case. Figure 3 shows the structure of the transition states and intermediates involved in the reaction of CO₂ and methanol to afford DMC with the [(CH₃)₂Sn(OCH₃)₂]₂ dimer as catalyst. The structures are similar when considering the [Ph₂Sn(OCH₃)₂]₂ dimer.

The potential energy surfaces for both catalysts are shown in Figure 4. It comes from the results that the steric hindrance, due to the presence of bulky phenyl groups, overrides the electronic effects in the dimer catalyst, which present a similar kinetic profile. Indeed, the Sn–OCO distance in TS1

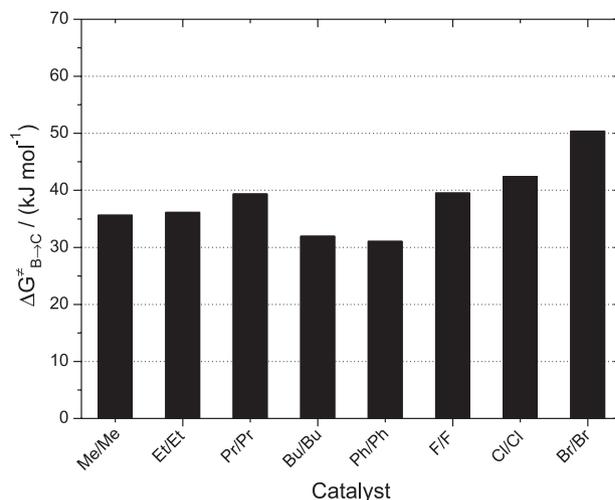


Figure 2. Effect of the substituent (R) on the kinetic parameter for the insertion of CO₂ molecule in the Sn–OCH₃ bond of the R₂Sn(OCH₃)₂ monomer.

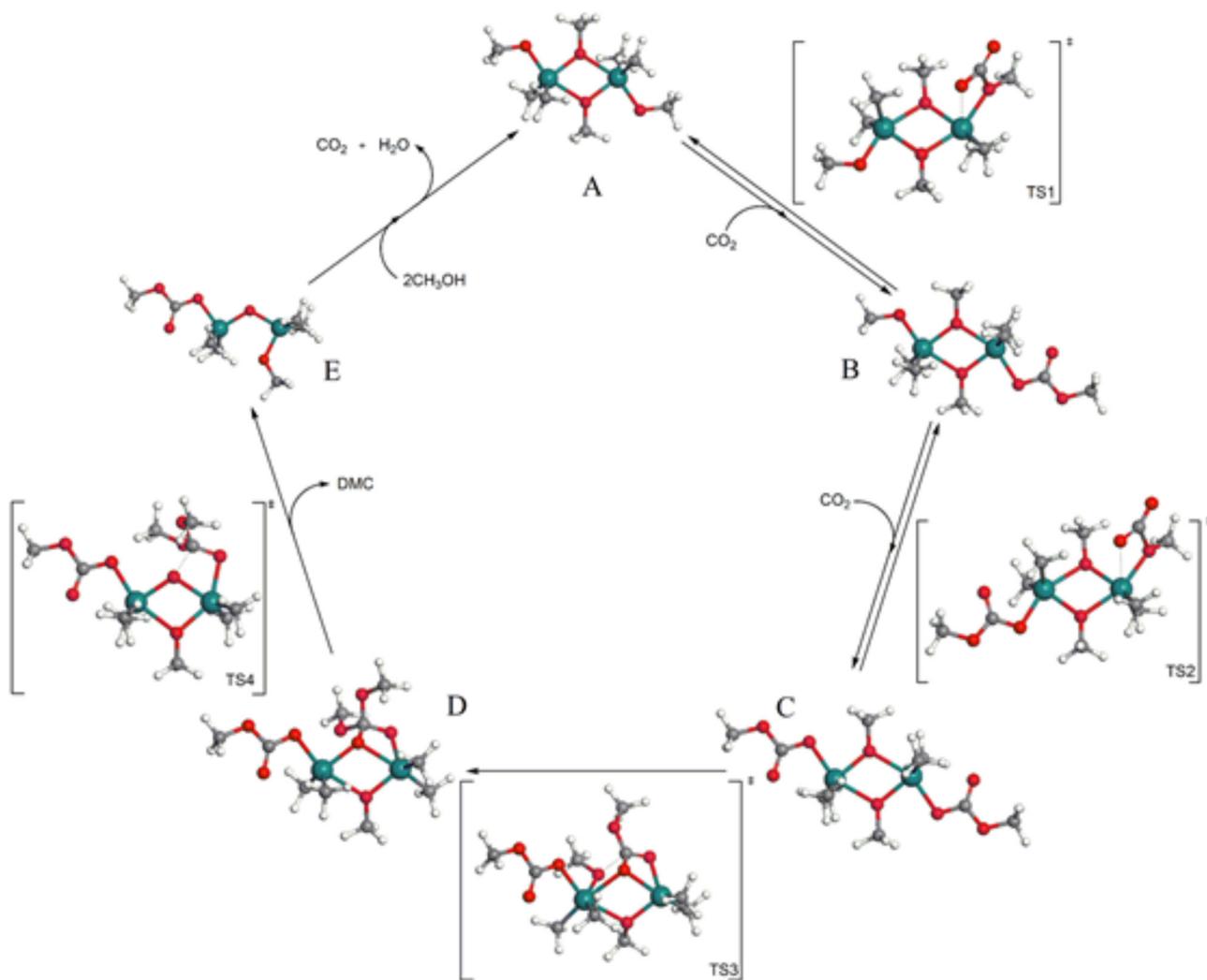
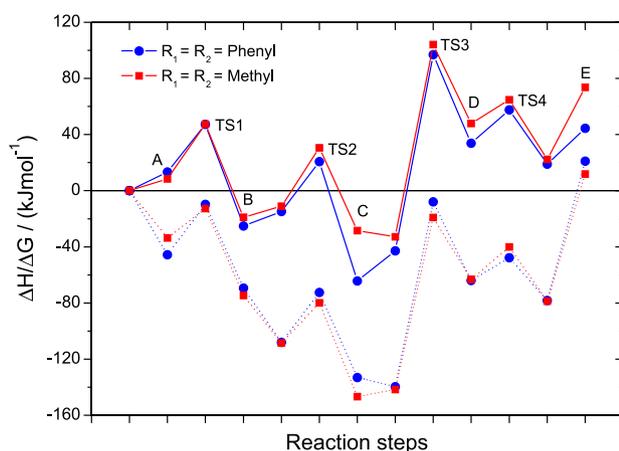


Figure 3. Calculated structures of the transition states and intermediates in the reaction of CO₂ with methanol to DMC, catalyzed by the (CH₃)₂Sn(OCH₃)₂ dimer.

Table 2. Kinetic parameters for the reaction of CO₂ with methanol to afford DMC, catalyzed by the R₁R₂Sn(OCH₃)₂ dimer, according to the mechanism depicted in Figure 3

Parameter	ΔH^\ddagger / (kJ mol ⁻¹)	$-T\Delta S^\ddagger$ / (kJ mol ⁻¹)	ΔG^\ddagger / (kJ mol ⁻¹)	k / s ⁻¹	E_a / (kJ mol ⁻¹)	A / (s ⁻¹ × 10 ¹¹)	ν^a / (cm ⁻¹)
Phenyl							
A→B	35.9	3.0	38.9	9.55×10^{04}	38.4	6.20	188.60
B→C	35.6	6.2	41.8	2.97×10^{04}	38.1	6.17	116.26
C→D	131.7	5.2	136.9	6.32×10^{-13}	134.2	6.18	231.38
D→E	16.2	0.6	16.8	7.01×10^{08}	18.7	6.22	214.60
Methyl							
A→B	20.9	13.0	33.9	7.18×10^{05}	23.4	6.12	108.37
B→C	28.6	6.8	35.5	3.76×10^{05}	31.1	6.17	106.17
C→D	122.5	17.3	139.8	1.98×10^{-13}	125.0	6.08	232.10
D→E	23.1	-1.5	21.6	1.03×10^{08}	25.5	6.24	212.57

^aImaginary frequency.

**Figure 4.** Thermodynamic and kinetic profile for the reaction of CO₂ with methanol to afford DMC, catalyzed by the R₁R₂Sn(OCH₃)₂ dimer, according to the mechanism depicted in Figure 3. Dashed lines (enthalpy) and solid lines (Gibbs free energy).

slightly increases from 2.56 Å to 2.60 Å when considering the dimeric form of the Ph₂Sn(OCH₃)₂ catalyst. This may be explained to the steric hindrance, whilst keeping the same value ($d_{\text{Sn}-\text{OCO}} = 2.70$ Å) for the dimeric form of the (CH₃)₂Sn(OCH₃)₂ catalyst. Entropic contributions do not significantly modify the kinetic profile of the reaction, which still shows an unfavorable thermodynamic energy. This may explain the low yields and conversions observed in the synthesis of DMC from CO₂ and methanol. The use of water suppressor is normally required¹⁷ to shift equilibrium and achieve higher yields of DMC.

The calculated kinetic parameters for the reaction steps involving the TS are shown in the Table 2. According to the results, the activation energy of the slowest step (step C→D) for the dimeric form of the Ph₂Sn(OCH₃)₂ catalyst is slightly higher compared to the (CH₃)₂Sn(OCH₃)₂ catalyst, probably due to steric reasons.

Conclusions

Calculations on the thermodynamic and kinetic profile of the insertion of CO₂ in the R₁R₂Sn(OCH₃)₂ catalysts were carried out at M062x/6-31G(d,p) level of theory. Regardless of the substituents on the tin complex, the interaction with the CO₂ molecule is not favored at room temperature and atmospheric pressure due to the entropic term. The insertion into the Sn–OCH₃ bond is thermodynamic favorable for all the catalyst, but the free energy of activation depends on the nature of the substituents. Phenyl groups showed the lowest barrier, whereas halogen atoms the highest, supporting the dependence of the kinetics on the electrophilicity/nucleophilicity of the Sn atom, caused by the substituents.

The entire mechanistic scheme was then calculated for the dimeric Ph₂Sn(OCH₃)₂ catalyst, showing that steric factors become predominant when considering the dimer as catalysts.

Acknowledgements

Authors thank FAPERJ (E-26/112.193/2012) and CNPq for financial support.

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Submitted on: August 14, 2014

Published online: October 10, 2014