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Kinetic modelling of the synthesis of diethyl carbonate and propylene carbonate from ethanol and 1,2-propanediol associated with CO₂

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Abstract

Organic carbonates have attracted considerable attention because of their numerous applications. The direct association of CO₂ and alcohol to synthesise these carbonates is one of the most promising routes, when considering the economic and the environmental aspects. A significant number of researchers have worked on the catalysis and the dehydration of these reactions, but very few have dealt with the study of the thermodynamic equilibrium and the kinetics of these reactions. The objective of this work is to study the synthesis of diethyl carbonate (DEC) and propylene carbonate (PC). A parametric study was conducted by varying the temperature, the pressure and the initial concentration. Equilibrium constants were determined experimentally and compared to available published data. Kinetic models are developed based on four mechanisms, two of which are the mechanisms of Langmuir-Hinshelwood and Eley-Rideal. Mean deviations between the experimental data and the modelling were below 10 % for all the mechanisms. The best fit was obtained for the mechanism of Langmuir-Hinshelwood for the synthesis of DEC and PC. Activation energies of 100 kJ/mol and 77 kJ/mol were determined for the synthesis of DEC and PC, respectively.

1. Introduction

Organic carbonates like dimethyl carbonate (DMC), diethyl carbonate (DEC) or propylene carbonate (PC) have attracted considerable attention over recent decades because of their specific properties (Kindermann et al., 2017; Sakakura and Kohno, 2009). They are considered to be building blocks in the chemical industry to produce polycarbonates or more complex carbonates (Ochoa-Gómez et al., 2009). They can also replace the highly toxic and hazardous phosgene in some reactions, like the synthesis of polyurethane (Fukuoka et al., 2003). Because of their low toxicity, organic carbonates can be used in replacement of some toxic or harmful solvents, like dichloromethane or toluene (Miao et al., 2008). DMC and DEC are often used as co-solvents in lithium batteries (Takeuchi et al., 2013) and also as a gasoline additive (Pandian et al., 2010, Szori et al., 2018).

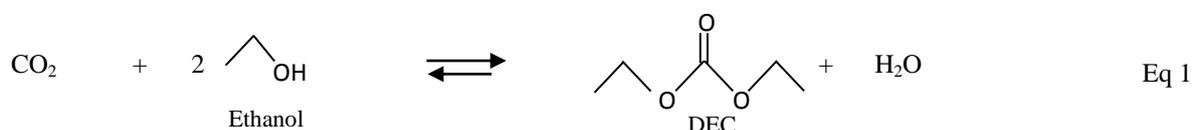
Conventionally, carbonates are produced by using certain highly toxic and harmful chemicals, like phosgene. To develop the market, a greener way of synthesis has to be found. New alternatives have been proposed in recent years (Huang et al., 2015). The most advanced alternative is the oxidative carbonylation of methanol or of methyl nitrile with CO. This synthesis is the most favourable in respect of thermodynamics, but it does use some toxic and corrosive chemicals. Today, new routes are being developed using CO₂. Indeed, reactions of CO₂ utilisation have been in development over the past few decades because CO₂ is a nontoxic and abundant molecule. The idea is to transform the most emitted greenhouse gas into valuable products to replace classical synthesis, which uses oil-derived products. In the case of organic carbonates, three routes are emerging. The first is the alcoholysis of urea generating carbonates during which NH₃ is evolved which can be converted back to urea by reacting with CO₂. The second is the transesterification of cyclic carbonates, which is performed in two steps: CO₂ reacts with epoxide to produce cyclic carbonate, which will then react with alcohol to produce linear carbonate. The last route is the direct association of CO₂ and alcohol to produce carbonate. A recent study highlights that this direct synthesis is one of the most promising routes, when considering the economic and the environmental aspects (Monteiro et al., 2009). Indeed, the only co-product of this synthesis is water, and the alcohol which can be produced from biomass, like it is for methanol (Galindo Cifre and Badr, 2007), ethanol (Sirajunnisa and Surendhiran, 2016) or 1,2-propanediol (Marinas et al., 2015).

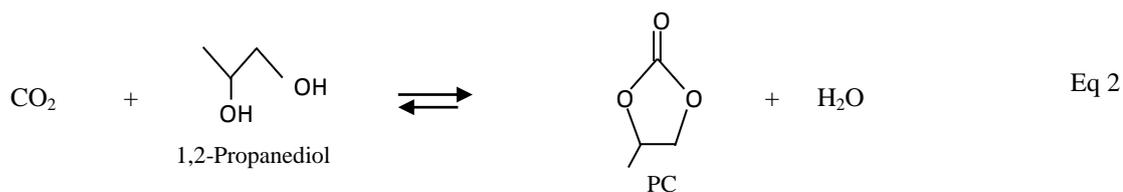
The growing interest in organic carbonates synthesis and CO₂ utilisation is leading researchers to work on this reaction. In the literature, many catalysts have been proposed; however, the yields obtained are still very low due to the unfavourable thermodynamics of the reaction (Honda et al., 2014a; Kindermann et al., 2017; Tamboli et al., 2017). Indeed, the reaction reaches a thermodynamic equilibrium. Removing water from the reaction mixture can shift this equilibrium and improve yields in carbonate. This dehydration can be made by

using a dehydrating agent like ketals (Tomishige and Kunimori, 2002), acetonitrile (Honda et al., 2010, 2009), benzonitrile (Honda et al., 2014a) or 2-cyanopyridine (Tomishige et al., 2019). This method improves the yield, but raises certain issues, like the separation of products and co-products at the end of the reaction. Some physical dehydration has been tested, such as the use of a molecular sieve (Choi et al., 2002) or a hydrophilic membrane (Décultot et al., 2019a; Dibenedetto et al., 2012; Li and Zhong, 2003). These methods are efficient to improve yields, but more studies are required in order to identify the best conditions of use (Aresta et al., 2017).

A significant number of researchers have worked on the catalysis and the dehydration of these reactions, but very few works deal with the study of the thermodynamic equilibrium and the kinetics of these reactions. However, these data are essential to understand the limitation of these reactions in order to find efficient solutions to improve the yields. Only three articles have studied the kinetics of the reaction of the synthesis of dimethyl carbonate (Fu et al., 2018; Marin et al., 2016; Santos et al., 2013). In each case, the initial kinetics are studied to estimate the activation energy. Two articles studied the kinetics based on the mechanisms of Langmuir-Hinshelwood and Eley-Rideal (Marin et al., 2016; Santos et al., 2013). However, the rate laws developed are different in the two articles.

The aim of this study is to develop a kinetic model for the synthesis of DEC and PC, for which no data has yet been found in the literature (Eq 1 and 2). A parametric study was performed using the catalyst CeO_2 , which gives good yields and very high selectivity (Yoshida et al., 2006). Thermodynamic constants were evaluated experimentally for different experimental conditions and compared with thermodynamic data found in the literature. Several kinetic models were developed based on different mechanisms, and rate constants were identified with the experimental data. The influence of several parameters such as temperature, pressure and initial concentrations of water and carbonates were studied.





2. Materials and methods

2.1. Materials

Cerium (IV) oxide with a purity of 99.5 % was purchased from Alfa Aesar. This catalyst was calcined at 600 °C for 4 h in the air. Absolute ethanol (>99.7 %) was purchased from VWR, DEC (>99 %) and 1,2-propanediol (>99,5 %) were purchased from Alfa Aesar and PC (>99 %) from Sigma Aldrich. All products were used as received.

2.2. Reactor unit

The reactor unit used to conduct the parametric study has been described in a previous work (Décultot et al., 2019a). A Parr autoclave with a capacity of 100 mL was used. It is equipped with a blade agitator, a valve to take samples during the reaction and two valves to add or remove CO₂. The temperature is controlled, and the pressure is read on a pressure gauge. For a typical experiment, 50 mL of ethanol are filled in the reactor with 2 g of CeO₂. Then, the reactor is purged three times with CO₂. Subsequently, the CO₂ is filled at the desired pressure by waiting for its solubilisation in ethanol for 45 min. The temperature is then increased up to the desired temperature. 1 mL of the sample is taken at selected times during the reaction. At the end of the reaction, the reactor is cooled down, and the pressure is decreased. For the determination of the concentrations of alcohol and carbonate, samples are diluted in methanol, with hexanol as an internal standard, and they are analysed by gas chromatography with a flame ionisation detector (FID) with an accuracy of 4 % (cf appendix for typical chromatogram). The initial amount of water was determined by a Karl-Fischer titration with a coulometric method, with an accuracy of 10 %. The protocol is similar for the reaction with 1,2-propanediol, but the solution is diluted in ethanol for the analysis. Table 1 presents the reaction operating conditions used for the experiments. Experiments can be classified into four groups. The first three correspond to the synthesis of DEC. The first one concerns reactions performed at different temperatures and similar pressures. For the second group, pressure was varied, but the temperature was the same. In the third group, different initial concentrations of water and diethyl

carbonate were tested. The fourth group corresponds to reactions performed with 1,2-propanediol with different temperatures and pressures.

Experiments	Reactant	Temperature (K)	Pressure (MPa)	Time (h)	Initial concentration of water (mol/L)	Initial concentration of DEC (mol/L)
<u>Group 1</u> : synthesis of DEC, various temperatures						
R1	Ethanol	398	5.8	48	0.035	-
R2	Ethanol	368	4.7	185	0.035	-
R3	Ethanol	370	4.6	170	0.035	-
R4	Ethanol	374	5.4	190	0.035	-
R5	Ethanol	382	5.2	185	0.035	-
R6	Ethanol	385	5.3	24	0.035	-
R7	Ethanol	391	5.6	24	0.035	-
R8	Ethanol	403	5.9	27	0.035	-
<u>Group 2</u> : synthesis of DEC, various pressures						
R9	Ethanol	398	2.4	52	0.035	-
R10	Ethanol	398	3.6	27	0.035	-
R11	Ethanol	398	4.4	28	0.035	-
<u>Group 3</u> : synthesis of DEC, various initial concentrations						
R12	Ethanol	398	5.7	24	0.021	-
R13	Ethanol	398	5.8	24	0.072	-
R14	Ethanol	398	5.8	24	0.115	-
R15	Ethanol	398	5.8	48	0.035	0.031
R16	Ethanol	398	5.8	28	0.035	0.076
<u>Group 4</u> : synthesis of PC, various temperatures and pressures						
R17	1,2-propanediol	376	5.8	24	0.070	-
R18	1,2-propanediol	386	5.6	24	0.070	-
R19	1,2-propanediol	393	5.2	75	0.070	-
R20	1,2-propanediol	399	5.2	27	0.070	-
R21	1,2-propanediol	405	5.8	24	0.070	-
R22	1,2-propanediol	413	5.8	32	0.070	-
R23	1,2-propanediol	399	2.8	28	0.070	-

Table 1. Experimental conditions for reactions of carbonation of ethanol or 1,2-propanediol with 2g of CeO₂

3. Results and discussion

3.1. Thermodynamic equilibrium

For the kinetic modelling, reaction equilibrium data are necessary. In the case of CO₂, there is an equilibrium between the gas and the CO₂ dissolved in the solvent. The activity of CO₂ can be expressed using a pressure or a concentration. For the concentration, the activity can be replaced by a concentration ratio using a reference concentration. With the same reference concentration for all compounds except CO₂, equation can be simplified by elimination of the reference concentration. The equilibrium constant (K_{eq}) is calculated based on the activity (a_i) and the stoichiometric coefficient (ν_i) of each component at the equilibrium (Eq 3). The activities of alcohol, carbonate and water can be expressed with concentrations. These two parameters are related by the Henry's law (Décultot et al., 2019b). In our case, pressure was chosen to simplify the expression. This approximation is justified by the fact that the conversion of alcohol is very low, assuming that CO₂ consumption is negligible, so the pressure is quite constant during all the experiments. Equilibrium constants are calculated with Eq 4 and Eq 5 for the synthesis of DEC and PC, respectively. P_0 and C_0 represent the standard pressure and concentration equal to 1 bar and 1 mol/L, respectively.

$$K_{eq} = \prod a_i^{\nu_i} \quad \text{Eq 3}$$

$$K_{eq} = \frac{[DEC]_{eq}[H_2O]_{eq}P_0}{[1,2PPD]_{eq}P_{CO_2}} \quad \text{Eq 4}$$

$$K_{eq} = \frac{[PC]_{eq}[H_2O]_{eq}P_0}{C_0[1,2PPD]_{eq}P_{CO_2}} \quad \text{Eq 5}$$

To ascertain the concentration of each component at equilibrium, reactions were performed over a long period of time (>24 h). The equilibrium is assumed to be reached when the concentration of DEC measured becomes constant. Concentrations of the other components are calculated from DEC and PC concentrations at the equilibrium:

$$[H_2O]_{eq} = [H_2O]_0 \quad \text{Eq 6}$$

$$[EtOH]_{eq} = [EtOH]_0 \quad \text{Eq 7}$$

$$[1,2PPD]_{eq} = [1,2PPD]_0$$

Eq 8

<u>Group 1</u> : synthesis of DEC, various temperatures						
Experiments	R4	R5	R1	R8		
Temperature (K)	374	382	398	403		
K_{eq}	$2.13 \cdot 10^{-7}$	$2.05 \cdot 10^{-7}$	$1.76 \cdot 10^{-7}$	$1.75 \cdot 10^{-7}$		
<u>Group 2</u> : synthesis of DEC, various pressures						
Experiments	R1	R11	R10	R9		
Pressure (MPa)	5.8	4.4	3.6	2.4		
K_{eq}	$1.76 \cdot 10^{-7}$	$1.88 \cdot 10^{-7}$	$2.24 \cdot 10^{-7}$	$2.29 \cdot 10^{-7}$		
<u>Group 3</u> : synthesis of DEC, various initial concentrations						
Experiments	R12	R1	R13	R14	R15	R16
$[H_2O]_0$	0.021	0.035	0.072	0.115	0.035	0.035
$[DEC]_0$	0	0	0	0	0.031	0.076
K_{eq}	$1.84 \cdot 10^{-7}$	$1.76 \cdot 10^{-7}$	$1.82 \cdot 10^{-7}$	$1.75 \cdot 10^{-7}$	$1.63 \cdot 10^{-7}$	$1.66 \cdot 10^{-7}$
<u>Group 4</u> : synthesis of PC, various temperatures and pressures						
Experiments	R19	R20	R21	R22	R23	
Temperature (K)	393	399	405	413	399	
Pressure (MPa)	5.2	5.2	5.8	5.8	2.8	
K_{eq}	$2.26 \cdot 10^{-5}$	$2.34 \cdot 10^{-5}$	$2.39 \cdot 10^{-5}$	$2.52 \cdot 10^{-5}$	$2.82 \cdot 10^{-5}$	

Table 2. Experimental equilibrium constants for the four groups of reactions

Experimental equilibrium constants are reported in Table 2 for the four groups of reactions. Equilibrium constants are calculated only when the equilibrium is reached. For some reactions, the time was not long enough for the DEC concentration to become constant. For group 3, it can be seen that similar equilibrium constants are obtained with different initial concentrations of water and DEC. This result confirms that the thermodynamic equilibrium is reached for each reaction. Concerning the effect of temperature, the equilibrium constant seems to

decrease when the temperature increases for the synthesis of DEC (group 1), and for the synthesis of PC (group 4) the contrary is true. It can also be seen that the equilibrium constant of synthesis of PC is 100 times higher than the equilibrium constant for the synthesis of DEC.

No experimental data are available in the literature about the determination of this equilibrium constant for the synthesis of DEC and PC. However, it is possible to compare it with theoretical values by using the Gibbs free energy at the temperature T ($\Delta_r G_T^0$) (Eq 9), calculated with the standard enthalpy of reaction $\Delta_r H_T^0$ and the standard entropy of reaction $\Delta_r S_T^0$ (**Error! Reference source not found.**Eq 12). These data are calculated using the standard enthalpy of formation $\Delta_f H_i^0$, the standard entropy S_i^0 and the heat capacity of each component C_p^i . By combining Eq 11, Eq 12 and Eq 13, it is possible to calculate directly the equilibrium constant (Eq 14).

$$\Delta_r G_T^0 = -RT \ln K_{eq} \quad \text{Eq 9}$$

$$\Delta_r G_T^0 = \Delta_r H_T^0 - T \Delta_r S_T^0 \quad \text{Eq 10}$$

$$\Delta_r H^0 = \sum v_i \Delta_f H_i^0 \quad \Delta_r S^0 = \sum v_i S_i^0 \quad \text{Eq 11}$$

$$\Delta_r H_T^0 = \Delta_r H^0 + \int_{T_0}^T \Delta_r C_p dT \quad \Delta_r S_T^0 = \Delta_r S^0 + \int_{T_0}^T \frac{\Delta_r C_p}{T} dT \quad \text{Eq 12}$$

$$\Delta_r C_p = \sum v_i C_p^i \quad \text{Eq 13}$$

$$\ln K_{eq} = \left[\frac{-\Delta_r G^0}{RT_0} \right] + \left[\frac{\Delta_r H^0}{RT_0} \left(1 - \frac{T_0}{T} \right) \right] + \left[-\frac{1}{RT} \int_{T_0}^T \Delta_r C_p dT + \frac{1}{R} \int_{T_0}^T \frac{\Delta_r C_p}{T} dT \right] \quad \text{Eq 14}$$

Table 3 shows the values of the standard enthalpy of formation and entropy of each component available in the literature, for the synthesis of DEC and the synthesis of PC (Vasil'ev et al., 1976; Gardner and Hussain, 1972; Gardner and Hussain, 1972; Moureu and Dode, 1937; Zaripov, 1982; Choi and Joncich, 1971; Vasil'eva et al., 1972; Leino et al., 2011; Shukla and Srivastava, 2018). For the synthesis of DEC, values given by Leino and colleagues and Shukla and colleagues are different. The data of Leino and colleagues are for gas components, and the data of Shukla and colleagues are for the liquid components, except for CO₂ which is considered as a gas in both cases. Liquid heat capacity was used for DEC, water and ethanol, and the gaseous heat capacity was used for CO₂. These data were found in the National Institute of Standards and Technology database (NIST). The influence of the value of heat capacity on the calculation of the equilibrium constant is negligible compared to

the enthalpy and entropy. To simplify the calculations, these heat capacities are assumed to be constant in the range of temperature studied (in line with the procedure used by Leino et al. in their calculations).

	$\Delta_f H^0$ (kJ/mol)		S^0 (J/mol/K)		C_p (J/mol/K)
	Leino et al., 2011	Shukla et al., 2018	Leino et al., 2011	Shukla et al., 2018	NIST
DEC	-637.9	-681.5	412.21	299.62	211
H ₂ O	-241.8	-285.83	188.8	69.95	76
CO ₂	-393.5	-393.52	213.8	213.79	37.1
C ₂ H ₅ OH	-234.8	-277.6	281.6	161	112
1,2-PPD	Vasil'eva et al., 1972	Choi and Joncich, 1971	Vasil'ev et al., 1976		Zaripov, 1982
	-613.1 ± 1	-631.8 ± 2.1	219.17		167.4
PC	Moureu and Dode, 1937	Gardner and Hussain, 1972	Gardner and Hussain, 1972		Vasil'ev et al., 1976
	-500.3 ± 1.8	-486 ± 3	180.9		189.9

Table 3. Standard enthalpy of formation, entropy and heat capacity of each component for the synthesis of DEC and PC

For the synthesis of PC, very limited data are available for the enthalpy, entropy and heat capacity of PC and 1,2-propanediol. The uncertainties surrounding these data are high, and this has an important impact on the calculation of the Gibbs free energy. In a more recent publication, Verevkin and colleagues confirm the formation enthalpy of PC (Verevkin et al., 2008). The value found was -614.1 ± 0.8 kJ/mol, which is near to that of Vasil'eva and colleagues (Vasil'eva et al., 1972). This value was chosen in this study for the calculation of equilibrium constants. For the 1,2-propanediol, two cases were studied: a) case 1, with the enthalpy of -486 kJ/mol (Gardner and Hussain, 1972); and b) case 2, with a value of -500.3 kJ/mol (Moureu and Dode, 1937). Only one value of entropy and one value of heat capacity were found for both PC and 1,2-propanediol. Recently, Yasir and colleagues tried to calculate the reaction enthalpy of the synthesis of PC, but the data used were different from those presented here, and the sources do not permit us to find the values (Yasir et al., 2017). We chose not to use these values.

Equilibrium constants for the synthesis of DEC were calculated using the data of Leino and colleagues and with the data of Shukla and colleagues, using liquid heat capacities with Eq 13. They are compared with the experimental data obtained in this work in **Error! Reference source not found.S1**. The experimental data are

close to the data obtained by Shukla and Leino. For each case, the equilibrium constant decreases with increasing temperature. Table S2 compares the values of equilibrium constants obtained experimentally and those calculated with the data found in the previous studies for the synthesis of PC. The enthalpy of formation of 1,2-propanediol has an important impact on the equilibrium constant. Between case 1 and 2, the values differ by two orders of magnitude for 393 K. The experimental results are closer to case 2. However, the equilibrium constant decreases when the temperature increases. Experimentally, it is the opposite. The uncertainties of the experimental data and the high uncertainties of the data can explain this difference of tendency.

Eq 15 is obtained by combining Eq 12 and Eq 14. By considering that the enthalpy and entropy of the reaction are constant within the temperature range studied, these two parameters can be estimated by plotting $\ln K_{eq}$ against the inverse of temperature. The results are presented in Figure 1 : Estimation of the enthalpy and the entropy of the reaction by plotting $\ln K_{eq}$ against $1/T$ for the experimental results and the thermodynamic data of Leino and colleagues and Shukla and colleagues and Table 4 for the synthesis of DEC.

$$\ln K_{eq} = \frac{-\Delta_r H_T^0}{RT} + \frac{\Delta_r S_T^0}{R} \quad \text{Eq 15}$$

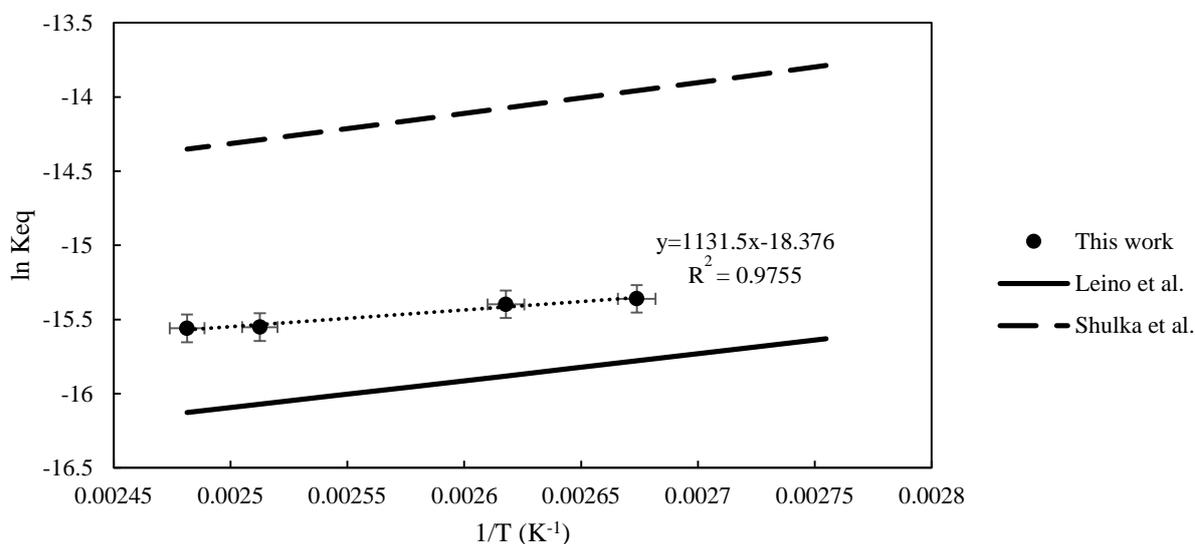


Figure 1 : Estimation of the enthalpy and the entropy of the reaction by plotting $\ln K_{eq}$ against $1/T$ for the experimental results and the thermodynamic data of Leino and colleagues and Shukla and colleagues, for the synthesis of DEC.

	$\Delta_r H_T^0$ (kJ/mol)	$\Delta_r S_T^0$ (J/mol/K)
Leino et al. 2011	-15.1	-172
Shukla et al. 2018	-17.1	-162
This work	-9.4	-153

Table 4. Estimation of the enthalpy and entropy of the reaction for the experimental results and the data of Leino et al. 2011 and Shukla et al. 2018

As we can see in Table 4, the enthalpy and the entropy estimated in this work are less negative than those determined with the data of Leino and colleagues 2011 and Shukla and colleagues 2018. There are several reasons for this difference. Only four experimental data sets were used to calculate these parameters, and the uncertainties concerning these experiments are high in comparison with the calculation. The calculation made to estimate the theoretical enthalpy and entropy does not take into account the pressure. For the experimental data, the pressure was not exactly the same for each experiment. This factor may influence the enthalpy and entropy of the reaction. To be coherent with our experiments, equilibrium constants for other reactions at different temperatures (R2, R3, R6 and R7) are estimated with Eq 14 by using $\Delta_r H_T^0 = -9.4$ kJ/mol and $\Delta_r S_T^0 = -153$ J/mol/K. These values were also used to estimate the equilibrium constant of the reaction with a variation of initial concentrations (R12-R16). The same equilibrium constant of $1.79 \cdot 10^{-7}$ was used for all calculations because the temperature and the pressure were the same.

To estimate the equilibrium constant of R17 and R18 in the case of the synthesis of PC, Eq 14 was used (Figure 2). The tendency of the experimental data for the variation of the equilibrium constant with the temperature is not in accordance with the physical behaviour. Anyway, considering that only 4 values have been calculated in a short temperature range (20 K) with an important uncertainty, these points could be in agreement of a positive slope leading to a slightly negative enthalpy as proposed in literature. The enthalpy of case 2 was -3.2 kJ/mol and for the entropy was -101 J/mol/K. The experimental enthalpy and entropy of reaction were used to calculate the equilibrium constant of R17 and R18.

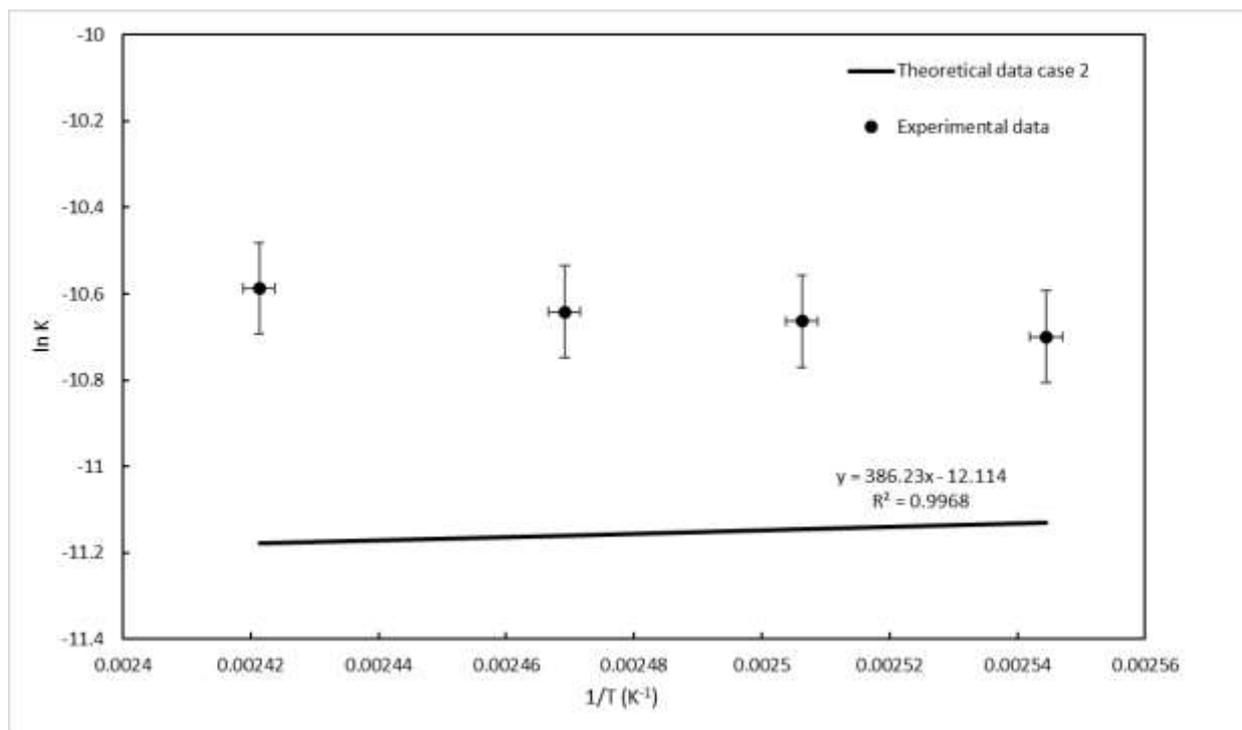


Figure 2. Determination of reaction enthalpy and entropy by plotting $\ln K_{eq}$ against the inverse of temperature, for the synthesis of PC

3.2. Mechanisms and reaction rates

Four mechanisms were developed from for the synthesis of DEC. The Langmuir-Hinshelwood and Eley-Rideal mechanisms are two classical mechanisms used to model the kinetics of reactions generated using heterogeneous catalysts. Santos and colleagues and Marin and colleagues used these two mechanisms to develop rate laws for the kinetic modelling of the synthesis of DMC from methanol and CO_2 (Marin et al., 2016; Santos et al., 2013). These mechanisms are represented in **Error! Reference source not found.** (mechanism A and B). In the case of the Langmuir-Hinshelwood mechanism, both CO_2 and ethanol are adsorbed on the catalyst. CO_2 and one molecule of ethanol adsorb on basic sites, and the second molecule of ethanol adsorbs on the acid sites (Kumar et al., 2016; Wang et al., 2013). They react together in step 3, and products desorb in steps 4 and 5. In the case of the Eley-Rideal mechanism, only ethanol is adsorbed on the catalyst, and an intermediate is formed in step 3. This intermediate is an ethylcarbonate ($\text{C}_2\text{H}_5\text{OCOO}$), which is described in some mechanisms used in other published works (Eta et al., 2011; Tomishige et al., 2000b). Some researchers experimentally studied the reaction to propose mechanisms that are more specific (Aresta et al., 2010; Chen et al., 2014). The mechanisms depend on the catalyst used and on the experimental conditions. Mechanism C is based on the Langmuir-Hinshelwood mechanism, but the second molecule of ethanol does not adsorb on the catalyst. This hypothesis is

based on the fact that it can be difficult to have a termolecular mechanism, and it is more likely that the second ethanol will not be adsorbed on the catalyst (Aresta et al., 2010). Mechanism D corresponds to the mechanism developed by Chen and colleagues in the case of the synthesis of DMC with the catalyst CeO_2 . It is based on the Eley-Rideal mechanism, its first two steps are similar to those of the Langmuir-Hinshelwood mechanism, but the CO_2 and the first molecule of ethanol will be adsorbed on the catalyst. The intermediate detected by Raman spectrometry is also different from that of Eley-Rideal, in that it is a carbomethoxy ($\text{EtOCO}=\text{C}_2\text{H}_5\text{OCO}$) (Chen et al., 2014).

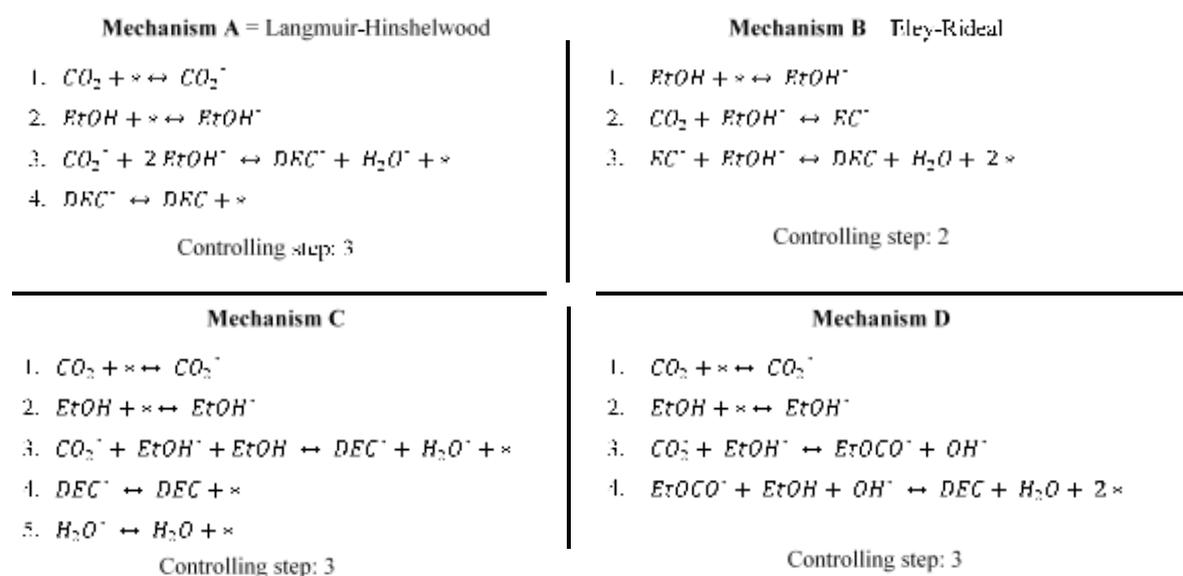


Figure 3 : Mechanisms used to develop rate laws for the synthesis of DEC

In the case of the synthesis of PC, very few mechanisms are available in the literature. Honda and colleagues propose a mechanism in three steps: adsorption of the 1,2-propanediol; insertion of CO_2 to form an intermediate; and nucleophilic attack of the OH group to produce the cyclic carbonate (Honda et al., 2014b). This mechanism corresponds to the Eley-Rideal mechanism. In this study, two mechanisms are used: Eley-Rideal and Langmuir-Hinshelwood.

The controlling step is assumed to be the step of reacting between CO_2 and alcohol for each mechanism. The other elementary steps are considered to be at the equilibrium and are defined with their equilibrium constant, named K_{A1} : the letter subscript corresponds to the mechanism and the number subscript corresponds to the elementary step. For the case of the synthesis of PC, the letters PC are added in superscript. To define these equilibrium constants, the parameter θ_* was used, which represents the fraction of free active sites. θ_i represents

the fraction of active sites occupied by the component i (Eq 16). The equilibrium constants are described for the case of the Langmuir-Hinshelwood mechanism for the synthesis of DEC in Eq 17.

$$1 = \theta_* + \theta_{CO_2} + \theta_{EtOH} + \theta_{DEC} + \theta_{H_2O} \quad \text{Eq 16}$$

$$K_{A1} = \frac{\theta_{CO_2} P_0}{P_{CO_2} \theta_*} \quad K_{A2} = \frac{\theta_{EtOH} C_0}{[EtOH] \theta_*} \quad K_{A4} = \frac{\theta_* [DEC]}{C_0 \theta_{DEC}} \quad K_{A5} = \frac{\theta_* [H_2O]}{C_0 \theta_{H_2O}} \quad \text{Eq 17}$$

The reaction rate is equal to the rate of step 3 in the case of mechanism A (Eq 18). The fraction of active sites for each component is replaced by using the equilibrium constant of each step. The rate law described in Eq 19 is obtained.

$$r_A = r_3 = k_3 \theta_{EtOH}^2 \theta_{CO_2} - k_{-3} \theta_{DEC} \theta_{H_2O} \theta_* \quad \text{Eq 18}$$

$$r_A = k_A \frac{\left(\frac{[EtOH]^2 P_{CO_2}}{C_0^2 P_0} - \frac{[DEC][H_2O]}{K_{eq} C_0^2} \right)}{\left(1 + K_{A1} \frac{P_{CO_2}}{P_0} + K_{A2} \frac{[EtOH]}{C_0} + \frac{[DEC]}{C_0 K_{A4}} + \frac{[H_2O]}{C_0 K_{A5}} \right)^3} \quad \text{Eq 19}$$

This equation corresponds to the equation usually obtained for the Langmuir-Hinshelwood mechanism (Santos et al., 2013). The equilibrium constants K_{eq} used are those determined experimentally in section 3.1. The rate laws for other mechanisms and for the PC synthesis are developed by the same method and are detailed in **Error! Reference source not found.** to Eq 24.

$$r_B = k_B \frac{\left(\frac{[EtOH]^2 P_{CO_2}}{C_0^2 P_0} - \frac{[DEC][H_2O]}{K_{eq} C_0^2} \right)}{\frac{[EtOH]}{C_0} \left(1 + K_{B1} \frac{[EtOH]}{C_0} + \frac{[DEC][H_2O]}{[EtOH] C_0 K_{B3} K_{B1}} \right)} \quad \text{Eq 20}$$

$$r_C = k_C \frac{\left(\frac{[EtOH]^2 P_{CO_2}}{C_0^2 P_0} - \frac{[DEC][H_2O]}{K_{eq} C_0^2} \right)}{\left(1 + K_{C1} \frac{P_{CO_2}}{P_0} + K_{C2} \frac{[EtOH]}{C_0} + \frac{[DEC]}{C_0 K_{C4}} + \frac{[H_2O]}{C_0 K_{C5}} \right)^2} \quad \text{Eq 21}$$

$$r_D = k_D \frac{\left(\frac{[EtOH]^2 P_{CO_2}}{C_0^2 P_0} - \frac{[DEC][H_2O]}{K_{eq} C_0^2} \right)}{\frac{[EtOH]}{C_0} \left(1 + K_{D1} \frac{P_{CO_2}}{P_0} + K_{D2} \frac{[EtOH]}{C_0} + 2 \sqrt{\frac{[DEC][H_2O]}{[EtOH] C_0 K_{D4}}} \right)^2} \quad \text{Eq 22}$$

$$r_A^{PC} = k_A^{PC} \frac{\left(\frac{[1,2PPD] P_{CO_2}}{C_0 P_0} - \frac{[PC][H_2O]}{K_{eq} C_0^2} \right)}{\left(1 + K_{A1}^{PC} \frac{P_{CO_2}}{P_0} + K_{A2}^{PC} \frac{[1,2PPD]}{C_0} + \frac{[PC]}{C_0 K_{A4}^{PC}} + \frac{[H_2O]}{C_0 K_{A5}^{PC}} \right)^2} \quad \text{Eq 23}$$

$$r_B^{PC} = k_B^{PC} \frac{\left(\frac{[1,2PPD] P_{CO_2}}{C_0^2 P_0} - \frac{[PC][H_2O]}{K_{eq} C_0^2} \right)}{\left(1 + K_{B1}^{PC} \frac{[1,2PPD]}{C_0} + \frac{[PC][H_2O]}{C_0^2 K_{B3}^{PC}} \right)} \quad \text{Eq 24}$$

k corresponds to the rate constant, which is a function of the temperature following an Arrhenius equation, where k_0 represents the pre-exponential factor, E_a is the activation energy, R is the ideal gas constant and T is the temperature.

$$k = k_0 e^{-E_a/RT} \quad \text{Eq 25}$$

The reaction rate depends on the concentration of DEC (or PC) as described in Eq 26:

$$r = \frac{d[DEC]}{dt} \quad \text{Eq 26}$$

Differential equations were solved in Matlab, using a method based on differentiation (numerical differentiation formulas, ODE15S). The objective function used is given in Eq 27. NP represents the number of experimental points. For the synthesis of DEC, we used 16 experiments, which represent 103 experimental points.

$$F_{obj} = \min \left[\sum_{i=1}^{NP} \left(\frac{|[DEC]_{model} - [DEC]_{exp}|}{[DEC]_{exp}} \right) \right] \quad \text{Eq 27}$$

3.3. Simulation results

The kinetic parameters obtained for the synthesis of DEC and for the synthesis of PC are listed in Table 5. For the synthesis of DEC, the activation energy is around 100 kJ/mol for the four mechanisms. No value was

found in the literature for the activation energy of the synthesis of DEC. The synthesis of DMC has received more scholarly attention, and the activation energies obtained with different catalysts are listed in Table 6. The value obtained in this study is near to the value obtained by Santos and colleagues and Marin and colleagues, who used commercial CeO₂ (Marin et al., 2016; Santos et al., 2013). Some researchers obtained lower activation energy by using other catalysts (Fu et al., 2018; Hofmann et al., 2012; Marin et al., 2016). This difference is due to the composition of the catalyst. Indeed, the quantity of acid and basic sites is directly related to the catalyst activity (Tomishige et al., 2000a; Wang et al., 2013). For 1,2-propanediol, the activation energy is lower, at 77 and 86 kJ/mol for the two different mechanisms. No data were found in the existing literature for the activation energy of the synthesis of cyclic carbonates. Pre-exponential factors are in the same order of 10⁸ and 10¹¹ mol/L/h. For each mechanism, this factor corresponds to a product of different equilibrium constants, so it is difficult to compare one to another. Equilibrium constants are different from one to another, they were determined by the modelling but they cannot be validated by experimental measurements of adsorption constants.

Mechanism		k ₀	E _a	K _{aCO₂}	K _{aEtOH}	K _{fDEC-PC}	K _{dDEC-PC}	K _{dH₂O}	MD
		mol/L/h	kJ/mol	-	-	-	-	-	%
A	Name	k _{0A}	E _{aA}	K _{A1}	K _{A2}		K _{A4}	K _{A5}	4.22%
	Value	3.61·10 ¹⁰	101	0.096	0.051		0.028	0.014	
B	Name	k _{0B}	E _{aB}		K _{B1}	K _{B3}			7.73%
	Value	1.39·10 ⁸	100		0.029	0.0025			
C	Name	k _{0C}	E _{aC}	K _{C1}	K _{2C}		K _{C4}	K _{C5}	4.25%
	Value	1.17·10 ¹²	104	2.14	5.26		0.001	0.0005	
D	Name	k _{0D}	E _{aD}	K _{D1}	K _{D2}	K _{D4}			7.41%
	Value	7.56·10 ⁹	97.8	0.128	0.423	1.33			
A ^{PC}	Name	k _{0A}	E _{aA}	K _{A1}	K _{A2}		K _{A4}	K _{A5}	7.20%
	Value	5.78·10 ⁹	77.2	1.491	9.751		0.0484	1.794	
B ^{PC}	Name	k _{0B}	E _{aB}		K _{B1}	K _{B3}			9.41%
	Value	5.99·10 ⁷	86.2		2.059	89.6			

Table 5. Kinetic parameters optimised from the experiments for the synthesis of DEC (R1 to R16) and PC (R17 to R23). K_{aCO₂} and K_{aEtOH}: adsorption constant of CO₂ and ethanol on the catalyst. K_{fDEC-PC}: constant of formation of DEC or PC. K_{dDEC-PC} and K_{dH₂O}: desorption of DEC, PC and water. MD: mean deviation

Article	Catalyst used	Ea (kJ/mol)
Santos et al., 2013	CeO ₂	107
Hofmann et al., 2012	CeO ₂ -ZrO ₂	75
Marin et al., 2016	commercial CeO ₂	117
	synthesised CeO ₂	65
Fu et al., 2018	CeO ₂	67.9
	Ti _{0.04} Ce _{0.96} O ₂	46.3

Table 6. List of activation energies obtained in the literature for the synthesis of DMC

Kinetic models based on the Langmuir-Hinshelwood and C mechanisms have the lowest mean deviations. This improved fit can be due to the fact that the quantity of rate constants is higher in the case of mechanisms A and C. By increasing the degree of freedom, the regression improves. The conclusion is the same for 1,2-propanediol, where the mean deviation is lower for the case of mechanism A.

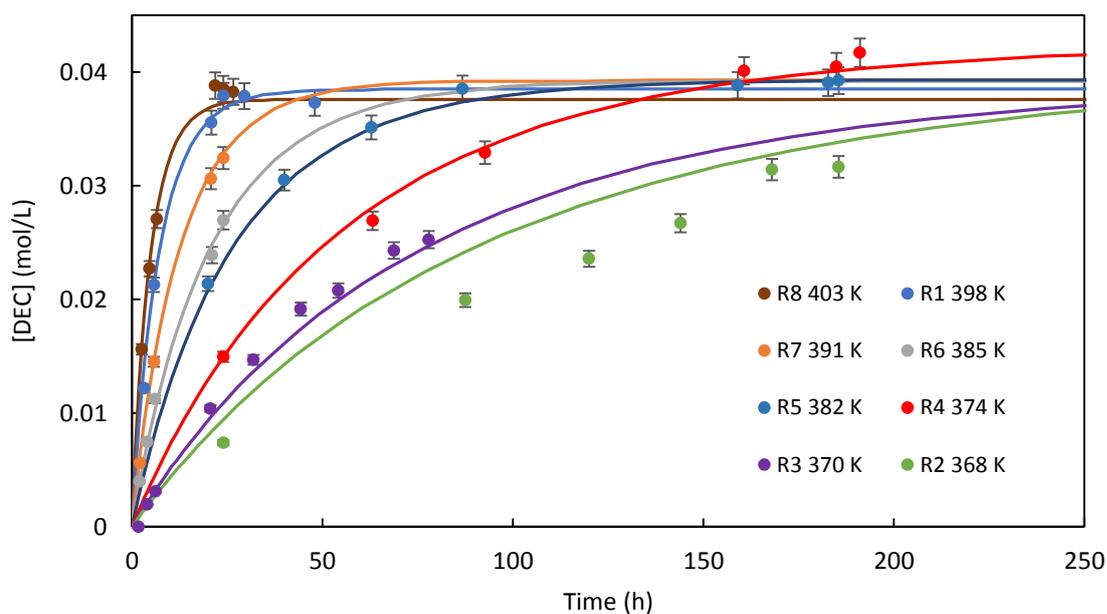


Figure 4 : Experimental DEC concentration during the time (points) and modelling with mechanism A (curves) for reactions with various temperatures (R1-R8)

Figures 4 to 6 present the evolution of the concentration of DEC during the experiments for the experimental values and the modelling for the case of the rate law based on mechanism A. **Error! Reference source not found.** represents the results obtained for reactions carried out at different temperatures. As the mean deviation is low, a good fit can be observed between the modelling and the experimental data. The worst fit is

obtained for the lowest temperature (R2). For this case, the equilibrium constant is not reached after 250 h. The elevation of the temperature has a strong impact on the kinetics. Moreover, the influence of the temperature on the thermodynamic equilibrium is very low; the concentration of DEC at the equilibrium is nearly the same for all the temperatures studied (Table 2). The use of a high temperature is an efficient solution to reduce the reaction time and to obtain a good conversion. **Error! Reference source not found.** represents reactions with various pressures. The fit is very good, which is mostly due to the fact that the direct experimental equilibrium was used in the kinetics. For the variation of initial concentrations of DEC and water (Figure 5), the same thermodynamic equilibrium was used for each experiment. The fit is good considering the uncertainties of the analysis of water. For reaction R16, there is no conversion because the concentration of DEC initially is higher than the concentration at the thermodynamic equilibrium.

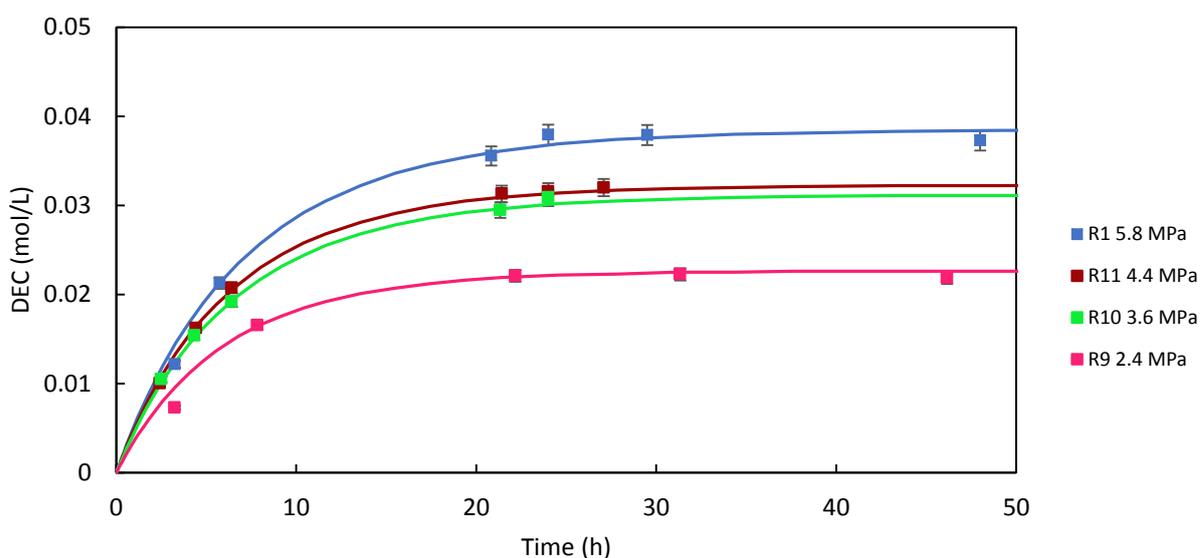


Figure 5 : Experimental DEC concentration during the time (points) and modelling with mechanism A (curves) for reactions with various pressures (R1, R9-R11)

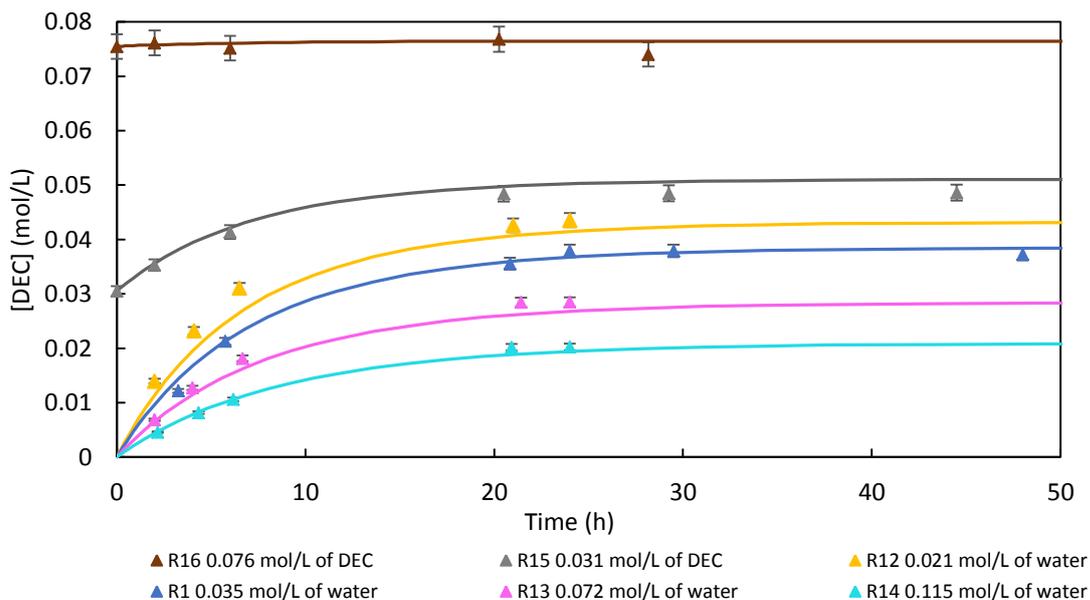


Figure 6 : Experimental DEC concentration during the time (points) and modelling with the mechanism A (curves) for reactions with various initial concentrations of water and DEC (R1, R12-R16)

Figure 6 represents the results obtained for the synthesis of PC. In that case, the mean deviation is higher, so the fit is less good than for the case of DEC. For the thermodynamic equilibrium, there are some differences between the experimental data and the modelling. This can be due to the analysis of water in the 1,2-propanediol, which is more difficult than for ethanol. As for the case of the synthesis of DEC, the temperature has an important impact on the kinetics. Moreover, in that case, the temperature increase seems to increase the concentration of DEC at the equilibrium. It can be concluded that the model shows a reasonable fit to the experimental data considering the uncertainties of the analysis of water.

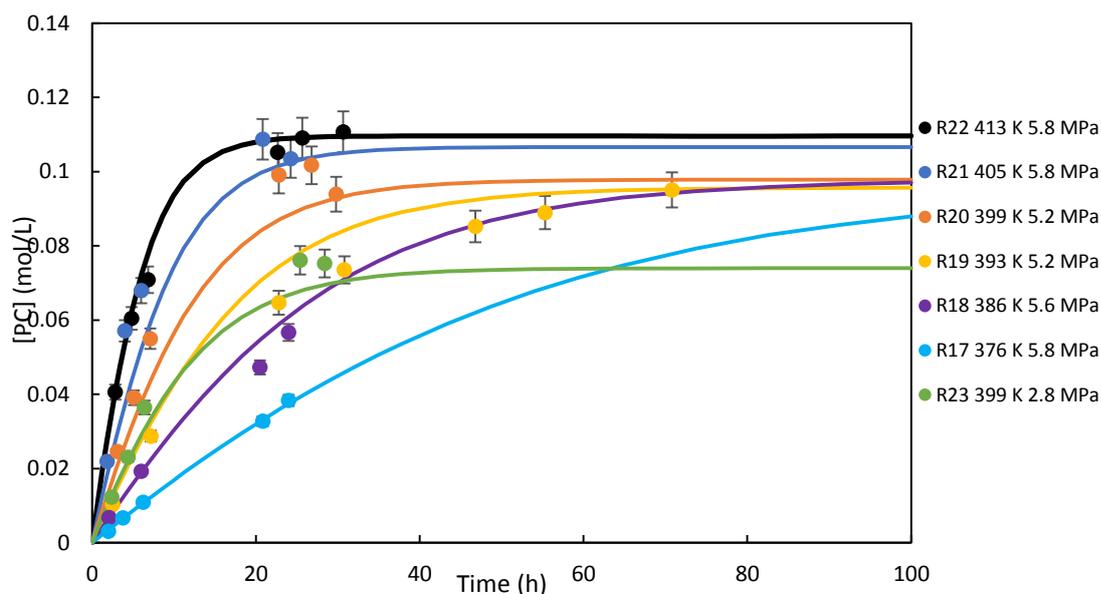


Figure 7 : Experimental PC concentration during the time (points) and modelling with mechanism A (curves) for reactions various temperatures and pressures (R17-R23)

The work of solving the equations was carried out for the 4 models considered. The mean standard deviations between these models and our experimental points are shown in Figure 8. First of all, we can see that for some conditions (R2, R12 and R13), whatever the model, the standard deviation is important. It is likely that in these cases, uncertainties related to the water analysis are the cause of this general shift. On the other hand, It appears that the mechanisms A and C allow better modelling of the experimental results. Mechanism B models the reactions R9, R10, R11 and R14 less well. Mechanism D is less efficient on reactions R2, R6, and R14.

Based on these findings, it is difficult to understand the origin of these discrepancies. However, we can put forward some hypotheses that further work could verify. In the A and C mechanisms, the desorption phase appears explicitly, allowing this phase to have an impact on the results of the model. The desorption phase is therefore perhaps limiting.

It also appears that the mechanisms presenting a termolecular (A,C) reaction are not discriminating in the case of this study. Assuming that the probability of occurrence of a termolecular reaction between adsorbed species is much more likely to occur between species within a liquid or gas, this finding is quite consistent.

Finally, from a mathematical point of view, the question of the number of estimated parameters could arise. Indeed, the greater the number, the greater the variance of the system and could allow a better identification of the parameters. However, in our case, the C mechanism, with 5 parameters, is not more efficient than the A mechanism with 4 parameters.

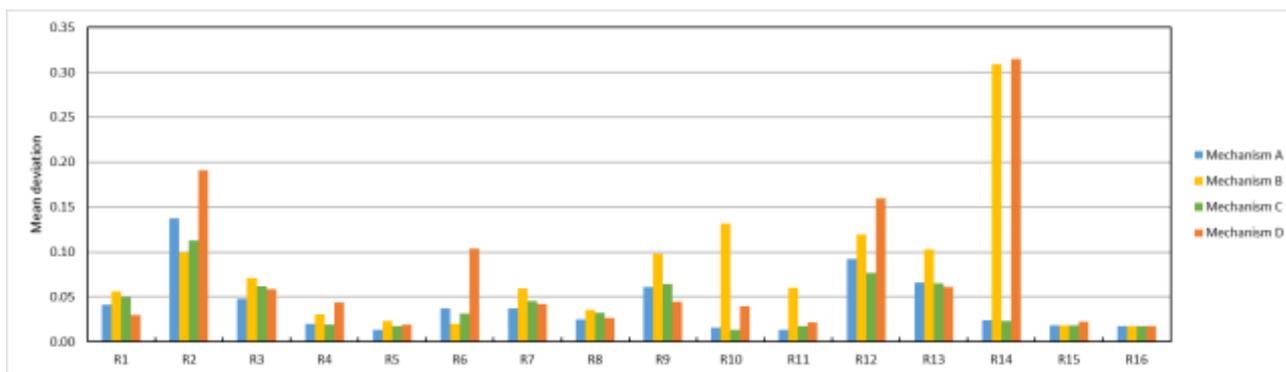


Figure 8. Comparison of standard deviation between the 4 models and our experimental data.

4. Conclusions

This article reports the first work on the development of a kinetic model for the direct synthesis of DEC and PC from alcohol and CO₂. A parametric study was performed using CeO₂ as a catalyst. The influences of temperature, pressure and initial concentrations of water and DEC were studied. Equilibrium constants were experimentally calculated for some experiments. Standard enthalpies and entropies of the reaction of -9.4 kJ/mol and -153 J/mol/K for the synthesis of DEC and -17.4 kJ/mol and -101 J/mol/K for PC were obtained. A difference was found between these values and the value obtained with the thermodynamic data taken from the literature. This difference can be attributed to the uncertainties of the experiments and to the uncertainties of the literature data. Indeed, several values were found for the enthalpy of formation or entropy of several compounds. Four reaction rate models were developed, based on different mechanisms for the synthesis of DEC, and two reaction rate models were developed for the synthesis of PC. The lower mean deviation between the experimental data and the modelling is obtained for the rate law based on the Langmuir-Hinshelwood mechanism for both cases. This difference is probably due to the higher number of degrees of freedom in the case of the Langmuir-Hinshelwood mechanism. An activation energy of about 100 kJ/mol for the synthesis of DEC was found, which is similar to the results obtained in the literature for the synthesis of DMC. For the synthesis of PC, the activation energy found is lower (77 and 86 kJ/mol). Good fittings with low mean deviations were obtained between the modelling and the experimental data for the case of the synthesis of DEC. For the synthesis of PC, the mean deviations are higher, but they remain under 10 %, which gives a reasonable fit when considering the uncertainties in the analysis of water. This work on the determination of the thermodynamic equilibrium and the development of the kinetics of these two reactions will be useful for the research of new processes.

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